DETERMINATION AND PREDICTION OF VAPOR-LIQUID EQUILIBRIA

Ph.D. Chemical Engineering

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DETERMINATION AND PREDICTION OF VAPOR-LIQUID EQUILIBRIA IN MIXTURES CONTAINING HYDROCARBONS, KETONES, ALCOHOLS AND ETHERS

ABSTRACT

The group solution model of Ratcliff and Chao for the prediction of the excess free energies of liquid mixtures has been tested and found to be satisfactory for eight mixtures of alkanes and ketones, and six mixtures of aromatic hydrocarbons and alcohols. The model was tested by comparing the predicted and experimental vapor-liquid equilibrium data. Data on one reference system was used in each case to generate group contribution functions. These functions were subsequently used to predict data on the remaining systems.

Data of aromatic hydrocarbon-alcohol systems were also predicted from the data of aliphatic CH_2/OH group mixtures and found to be very satisfactory.

Experimental data of alkane-ketone mixtures were determined at $65^\circ C$ using a modified Gillespie still. Aromatic hydrocarbon-alcohol mixture data were taken from the literature.

Vapor-liquid equilibrium data at $90^\circ C$ of three alkane-ether systems were also measured and found to be nearly ideal.

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A
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1. INTRODUCTION

Knowledge of precise vapor-liquid equilibria is a prerequisite to the detailed design of distillation equipment. However, such knowledge is limited, and usually not available when new systems are under consideration, because it is difficult and laborious to obtain the data experimentally. Predictive methods are therefore valuable for process evaluation and design.

Liquid state is highly complex for any general description, being in the 'in between' state of 'orderly' solids and 'disorderly' gases. Our lack of knowledge of the liquid state precludes the prediction of solution properties from those of the pure components which are, in most cases, either readily available or easily estimated, and forces us to develop empirical methods.

The main objective of the present work is the prediction of vapor-liquid equilibria from a minimum of experimental data. The second objective of determining equilibrium data was prompted by a lack of systematic experimental data for use in the predictive method.

Group contribution methods have been shown to be suitable for predicting a number of thermodynamic and transport properties (1,2,3,4)*. The present work is an extension of the work of Ratcliff and Chao (1) on the prediction of

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* Numbers indicate references at the end of the Introduction.

vapor-liquid equilibrium, and is concerned with mixtures of alkanes, ketones, ethers, and aromatic hydrocarbons.

The thesis is divided into seven chapters and three appendices. Each chapter is complete with its own bibliography and nomenclature. There is first, in chapters 2 and 3, a general outline of classical thermodynamics applied to mixtures, and a literature survey on the available methods for predicting vapor-liquid equilibria. Chapters 4 and 5 deal with the apparatus for determining the equilibrium data, experimental procedure and testing of the still for reliability. Experimental data, smoothing procedure, the predictive method, and a comparison of experimental and predictive data are presented in chapters 6 and 7. All the auxiliary information, such as the calibration data and computer programs, is included in the appendices.

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2. VAPOR-LIQUID EQUILIBRIUM

2.1 Introduction

The development, design and operation of equilibrium stage processes require a detailed knowledge of the composition of coexisting phases at equilibrium, and the effect of temperature and pressure on this composition. With the rise of petrochemical industry and the rapid increase in the number and quantity of solvent type compounds, there is a concentrated attention on matters relating to distillation in general, and vapor-liquid equilibria in particular. Vapor-liquid equilibria are studied primarily with either one or both of the following objectives in mind: (1) to collect the necessary equilibrium data for design of chemical process equipment, and (2) to provide the essential data needed to formulate models for the prediction of solution properties and test existing models.

Classical thermodynamics of solutions provides us with ways and means of treating and testing experimental data, but it is of very little use in predicting system properties.

Although determination and prediction of vapor-liquid equilibria are the broad objectives of the present study, some of the basic principles of classical thermodynamics applied to vapor-liquid equilibrium, nevertheless, need a brief review. This should serve the purpose of providing the background information needed for the chapters that follow. The present chapter is, therefore, intended to give an outline of solution thermodynamics applied to vapor-liquid equilibrium and data treatment methods.

2.2 Fundamental Principles

Systematic and exhaustive treatment of fundamental principles of classical thermodynamics of non-electrolyte solutions has been done in a number of text books (1,2,3,4,5, 6). Otto Redlich's article (7) on old and new problems in vapor-liquid equilibria gives a good critique on the subject. Van Ness (6) has written an excellent monograph on the classical thermodynamics of non-electrolyte solutions. Only relevant equations and principles are sketched below, and are mostly taken from the above source of reference.

The relationship between the composition of vapor and liquid at equilibrium and their temperature and pressure dependence is customarily developed from Gibbsian criterion of equality of partial molal free energy of each component in both phases. Expressed mathematically:

$$\bar{G}_{il} = \bar{G}_{iv} \qquad (2.1)$$

where $\bar{G}_{il}$ = partial molal Gibbs free energy of component i in liquid

$\bar{G}_{iv}$ = partial molal Gibbs free energy of component i in vapor

By definition, fugacity is given by

$$(d\bar{G}_i = RTd\ell n\hat{f}_i)_T \qquad (2.2)$$

where $\hat{f}_i$ = partial fugacity of component i in solution (not a partial molal quantity).

The definition of $\hat{f}_i$ is completed by arbitrarily specifying that

$$\lim_{P\to 0} \frac{\hat{f}_i}{x_i P} = 1 \tag{2.3}$$

where x_i = mole fraction of component i in solution

P = system pressure.

By definition, the activity coefficient of a constituent in a solution is given by

$$\gamma_i = \hat{f}_i / x_i f_i^* \tag{2.4}$$

where f_i^* is the fugacity of the constituent i in some arbitrarily chosen, convenient standard state.

The standard state for a constituent is selected with some limitations; the fundamental limitation being that the temperature of the standard state must always be that of the solution. Thus, the standard state temperature varies with solution temperature. The standard state of any constituent must be taken at a fixed composition of solution and may be arbitrary. This may be, but not necessarily, the same for all constituents. However, it is customary to take the standard state as the pure component at the temperature and pressure of the solution. Numerical value of the activity coefficient would be meaningless unless the standard state is fully described. In the present work the standard state is taken as that of the pure component at solution temperature and pressure. Thus the activity coefficient becomes

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i} \tag{2.5}$$

where f_i = fugacity of pure i at the temperature and pressure of solution.

An ideal solution is defined as the one which obeys Lewis and Randall rule for fugacities:

$$\hat{f}_i = x_i f_i \tag{2.6}$$

For an ideal solution the following relationships could be shown to be valid:

$$\Delta G^{id} = RT \sum_i x_i \ell n x_i \tag{2.7}$$

$$\Delta S^{id} = -R \sum_i x_i \ell n x_i \tag{2.8}$$

$$\Delta H^{id} = 0 \tag{2.9}$$

$$\Delta V^{id} = 0 \tag{2.10}$$

where Δ denotes the change of property due to mixing, and

G = Gibbs free energy

S = entropy

H = enthalpy

V = volume

From Equations (2.5) and (2.6) it can be recognized that the activity coefficient is a measure of the degree of nonideality of a solution. It is related to other excess properties of mixing (excess property is the difference between the actual property of solution and that of an ideal mixture) by the following expressions:

$$S^E = -RT\left(\sum_i x_i \frac{\partial \ln \gamma_i}{\partial T}\right) - R\left(\sum_i x_i \ln \gamma_i\right) \qquad (2.11)$$

$$H^E = -RT^2\left(\sum_i x_i \frac{\partial \ln \gamma_i}{\partial T}\right) \qquad (2.12)$$

$$G^E = RT\left(\sum_i x_i \ln \gamma_i\right) \qquad (2.13)$$

$$V^E = RT\left(\sum_i x_i \frac{\partial \ln \gamma_i}{\partial P}\right) \qquad (2.14)$$

A complete listing of the other thermodynamic properties can be found in Reference (6). Thus, a knowledge of the activity coefficients and their variation with temperature and pressure would enable us to compute other thermodynamic properties of solutions.

From Equations (2.1) and (2.2) the criterion for vapor-liquid equilibrium in terms of fugacities would be

$$\hat{f}_{il} = \hat{f}_{iv} \qquad (2.15)$$

where $\hat{f}_{il}$ = partial fugacity of component i in liquid

$\hat{f}_{iv}$ = partial fugacity of component i in vapor.

In terms of activity coefficients, the relationship is given by

$$\gamma_i^L x_i f_i^L = \gamma_i^V y_i f_i^V \qquad (2.16)$$

Vapor phase fugacities could be calculated using an equation of state applicable to the component under consideration, and liquid phase fugacities from that of the vapor using conventional techniques. At moderate pressure, the virial equation of state truncated to two terms could be suitably employed (6) to evaluate fugacities. Complete development of equations is given by Van Ness. Using the virial equation of state, for a binary solution, liquid phase activity coefficient could be shown to be given by

$$\ln \gamma_1^L = \ln \frac{\pi y_1}{x_1 P_1^o} + \frac{(\beta_1 - v_1^L)(\pi - P_1^o)}{RT} + \frac{\pi \delta_{12} y_2^2}{RT} \qquad (2.17)$$

where $\delta_{12} = 2\beta_{12} - \beta_1 - \beta_2$

β_{12} = interaction cross coefficient, related to mixture virial coefficient β by

$$\beta = y_1^2\beta_1 + 2y_1y_2\beta_{12} + y_2^2\beta_2$$

β_1 & β_2 = component virial coefficients

π = total pressure

P^o = pure component vapor pressure at solution temperature T

x = mole fraction in liquid phase

y = mole fraction in vapor phase

v^L = component liquid molal volume at solution temperature.

A similar expression could be written for the second component. Equation (2.17) allows the calculation of liquid phase activity coefficient from vapor-liquid equilibrium data, volumetric information and pure component vapor pressure. Conversely, if liquid phase activity coefficients, volumetric information and vapor pressures are available, precise vapor-liquid equilibrium data could be computed.

Experimental virial coefficients may be used in Equation (2.17) when such data are available. In the absence of experimental data, these coefficients are usually estimated. A number of authors (8,9,10,11,12,13) have correlated virial coefficient data as a function of critical constants and reduced temperature and other characteristic parameters like the acentric factor. Prausnitz (14) has correlated mixture virial coefficients from pure component virial coefficients and suitable combining rules. In the same article he presents equations for vapor phase activity coefficients of a gas mixture, and gives several excellent illustrative examples. However, the combining rules for highly polar gas mixtures are not sufficiently accurate and further work in this direction would be of immense use.

The third term in the right-hand side of Equation (2.17) represents vapor phase activity coefficient which is a measure of nonideal solution behavior in the vapor phase. The second term represents the departure of gas phase from ideal gas law behavior and the effect of pressure on liquid fugacity. If the gas phase is ideal with respect to both solution and gas behavior and the effect of pressure on liquid fugacity is neglected, liquid phase activity coefficients in a binary are given by the more familiar expressions

$$\gamma_1^L = \frac{\pi\, y_1}{P_1^o x_1} \tag{2.18}$$

$$\gamma_2^L = \frac{\pi\, y_2}{P_2^o x_2} \tag{2.19}$$

The effect of temperature and pressure on activity coefficients is given by the following expressions:

$$\left(\frac{\partial \ell n \gamma_i}{\partial T}\right) = \bar{H}_{iR}/RT^2 \qquad (2.20)$$

$$\left(\frac{\partial \ell n \gamma_i}{\partial P}\right) = \bar{V}_{iR}/RT \qquad (2.21)$$

where $\bar{H}_{iR}$ = relative partial molal enthalpy of solution

= difference between molal enthalpy of pure liquid and partial molal enthalpy in the solution at the composition under consideration

$\bar{V}_{iR}$ = relative partial molal volume

= difference between molal volume of pure liquid and partial molal volume in the solution under consideration.

2.3 Testing and Correlation of Vapor-Liquid Equilibrium Data

2.3.1 Gibbs-Duhem Equation

The fundamental consideration in the validity of phase equilibrium data is how well the data obey the Gibbs-Duhem equation. This equation, as is well known, could be derived in the differential form from the principles of classical thermodynamics. It expresses the variation of partial molal excess Gibbs free energy with composition, and cannot be integrated in a rigorous way. However, it serves as a powerful guide in correlating and testing phase equilibrium data.

In terms of fugacity, the Gibbs-Duhem equation for a binary mixture could be expressed as

$$x_1 d\ell n\hat{f}_1 + x_2 d\ell n\hat{f}_2 = \frac{1}{RT}(vdP - sdT) \qquad (2.22)$$

where s = molal entropy

v = molal volume of the liquid mixture.

The above expression is a general form of the Gibbs-Duhem equation applicable to vapor-liquid equilibrium and has been used extensively in much simpler forms. It is possible to simplify the equation by confining the system to constant temperature or pressure. It is not possible to restrict vapor-liquid equilibrium problems to both constant temperature and pressure because of the phase rule constraints. It can be shown from Equation (2.22) that at constant temperature

$$\frac{d\ell n\gamma_1}{d\ell nx_1} - \frac{d\ell n\gamma_2}{d\ell nx_2} = \frac{\Delta V}{RT}\left(\frac{dP}{dx_1}\right) \qquad (2.23)$$

and at constant pressure

$$\frac{d\ell n\gamma_1}{d\ell nx_1} - \frac{d\ell n\gamma_2}{d\ell nx_2} = -\frac{\Delta \bar{H}}{RT^2}\left(\frac{dT}{dx_1}\right) \qquad (2.24)$$

where ΔV = volume change on mixing

ΔH = integral heat of mixing per mole of solution.

The right-hand side of these two expressions must be evaluated from volume and enthalpy of mixing measurements, and the left-hand sides by differentiation of x-$\log\gamma$ data.

2.3.2 Thermodynamic Consistency

2.3.2.1 General Problem

Gibbs-Duhem equation and its special integral forms are quite extensively used to test the thermodynamic consistency of vapor-liquid equilibrium data. Dodge (1) and Smith (5) give several illustrative examples on testing of experimental data for consistency.

Because inaccuracies often appear in experimental data through human and mechanical errors, the subject of consistency of data is often given careful consideration. If erroneous data go undetected, incorrect conclusions might be drawn about a design or theory. Although consistency tests are designed to aid in screening correct data from erroneous data, approximate forms of these tests might indicate that erroneous data are consistent or vice-versa. On the other hand, rigorous compliance of the data with the tests based on the Gibbs-Duhem equation need not necessarily be correct since incorrect data might fortuitously satisfy the equation. However, those data that do not obey the Gibbs-Duhem relationship may be rejected as erroneous.

A number of methods have been described in the literature for the treatment and correlation of activity coefficient data. Lu, Spinner and Ho (15) have made a complete review and proposed a number of visual methods for testing thermodynamic consistency of binary vapor-liquid equilibrium data. A system of flexible methods of thermodynamic analysis of experimental vapor-liquid equilibrium data have been reviewed by Redlich, et al. (16) and Murthy, et al. (17). Edmister and Robinson (18) have made a systematic treatment and critical review of the methods available to test data and show the discrepancy associated with the universal neglect of heats of mixing and volumes of mixing terms in the Gibbs-Duhem equation, and general inadequacy of the area test. The following is a brief outline of the commonly used thermodynamic consistency tests.

2.3.2.2 Differential Method

At constant temperature and pressure, the Gibbs-Duhem equation for a binary mixture can be rearranged to give

$$\frac{d\ell n\gamma_1}{dx_1} = \frac{x_2}{x_1}\frac{d\ell n\gamma_2}{dx_2} \qquad (2.25)$$

Thus, the slopes of x-$\ell n\gamma$ curves form the basis of detecting systematic experimental errors. In a rigorous thermodynamic sense, the sum of the two terms in Equation (2.25) must equal the correction factors which take into account the effect of neglecting the heats or volumes of mixing terms in the general Gibbs-Duhem equation. However, the magnitude of such corrections may be, in many cases, much smaller compared to the uncertainty in determining slopes from slightly scattered experimental data.

2.3.2.3 Integral Methods

There are a number of mathematical expressions which satisfy the Gibbs-Duhem equation and are inherently thermodynamically consistent. These algebraical expressions could be regarded as particular solutions of the Gibbs-Duhem equation. The method of treating data under this category involves the choosing of a proper suffix equation that represents the activity coefficient composition data best. However, inadequacy of the selected equation to represent experimental data need not necessarily mean that the data are inconsistent.

The excess Gibbs free energy represents nonideal behavior in a solution due to intermolecular forces, and differences in size and shape of the molecules. Wohl (19) has developed a general expression to represent excess free energy in terms of composition, effective molal volume and volumetric composition. Based on Wohl's equations, several simpler equations have been developed. Two and three suffix, van Laar and Margules equations may be cited under this category. Redlich and Kister have expressed variation of activity coefficients with composition in a polynomial form, and modifications of these equations presented by Chao have been used extensively. All these algebraical equations are given in Reference (3).

Wilson (20) has recently developed a semi-theoretical expression to represent the excess Gibbs free energy and hence activity coefficients. His expressions for activity coefficients are given by

$$\ell n\gamma_1 = -\ell n\,(x_1+\Lambda_{12}x_2) + x_2\,\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right] \qquad (2.26)$$

$$\ell n\gamma_2 = -\ell n\,(x_2+\Lambda_{21}x_1) - x_1\,\left[\frac{\Lambda_{12}}{x_1+\Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1+x_2}\right] \qquad (2.27)$$

where Λ_{12} and Λ_{21} are Wilson's parameters.

Orye and Prausnitz (21) have tested the usefulness of Wilson's equation, and from the results of about sixty binary mixtures of varied chemical structure, they concluded that Wilson's equation was the best two-parameter equation available.

Renon and Prausnitz (22) later proposed a three-parameter equation, similar to that of Wilson, after a critical discussion on the use of local compositions to represent the excess Gibbs free energies of liquid mixtures. This equation is based on Scott's two-liquid model and an assumption of non-randomness similar to that of Wilson. They also present a general discussion on Wilson and Heil's (23) equations. The superiority of their N.R.T.L. (non-random two-liquid) equation, particularly to represent mixtures of limited miscibility, for which Wilson's equations totally fail, is also clearly demonstrated.

All the analytical equations used to represent activity coefficients have four principal uses:

1. Correlation of scattered data; a smoothed line which is thermodynamically consistent will greatly simplify correlation of scattered data points.

2. Calculation of complete vapor-liquid equilibrium data from only one precise experimental measurement such as the azeotropic point.

3. Storage of a vast amount of experimental data by just specifying the equation and its constants.

4. Prediction of multicomponent data from sets of binary data.

2.3.2.4 Redlich-Kister Area Criterion

The area test for thermodynamic consistency developed by Redlich and Kister could be summarized by

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad (2.28)$$

i.e., the algebraic sum of the areas under x_1 versus $\log \gamma_1/\gamma_2$ curve should be equal to zero. This is strictly true for constant temperature and pressure, and correction factors must, therefore, be applied for accurate application of the area test. Further, as demonstrated by Steinhauser and White (24), the data in the dilute concentration zones are most unreliable, making smoothing in this region of questionable accuracy. Thus, the area test would give no indication of the correctness of the data when the validity of the smoothed line itself is questionable.

2.3.2.5 Herington's Criterion

The area test for constant pressure systems should be

$$\int_0 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = \int_0^1 - \frac{\Delta H}{2.303RT^2} \left(\frac{dT}{dx_1}\right) dx_1 \qquad (2.29)$$

Herington (25) has devised a testing method for these non-isothermal systems given by

$$D - J < 10$$

where $D = \frac{|I|}{\Sigma'} (100)$

$J = 150\ (\theta)\ /\ T_{max}$

$$I = \int_0^1 \log \frac{\gamma_1}{\gamma_2} dx_1$$

$$\Sigma' = \int_0^1 \left|\log \frac{\gamma_1}{\gamma_2}\right| dx_1$$

$$\theta = T_{max} - T_{min}$$

T_{max} = maximum temperature

T_{min} = minimum temperature

Herington's criterion is also subject to the same weakness as the area test, particularly when dealing with scattered data.

2.3.2.6 Lu, et al., Local Consistency Test

Lu, Spinner and Ho (15) have presented several useful visual aids in checking the data. They are:

1. when x = 0.5

$$\frac{d\log\gamma_1}{dx_1} = -\frac{d\log\gamma_2}{dx_1} \qquad (2.30)$$

Therefore, at x = 0.5, the slopes of the x-logγ curves should be equal but opposite in sign.

2. The points of intersection of the curves with the vertical axes are designated as "end values" defined by

$$\lim_{x_1 \to 0} \log\gamma_1 = A_{12}$$

$$\lim_{x_1 \to 0} \log\gamma_2 = A_{21}$$

At $x_1 = 0.5$

$$\log\gamma_1 = 0.25\ A_{21}$$

$$\log\gamma_2 = 0.25\ A_{12}$$

This is not strictly true but a convenient approximation. It should serve as a useful guide while smoothing erratic and inadequate data.

3. At $x_1 = 0.25$

$$\log\gamma_1 \approx \log\gamma_2 \quad \text{at} \quad x_1 = 0.75$$

This, again, is an approximation.

4. If there is no maximum or minimum in the curves, all data points should be on the same side of the composition axis.

5. If there is a maximum or minimum in one curve, there should be a corresponding minimum or maximum in the other curve.

2.3.2.7 Van Ness' Composition Resolution Test

Integral and area tests rely on an overall evaluation in which regional inconsistencies may be obscured due to mutual cancellation. To overcome this difficulty Van Ness (6) has described a composition resolution test for checking the local consistency of activity coefficient data.

Thermodynamic consistency of experimental data is assessed by resolving the function G^E/x_1x_2RT into a set of thermodynamically consistent activity coefficient functions. A comparison of calculated and experimental coefficients provides an assessment of the local consistency. For a binary the following relations are valid:

$$\frac{\ell n \gamma_1}{x_2} = x_2 \left[\frac{2G^E}{x_1 x_2 RT} - I_0\right] - \delta \qquad (2.31)$$

$$\frac{\ell n \gamma_2}{x_1} = x_1 \left[\frac{2G^E}{x_1 x_2 RT} - I_0\right] + \delta \qquad (2.32)$$

where $\delta = - \frac{H^E}{RT^2} \frac{dT}{dx_1}$ for isobaric data (2.33)

$\delta = - \frac{V^E}{RT^2} \frac{dP}{dx_1}$ for isothermal data (2.34)

I_0 & I_1 = intercepts of the tangent to the free energy function at the composition under consideration.

2.3.2.8 Discussion

It is easily recognizable that any rigorous test for thermodynamic consistency inevitably requires data on heats of mixing or volumes of mixing, depending on whether the experiment is carried out under isobaric or isothermal conditions. Such data are seldom available. Further, there is no generally acceptable smoothing technique for scattered data. The degree of scatter depends on several factors, such as the analytical accuracy achieved in the analysis of the phases, random errors in temperature and pressure measurement, and the concentration range under consideration. Available testing procedures are invaluable in detecting systematic errors, but there is no method for designating experimental data as unquestionably correct.

The most serious error in vapor-liquid equilibrium measurement from which activity coefficient data are usually derived is the achievement of improper equilibrium between phases. Errors might also be introduced due to poor still design, particularly those due to superheating and condensation effects. These systematic errors could be overcome by proper choice of the still, and testing the still with mixtures for which independent experimental data are available for comparison. Once there is sufficient degree of confidence in the performance of the still, and the measurement of the true equilibrium temperature and pressure, the accuracy of data would then depend on the analytical technique. However, random errors cannot be avoided in experimentation though they could be minimized by proper analytical and sample handling techniques. Once these conditions are achieved in practice, subjecting data to consistency tests need not be essential, if the general guidelines are observed in smoothing scattered data. Selection of proper analytical equations which are thermodynamically consistent and fitting experimental data to these equations would serve at least the same purpose as subjecting the data to uncertain test procedures.

Nomenclature

A_{12}	end value of $\log\gamma_1$
A_{21}	end value of $\log\gamma_2$
D	parameter in Herington's criterion
f	fugacity

$\hat{f}$	partial fugacity given by Equation (2.2)
G	Gibbs free energy
H	enthalpy
$\overline{H}_{iR}$	relative partial molal enthalpy of solution
I_0 & I_1	intercepts of the tangent to the free energy function
J	parameter in Herington's criterion
P	pressure
P^o	pure component vapor pressure
R	gas constant
S	entropy
T	temperature (absolute)
v	molal volume
$\overline{V}_{iR}$	relative partial molal volume of solution
x	mole fraction in liquid
y	mole fraction in vapor

Greek Letters:

β	virial coefficient
β_{12}	mixture virial coefficient
γ	activity coefficient
Δ	change of property
δ	parameter given by Equations (2.33) and (2.34)
Λ_{12} & Λ_{21}	Wilson's parameters
θ	$T_{max} - T_{min}$
π	total pressure

Subscripts:

i	component i

il	component i in liquid
iv	component i in vapor
max	maximum
min	minimum
1	component 1
2	component 2

Superscripts:

L	liquid
V	vapor
id	ideal
*	standard state value

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3. PREDICTION OF VAPOR-LIQUID EQUILIBRIUM

3.1 Introduction

Much investigation is being carried out in the field of predicting thermodynamic properties of non-electrolyte solutions with particular attention to vapor-liquid equilibria, primarily to provide data for use in engineering design and for the formulation of thermodynamic models. Work on the nature of intermolecular forces and theories of solution is also quite considerable. An up-to-date review of the work in this field appears regularly in Annual Reviews of Physical Chemistry. Guggenheim (1) and Prigogine (2) have written excellent monographs on the theories of solution.

In spite of the vast amount of fundamental work on mixtures, the theoretical description of solution phenomena is far from satisfactory. This is particularly true for mixtures involving polar compounds which are of great practical interest to the chemical engineer.

Semi-empirical methods, on the other hand, appear to be quite promising in providing guidelines in predicting data for applied needs, particularly in screening of separation processes. For our discussion, these methods could be classified into two categories: (1) extension of Hildebrand's regular solution theory, and (2) group contribution methods.

The present chapter gives a general review of the previous work on the prediction of liquid phase activity coefficients in mixtures containing polar compounds. Detailed and complete reviews can be found elsewhere (3) and only work relevant to the present study is included here.

3.2 Regular Solution Theory and Its Extension

Scatchard and Hildebrand's (4) theory of regular solutions, sometimes referred to as solubility parameter theory, assumes that:

1. the molecules are spherical and nonpolar;
2. only London dispersion forces prevail and molecular orientation is random;
3. the volume change on mixing is zero.

Their expression for excess Gibbs free energy and activity coefficients for a binary solution are given by

$$G^E = (x_1v_1 + x_2v_2)(C_{11} + C_{22} - 2C_{12})\, z_1z_2 \quad (3.1)$$

$$\log\gamma_1 = \frac{v_1 z_2^2}{2.303RT}(\delta_1 - \delta_2)^2 \quad (3.2)$$

$$\log\gamma_2 = \frac{v_2 z_1^2}{2.303RT}(\delta_1 - \delta_2)^2 \quad (3.3)$$

where C_{11} & C_{22} = cohesive energy densities (also called internal pressures) of like pairs of molecules given by Equations (3.6) and (3.7)

C_{12} = cohesive energy density of unlike pair molecules given by Equation (3.8)

$$z_1 = x_1v_1/(x_1v_1 + x_2v_2) \quad (3.4)$$

$$z_2 = x_2v_2/(x_1v_1 + x_2v_2) \quad (3.5)$$

δ_1 & δ_2 = solubility parameters of components 1 and 2, and given by Equations (3.6) and (3.7)

$$C_{11} = \delta_1^2 = (\Delta H_{1vap} - RT)/v_1 \qquad (3.6)$$

$$C_{22} = \delta_2^2 = (\Delta H_{2vap} - RT)/v_2 \qquad (3.7)$$

ΔH_{1vap} & ΔH_{2vap} = latent heats of vaporization of components 1 and 2, respectively

x_1 & x_2 = mole fractions

v_1 & v_2 = molar volumes

T = temperature

R = gas constant

In arriving at Equations (3.2) and (3.3), it is further assumed that Berthelot's geometric mean rule is applicable for unlike pair cohesive energy density, giving

$$C_{12} = \sqrt{C_{11}\, C_{22}} \qquad (3.8)$$

The solubility parameter theory is a very good approximation for non-polar molecular systems, but it should not be used when there are reasons for suspecting the validity of the fundamental assumptions involved. In particular, it should not be expected to be applicable to systems involving polar compounds.

The importance of polarity of molecules in solution behavior is easily recognized and attempts have been made to take into account the effects of polarity into solution nonideality. Van Arkel (5) introduced into Hildebrand's equation for limiting activity coefficient a correction factor to account for the orientation forces. His expression is given by

$$\log\gamma_i = \frac{v_i}{2.303RT} z_j^2 [(\delta_i-\delta_j)^2+(\omega_j-\omega_i)^2] \qquad (3.9)$$

The term $(\omega_j-\omega_i)$ is given by the relation

$$(\omega_j-\omega_i) = \frac{3.25 \times 10^7}{v_j^2\ RT} [\frac{\mu_j^2}{\sqrt{v_j}} - \frac{\mu_i^2}{\sqrt{v_i}}] \qquad (3.10)$$

where μ_i & μ_j = the dipole moments of pure components.

Quantitative testing of this extension does not appear to have been carried out, perhaps because of the obvious inadequacy of the equation to predict negative deviations from Raoult's law.

Martire (6) introduced as an improvement a semi-empirical parameter K given by

$$K = C \frac{\delta_j\ v_i}{\delta_i\ v_j} \qquad (3.11)$$

The constant C can be determined for a whole group of compounds from gas chromatographic measurements. Martire's equation for limiting activity coefficient is given by

$$\log\gamma_i^o = \frac{v_i}{2.303RT} [(\delta_j-\delta_i)^2+(\omega_j-\omega_i)^2-K] \qquad (3.12)$$

The derivation and method of determining C for a homologous series is given in Reference (6). The author tested this equation on many systems composed of polar and nonpolar constituents with an average deviation in the limiting value of about ± 3 percent. But this method suffers from the disadvantage that the value of C must be determined experimentally.

Finch and Van Winkle (7) made an extension of regular solution theory on the same lines as suggested by Van Arkel and devised empirical correction factors correlated in terms of "internal pressures; polar and nonpolar". They have tested the modified form on twelve polar-nonpolar binaries with a maximum deviation in the predicted value of y of about 15 percent and an average deviation of 4 percent.

Erdos (8) joined Scatchard's method with Langmuir's (9) concept of surface area of the molecule as being related to molecular interaction and derived an equation which can be written in the form,

$$\log\gamma_i^o = \frac{[P_i]^{2/3}}{2.303RT}(\delta_i' - \delta_j')^2 \qquad (3.13)$$

where $[P_i]$ denotes the parachor of the pure component i. The adjusted solubility parameters are defined by the equations

$$(\delta_i')^2 = \frac{\Delta H_{ivap} - RT}{[P_i]^{2/3}} \qquad (3.14)$$

$$(\delta_j')^2 = \frac{\Delta H_{jvap} - RT}{[P_i]^{2/3}} \qquad (3.15)$$

Erdos tested his equation on eleven binary mixtures of alcohols and water to predict van Laar's constants within 3 percent. This method again is applicable for mixtures showing positive deviations only, but has the advantage of using only pure component data to predict binary vapor-liquid equilibrium. Erdos also assumes as in Scatchard's theory that the entropy of mixing is that of an ideal solution.

Gilmont, Zudkevitch and Othmer (10) modified Erdos' method by adding an adjustable parameter, called the "field factor", to take into account the error introduced due to assuming ideal entropy of mixing in Erdos' model. They divided the pure components into ten classes, an extension of Ewell's (11) classification of liquids based on their tendency to form hydrogen bonds, and every binary combination of these compounds is characterized by a field factor. The authors tested their method on a large variety of binary mixtures and claimed an accuracy of 1.7 percent in the predicted value of y. Subsequent testing of the method by Hala, et al. showed "much worse agreement" than was originally claimed by the authors.

Redlich, Kister and Turnquist (12) have presented relations for approximate calculation of the constants in their third order activity coefficient equations for systems whose constituents neither associate nor form hydrogen bonds. Their expressions for B and C are given by

$$B = 0.869\left(\frac{\delta_1}{\sqrt{v_1}} - \frac{\delta_2}{\sqrt{v_2}}\right)^2 \frac{v_1 v_2}{RT(v_1+v_2)} \tag{3.16}$$

$$C = B\,(v_2-v_1)/(v_2+v_1) \tag{3.17}$$

where δ_1 & δ_2 are the solubility parameters, v_1 & v_2 the molar volumes, and B & C are the constants in their two constant equations representing activity coefficient as a function of composition. Though the method gave satisfactory agreement for nonpolar mixtures, it cannot be expected to provide similar estimates for mixtures involving polar compounds.

Prausnitz and Anderson (13), in an excellent article on the solvent selection in hydrocarbon extractive distillation, discuss the various forces that contribute to nonideality and present a thermodynamic and physico-chemical analysis of the solution phenomenon. In a later article Weimer and Prausnitz (14) take into account these physico-chemical effects in a quantitative way and present a correlation to predict activity coefficient at infinite dilution for paraffins, naphthenes, pentene and benzene in a large variety of polar solvents. The model is essentially an extension of regular solution theory and their final expression for excess Gibbs free energy is given by

$$G^E = z_1 z_2 (x_1 v_1 + x_2 v_2)[(\delta_1 - \delta_2)^2 + \tau_1^2 - 2\psi_{12}] + x_1 \ln \frac{z_1}{x_1} + x_2 \ln \frac{z_2}{x_2} \qquad (3.18)$$

where δ_1 & δ_2 = nonpolar solubility parameters
τ = polar solubility parameter
ψ_{12} = term representing induction energy between the polar and nonpolar species

They have described Bondi and Simkin's (15) "homomorph" approach as modified later by Anderson (13) to evaluate the nonpolar cohesive energy density. The polar and nonpolar solubility parameters were thus computed for forty polar solvents. They have correlated infinite dilution activity coefficient data to within ± 10 percent, and present empirical relations for the induction energy term for paraffins, pentene and benzene in a number of polar solvents as a function of nonpolar solubility parameter.

Helpinstill and Van Winkle (16) adopted the same lines of thought as Weimer and Prausnitz and extended their correlation to include the case where both components are polar. The concept of dividing the solubility parameter into polar and nonpolar parts and their computation using homomorph plot is similar to that of Prausnitz. Their data on infinite dilution activity coefficients for a number of hydrocarbons in polar solvents showed agreement within ± 13.5 percent. The correlations are reported to be valid over a wide range of temperature between $0^\circ C$ to $125^\circ C$.

3.3 Group Contribution Methods

Prediction of pure component properties using the method of group contributions from the atoms and groups of atoms present in the molecule has become highly successful (17). A summary of the different methods is given by Janz (18). However, a similar analogy to represent mixture properties is poor. In the case of pure components we are concerned with intramolecular forces; but in mixtures, intermolecular forces and specific interactions like hydrogen bonding are encountered. Nonetheless, attempts have been made to predict solution properties considering it to be a mixture of the groups which make up the components of the solution.

Deal and Derr (19) have recently made an extensive review of the ways in which activity coefficients of components in solution can be predicted by using the idea of characteristic structural group contributions. Nonetheless, a brief review of the important works in this line is in order.

The earliest description of a model to predict mixture properties appears to have been proposed by Langmuir (9) with the formulation of his "principle of independent surface action". He arrived at the following expressions for the partial vapor pressures in a mixture of two components.

$$p_1 = P_1 x_1 e^{S_1 \emptyset \alpha_2^2 / kT} \tag{3.19}$$

$$p_2 = P_2 x_2 e^{S_2 \emptyset \alpha_1^2 / kT} \tag{3.20}$$

where p_1 & p_2 = partial pressures

P_1 & P_2 = pure component vapor pressures

S_1 & S_2 = surface areas of the molecules

α_1 & α_2 = surface fractions

k = Boltzman constant

$\emptyset$ = "mixture energy constant", function of surface fractions and interfacial energy.

Langmuir, in spite of his initial enthusiastic description of the model, did not pursue it further for testing. Smythe and Engel (20) applied Langmuir's model to test vapor-liquid equilibrium in a number of polar-nonpolar mixtures, and attributed the failure of the model to its inadequacy to consider size and shape of the molecules, particularly molecular dipole interactions.

Butler (21) measured Henry's law constants and arrived at simple correlations relating terminal activity coefficients to solute carbon number. He indicated the systematic shift of these graphical correlations depending upon the nature of the polar grouping in the solute.

Redlich, Derr and Pierroti (22) proposed a group interaction model essentially on the same lines as Langmuir. They assumed that the interaction energy can be represented as the sum of the contributions of pairs of interacting groups. The contribution of each pair of groups is assumed to be independent of the nature of the molecules involved and dependent on the group concentration. Papdopoulos and Derr (23) predicted enthalpies of hydrocarbon mixtures using the model, and insufficient experimental data at that time hindered conclusive tests on the model. Chao and co-workers (24) later modified Redlich's model to apply to solutions containing polar substances by taking local group concentrations into account as described by Wilson (25). They also described a method of evaluating group surfaces using covalent and van der Waal's radii. The model appears to predict heats of mixing of a number of polar-nonpolar mixtures quite satisfactorily. Extension of the model to excess free energies of mixing by combining with suitable expression for entropies of mixing would be interesting. However, the understanding of solution entropy is very limited at the present time.

One of the significant advancements in the correlation and prediction of activity coefficients, based on group contributions, was presented by Pierroti and co-workers (26). Structural parallelism based on observed changes of the limiting activity coefficient with molecular weight, molecular configuration and function group type form the basis of their correlations. The authors correlated the activity coefficients at infinite dilution for many classes of substances in a few solvents such as water, paraffins, alcohols and ketones. Their equation for γ^o is given by

$$\log\gamma_1^o = A_2 + B_2 n_1/n_2 + C_1/n_1 + D(n_1-n_2)^2 + F_2/n_2 \qquad (3.21)$$

A_2, B_2, C_1, D and F_2 in the above equation are characteristic constants, and n_1 and n_2 are the number of carbon atoms in the hydrocarbon radicals. A similar expression is given for $\log\gamma_2^o$. The procedure of obtaining γ^o values is quite simple, merely involving the substitution of the constants in the equations. The authors have tabulated these constants for various temperatures. However, this method, though very approximate (deviation in γ^o value ranging from ± 3 percent to ± 84 percent), is applicable only for five systems; that is, only for five systems can both $\log\gamma_1^o$ and $\log\gamma_2^o$ be computed. For all the other systems listed, only the solute $\log\gamma^o$ can be computed. The five systems which can be calculated are n-alcohols-water, n-ketones-water, sec-alcohols-water, n-ketones-paraffins and ethyl alcohol-paraffins.

Wilson and Deal (27) have proposed a model for predicting activity coefficients as a function of composition. Their "solution of groups" approach estimates the partial molal excess Gibbs free energy as the sum of group contributions and provides a concentration dependency of these group contributions. The model is based on four postulates which state that:

1. Experimental activity coefficient could be divided into two parts: (1) group contribution due to interaction of groups, and (2) entropy contribution associated with size effects. Mathematically,

$$\log\gamma_K = \log\gamma_K^G + \log\gamma_K^S \tag{3.22}$$

where γ_K = molecular activity coefficient

γ_K^G = group contribution

γ_K^S = size contribution

2. Size contribution is given by Flory-Huggins (28,29) expression developed for athermal solutions.

3. The group contribution is assumed to be the sum of contributions of each group referred to the same standard state.

4. The group contribution is a unique function of a group composition.

Wilson and Deal applied their model to a number of binaries and fairly good agreement between experiment and prediction was realized. The general agreement in logarithms of the activity coefficients were estimated to be within about 10 percent. However, in fitting data on systems containing water, they assumed water molecule to be consisting of 1.5 hydroxyl groups.

Scheller (30) later used Wilson's model to predict activity coefficients in alcohol-water systems and certain polyols. He has calculated the term with molar volumes rather than group numbers as was originally used by Wilson. He arrived at a value of 1.6 hydroxyl groups for water to reasonably fit the experimental data (within 10 percent in γ).

Ratcliff and Chao (31) modified Wilson's model by replacing the entropy term (given by Flory-Huggins equation) with a skeletal contribution term given by Broensted and Koefoed's (32) theory of congruence. The authors gave a more meaningful interpretation to the standard state group activity coefficients and successfully predicted vapor-liquid equilibrium data on a number of alcohol-water systems without having to assume water to be made up of 1.5 hydroxyl groups. Testing of the model on other systems was hampered due to lack of sufficient data. Ratcliff and Chao's model has been extended successfully (33,34) to predict heats of mixing and viscosities of mixtures.

During the preparation of the present thesis, some rather interesting work of Derr and Deal (35) has appeared which extends Wilson's model to an "analytical solution of groups". This involved representing group activity coefficient-group composition data by Wilson's (26) activity coefficient expression and evaluating the interaction parameters. Use of binary interaction parameters to predict multigroup activity coefficients seems to be very promising and their results quite encouraging. They have demonstrated the calculations on a large variety of polar-nonpolar mixtures.

Barker (36) has used a quasi-lattice picture of the mixture to predict solution properties. Each molecule in the solution is assumed to occupy certain number of sites on a well-defined lattice. Each site so occupied is identified with a particular group of a molecule. Each site is considered to have a certain coordination number which refers to the number of possible directions on surfaces of contact of the group at a given site with other groups of either the same molecule or a different molecule. Barker applied his theory to fit the experimental free energy and heats of mixing data for methanol-benzene and methanol-carbontetrachloride systems. Representation of the data by the model appears to be satisfactory.

Sweeny and Rose (37), in an application of Barker's theory to alcohol-ester systems, represented the physical picture of the liquid similar to that of Barker and evaluated the various interaction energies from one base system and used these parameters to predict the data on other systems. The predicted vapor-liquid equilibrium data are reported to be within the experimental error and the activity coefficients to be within about 10 percent.

Lewell and Kristmanson (38) applied the same model to binary mixtures containing alcohols and ketones. They have used isobaric data from the literature and report the accuracy of prediction to be falling as the boiling point difference between the two components widens.

Except for the tedious trial-and-error calculations involved in the model to obtain interaction parameters, after a particular configuration is given to the molecule on the lattice, Barker's approach might offer grounds for further study.

3.4 Summary and Conclusions

Though there are a number of different methods available for the estimation of activity coefficient data, there appears to be no suitable model applicable for all systems. Regular solution theory, although it requires data only on pure components, is applicable only to a few special mixtures of nonpolar compounds. Serious errors can result if the model is applied to systems involving polar compounds unless accommodation is made for polarity effects. Attempts to account for polarity in a quantitative way have resulted only in little success. The extensions of regular solution theory proposed by Weimar and Prausnitz, and Helpinstill and Van Winkle, correlate only the infinite dilution activity coefficients of hydrocarbons in other solvents. Neither of the correlations are applicable to strongly polar solutes, nor to compounds which are strongly associating such as alcohols.

Group solution models have the advantage of being able to predict activity coefficients from a minimum of experimental information. Ratcliff and Chao's model has been applied successfully to some strongly polar mixtures. However, further testing of the model on systems involving other functional groups is hampered by a lack of systematic isothermal equilibrium data (activity coefficients are more sensitive to temperature than pressure, and as such isothermal data are preferred for model testing). Such data is very much needed for testing and extension of the group solution to other functional group systems.

Nomenclature

A	constant
B	constant
C	constant
C_{11} & C_{22}	cohesive energy densities of like pairs of molecules (1,1 and 2,2)
C_{12}	cohesive energy density of unlike pair of molecules (1,2)
D	constant
F	constant
G	Gibbs free energy
ΔH_{vap}	latent heat of vaporization
k	Boltzman constant

K	parameter in Equation (3.12)
n	number of carbon atoms in hydrocarbon radical
p	partial pressure
P	pure component vapor pressure
$[P]$	parachor
R	gas constant
S	surface area of molecule
T	absolute temperature
v	molar volume
w	correction factor in Equation (3.9)
x	mole fraction in liquid
z	volume fraction

Greek Letters:

α	surface fraction
γ	molecular activity coefficient
δ	solubility parameter
δ'	adjusted solubility parameter
ϕ	mixture energy constant
ψ_{12}	induction energy term in Equation (3.18)
μ	dipole moment
τ	polar solubility parameter

Subscripts:

1 & 2	components 1 and 2
i, j & k	molecular species i, j and k

Superscripts:

E	excess property
G	group term
o	terminal value
S	size term

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4. EXPERIMENTAL METHOD

4.1 Introduction

Almost all solutions of practical interest neither exhibit ideal behaviour, nor can their equilibrium relations be predicted from purely theoretical considerations. Recourse to experimental measurement will undoubtedly be required in arriving at equilibrium data necessary for engineering designs and testing of models until satisfactory methods of estimation are developed.

Measurement of activity coefficients in solution and, hence, the determination of the properties of coexisting phases at equilibrium as a function of composition, can be achieved in a number of ways. Hala et al. (1) have described in detail the various techniques employed for this purpose. The two most commonly used methods are:

1. the total pressure-composition method
2. direct measurement of the composition of equilibrium phases at constant temperature or pressure.

In the former case, a liquid of known composition is placed in a measuring cell, the air is evacuated from the apparatus, and the liquid and vapor phases are allowed to reach equilibrium. The resulting total pressure is measured for a number of liquid compositions and the vapor compositions are calculated (1,2,3,4,5,6). In the latter method, the two phases are brought into equilibrium in a still, operating either at constant temperature or pressure, and their compositions are analysed separately to determine the activity coefficients. Direct method is the most widely used technique to collect vapor-liquid equilibrium data. Hala et al. (1) have given a summary of the types, construction and capabilities of the various stills employed in this class of study. Because of the simplicity in construction and operation, and the ability to measure true equilibrium temperature, the Gillespie still (7) is quite extensively used.

A modified design of the Gillespie still was built for the purpose of this investigation. A description of the apparatus, the experimental and analytical techniques employed in the present study, are discussed in the following sections.

4.2 Description of the Apparatus

The equilibrium still used in the present study retains the essential features of the Gillespie still as described by Lu et al. (8). A few modifications are incorporated in the present design and are discussed in Section 4.3.

Details of the still and the experimental set-up are shown in Figures 4.1 and 4.2. The still primarily consists of a reboiler (R) which is filled with the mixture (about 250 ml.) for which data are to be measured. Heating the still is accomplished by an external electrical chord heater (H) wound over the reboiler. Heat input to the reboiler is controlled by regulating the voltage across the heater by a variac (not shown). As the liquid is vaporized, slugs of liquid and vapor are carried through the Cottrell tube (C) to the equilibrium chamber (E), after impinging on the thermowell (T). The thermowell is double-jacketed and vacuum sealed. It contains a copper-constantan thermocouple dipped in a few drops of oil placed in the well. The temperature of the boiling mixture is measured by this thermocouple. The vapor and liquid phases separate in the equilibrium chamber. The vapor travels upward in the annulus, countercurrent to the downcoming heterogeneous mixture, and provides a vapor jacket. The vapor is condensed in a total condenser-subcooler (CR). The liquid sample, disengaged from the vapor, travels through the downcomer (D). The condensed vapor and liquid samples then pass through double-jacketed sampling cells (SC1,SC2), and drop counters. The two samples then enter the return line (RL) and are circulated into the reboiler. The return line from the sampling cells to the reboiler is of capillary construction (2 mm. dia.) to provide dampening effect when the solution is boiling. The sampling cells are provided with sampling ports (SP1,SP2) fitted with 2 mm. bore teflon stopcocks. The equilibrium still is completely made of pyrex glass.

The condenser is connected to a vacuum pump through a flash pot (FP), calcium chloride drying bottle (DR), a large surge tank (ST), and a manostat (MA) by thick-walled rubber tubing. The flash pot serves the emergency purpose of holding any flashed liquid due to the upsets in the still. This prevents contamination and blocking of lines and equipment downstream. A mercury manometer (MN) is connected to the still to indicate the pressure. The needle valve (NV) is used to provide a bleed of air into or out of the system depending on the system pressure. The three-way stopcock (SP) is used to connect the still to either the pressure or vacuum system.

4.3 Present Modifications

The Gillespie still as described by Lu et al., in spite of its accuracy in measuring equilibrium temperature, lacks some features, the absence of which will contribute to errors in the data obtained. They involve:

1. provision for a thorough and immediate mixing of the condensed vapor and liquid samples joining the reboiler
2. adequate mixing of the vapor and liquid samples in their respective cells
3. provision to eliminate contamination of the equilibrium samples by non-equilibrium vapor condensate at the end of the run.

Inadequate mixing of the returning liquid from the sampling cells with the main body of the liquid in the reboiler, can result in several errors. If this liquid is not well mixed immediately on entering the reboiler, concentration gradients will exist resulting in severe flashing. The seriousness of this error will depend on the relative volatilities of the components involved. Second, the vaporization process occuring in the reboiler can be chaotic. Considering a small element of liquid with local concentration gradients moving into the proximity of the heater, there is little certainty of the extent to which this element will be vaporized before being swept away. This results in only pseudo-equilibrium conditions, i.e. small packets of vapor and liquid swept into the Cottrell tube may very well be close to equilibrium on a local basis but may be far from it on a gross basis. A magnetic stirrer coated with teflon (S) is provided in the reboiler to reduce such a possible source of error. This resulted in excellent mixing of the liquid in the reboiler and the start of a nice bubble nucleation from the surface of the stirrer. Further, the vapor bubbles are thoroughly mixed with the boiling liquid before being carried away into the Cottrell tube. This provision also eliminates local hot spots on the still walls and any non-equilibrium vaporization and superheating.

Lu et al. provided double-jacketed sampling cells to facilitate better mixing. In spite of this provision, very clear convection currents could be observed indicating poor mixing of the liquid in the cells. This increases the time to reach equilibrium and also the samples withdrawn may not be representative of equilibrium phase compositions. Adequate mixing is achieved by providing a teflon-coated micromagnetic stirrer in each cell.

The thermal capacity of the heater causes continued vaporization even after the heat to the reboiler is cut off, but the vapors generated are not sufficient to carry the liquid slugs. This pseudo-equilibrium vapor condenses and contaminates the condensed equilibrium vapor sample in the cell. A by-pass line (BP), as shown in Figure 4.1, is provided to overcome this type of error. The sampling cells can be completely isolated by suitably manipulating the stopcocks T1, T2 and T3. The extent of contamination of the samples by the condensed vapor due to surface evaporation can be high in systems with wide relative volatility differences.

As a further improvement, the heat loss from the Cottrell tube and equilibrium chamber is minimized by providing compensatory heating. An external heating tape is wrapped around the asbestos insulation. Temperature at about 3/4 in. from the wall of the equilibrium chamber is measured by a copper-constantan thermocouple and is controlled within ± 2°C of the boiling point of the mixture by an on-off controller. This method, though approximate, certainly decreases the temperature gradient and heat loss. In effect, local condensation is greatly reduced.

4.4 Operation of the Still and Experimental Procedure

The still can be used to determine either isobaric or isothermal equilibrium data. Operation for isobaric data is fairly straightforward. Isothermal determinations, on the other hand, are somewhat difficult involving trial-and-error procedure to arrive at the equilibrium pressure.

After usual cleaning and drying of the still, the needle valve NV (Figures 4.1 and 4.2) is completely opened and the stopcocks T1 and T2 turned to connect the reboiler to the sampling cells. Stopcock T3 is open and SP1, SP2 and SP3 closed. The vacuum pump is started and a slight vacuum (about 200 mm.) is applied by adjusting the bleed through NV. The mixture for which equilibrium data is to be measured is made up into an approximate composition (starting from the dilute end) and charged into the partially evacuated still through SP1, SP2 and SP3 until the two sampling cells and the reboiler are full. The amount of liquid in the reboiler is critical for proper functioning of the still. Lower liquid levels will result in no liquid being pumped through the Cottrell tube, and overfilling of the reboiler will cause excessive level fluctuations and back mixing in the sampling cells. The right amount to be charged can be easily established by running the still a few times and this is usually about 10 to 15 ml. less than the volume of the reboiler. This amount should be just sufficient to fill the reboiler after expansion when heated up to the boiling point.

If operating under constant pressure, the still pressure is adjusted to the required value by the vacuum pump or compressed air (max. 2 atm.) and the manostat is set to control the pressure at this value. The three magnetic stirrers are turned on and cooling water is allowed to circulate through the condenser. Heat is slowly applied to the reboiler and the boiling rate is controlled by adjusting the voltage across the heater so that gentle boiling is achieved and the liquid levels in the drop counters show a slow pulsating action. The temperature controller on the compensatory heating tape is set such that the temperature measured by the two thermocouples are sufficiently close. After a while, usually about two to three hours, the boiling point of the mixture will reach a steady value indicating equilibrium. The still is run for at least another hour to be certain of the equilibrium and the boiling point is measured. Now, the stopcock T3 is closed and T1 and T2 are quickly and simultaneously turned to the by-pass position isolating the cells. The power supply to both heaters is turned off. The sampling cells are chilled by surrounding them with crushed ice. After the evaporation from the still is completely stopped, the still is brought to atmospheric pressure if it was operating under vacuum. If the still is at above atmospheric pressure, it is unnecessary and perhaps unsafe to reduce the pressure. Any sudden reduction in pressure will result in dangerous flashing.

The sampling ports are flushed well with the sample before any attempt is made to collect the samples for analysis. A hypodermic syringe, the needle of which is bent into the form of 'V', is used to withdraw the sample. The needle is inserted into the capillary opening of the sampling port and the sample is allowed to run through the port. The sample is then slowly withdrawn, exercising sufficient caution not to allow any vaporization in the syringe during the process of sampling. The samples are analysed immediately for composition.

The composition change in the still for the next run is achieved by charging the proper pure component to fill the sampling cells.

When operating under isothermal conditions, an approximate guess of the total pressure is made and the still is operated at this pressure to near equilibrium as in the isobaric case. The temperature is measured and compared with the set value for the data. The pressure is adjusted in the right direction to alter the boiling point to the required values and the experiment repeated. These trials are continued until the correct temperature is reached and equilibrium pressure and composition are measured. It is quite advantageous to start with lower pressure and increase it as the trials proceed. As mentioned earlier, it is extremely important not to reduce the pressure of the still suddenly during the run as this might result in very dangerous flashing. If the pressure is to be reduced, the heat to the reboiler must be turned off and the still allowed to cool sufficiently. The pressure is then reduced very cautiously.

4.5 Temperature Measurement and Control

The thermocouples were calibrated at ice point and steam point against a standard thermocouple certified by the National Bureau of Standards, and the voltages generated were identical to the standard copper-constantan thermocouple (within ± 0.5μV; less than ± 0.02°C). As such, the standard calibration data for copper constantan thermocouples in NBS circular 561 were directly used.

The cold junction of the thermocouple is placed in an ice bath. The voltage generated by the thermocouple is measured using a Leeds and Northrup, type K3, potentiometer capable of measuring up to ± 0.5μV. An L & N 9834 electronic null detector is employed to detect the null point. A constant voltage supply source supplied by the same company is used in the potentiometer circuit in conjunction with an Eppley Laboratory Inc. made standard cell (1.0193 volts at 22°C) for current standardization of the potentiometer. The method of standardizing the potentiometer and measurement of E.M.F. are described in detail in the manufacturer's bulletin (9).

In isothermal data measurements, temperature control of the still is indirectly achieved by the control on still pressure. A Fisher supplied thermistemp temperature controller is used to maintain control action on the compensatory heating tape and the temperature is expected to be within 2°C of the boiling point of the mixture.

4.6 Pressure Measurement and Control

The pressure measuring and control system is illustrated in Figure 4.2. A cartesian manostat and a needle valve (NV) are used to control the pressure. The differential pressure is measured by a mercury-in-glass manometer, one limb of which is connected to the system and the other exposed to the atmosphere. Mercury levels are read by a cathetometer. A constant check on atmospheric pressure fluctuation is maintained and the manostat is readjusted accordingly. A Welch duo-seal vacuum pump is used to generate vacuum in the system. When pressure above atmospheric is encountered in the still, it is maintained by a compressed air cylinder connected to the system through a reducing valve and two needle valves in series. When dealing with chemicals that react with air under the conditions of the experiment (like aldehydes), nitrogen is to be used. The method of operation of the cartesian manostat is described in the supplier's bulletin (10).

4.7 Analytical Technique

Samples of equilibrium mixtures were analysed using either refractive index or gas chromatography. The compositions of these samples were determined from calibration charts.

4.7.1 Gas Chromatography

Gas chromatography is employed as the analytical technique in much of the experimental work. A Perkin-Elmer, model 820, gas chromatograph with hydrogen flame ionization detector coupled with a Leeds and Northrup 1mV recorder is used for the purpose. For some systems, the recorder is connected to a Perkin-Elmer, model 194B, digital integrator, to get the area under each peak. The fractional height of the component peak is defined as

$$\text{F.H.C.P.} = \frac{\text{height of the peak of the component}}{\text{sum of the heights of all peaks}}$$

The fractional area of the peak is defined in a similar way. It is evaluated and plotted against the mole fraction to arrive at the calibration chart.

Stainless steel columns (6 ft. by 1/8 in.) containing 3.8 percent "Hallcomid 18" and 0.5 percent "carbowax-600" are used in the chromatograph. The samples are injected manually using Hamilton micro-syringes.

The complete description of the chromatograph and the integrating mechanism is available in the manufacturer's catalogue (11).

The gas flow rates and other conditions of operation are included in the data section and presented for each system separately.

4.7.2 Refractive Index

Refractive indices are measured using a Carl Zeiss refractometer 44143 and sodium light. The refractometer is capable of reading up to ± 1 in the fourth decimal place of the refractive index. The prisms of the refractometer are maintained at constant temperature (± 0.02°C) by water circulated from a constant temperature bath.

4.8 Auxiliary Equipment

A packed, batch distillation column with a reflux arrangement is employed to purify the chemicals. This consists of three 22 mm. I.D. glass sections with 24/40 joints, each section containing 48 cm. of packing. Porous porcelain beads of 6 mm. diamter are used as the packing material. The column is estimated to consist of approximately 40 theoretical stages.

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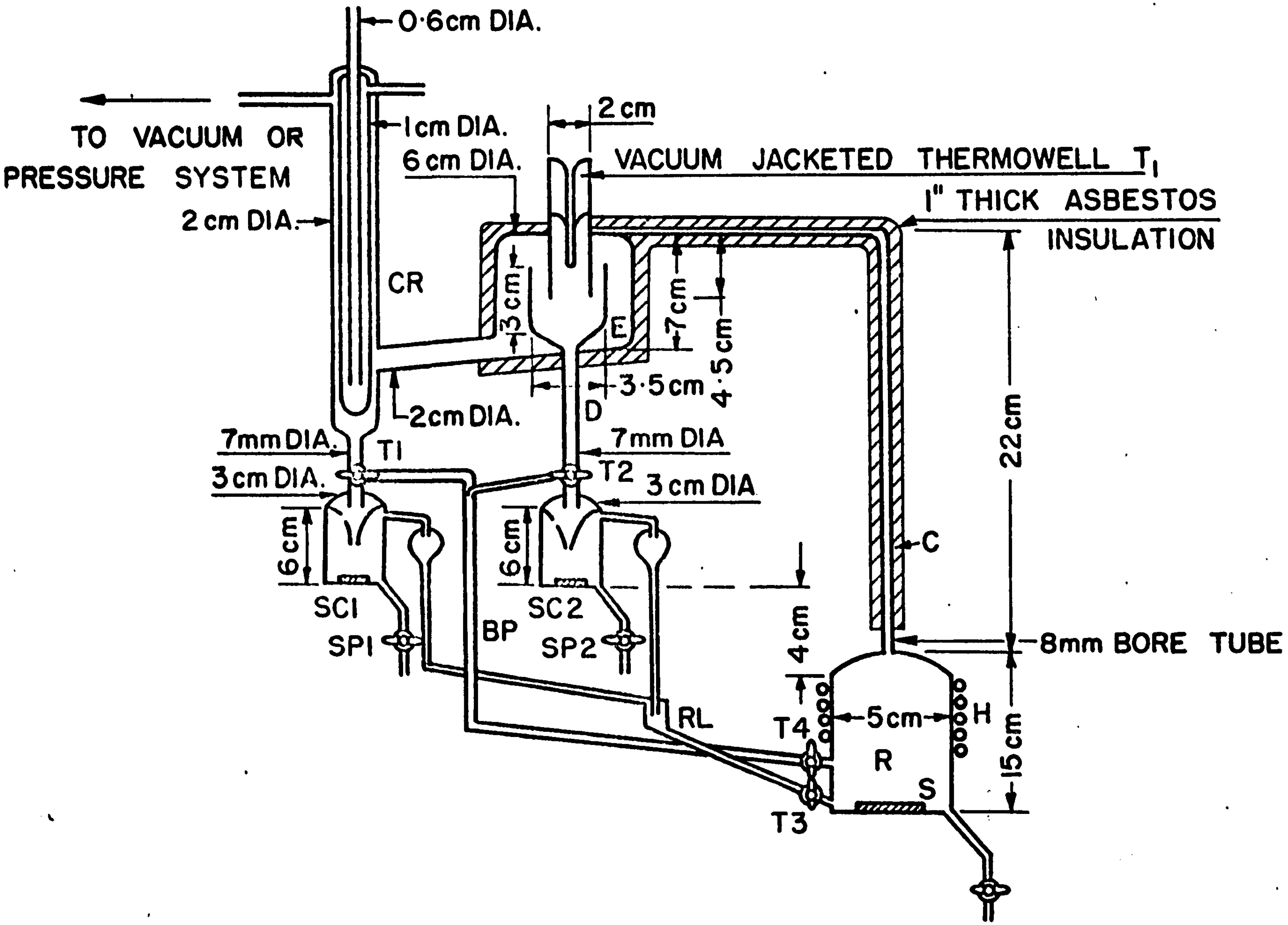

FIGURE 4.1 Modified Gillespie Still

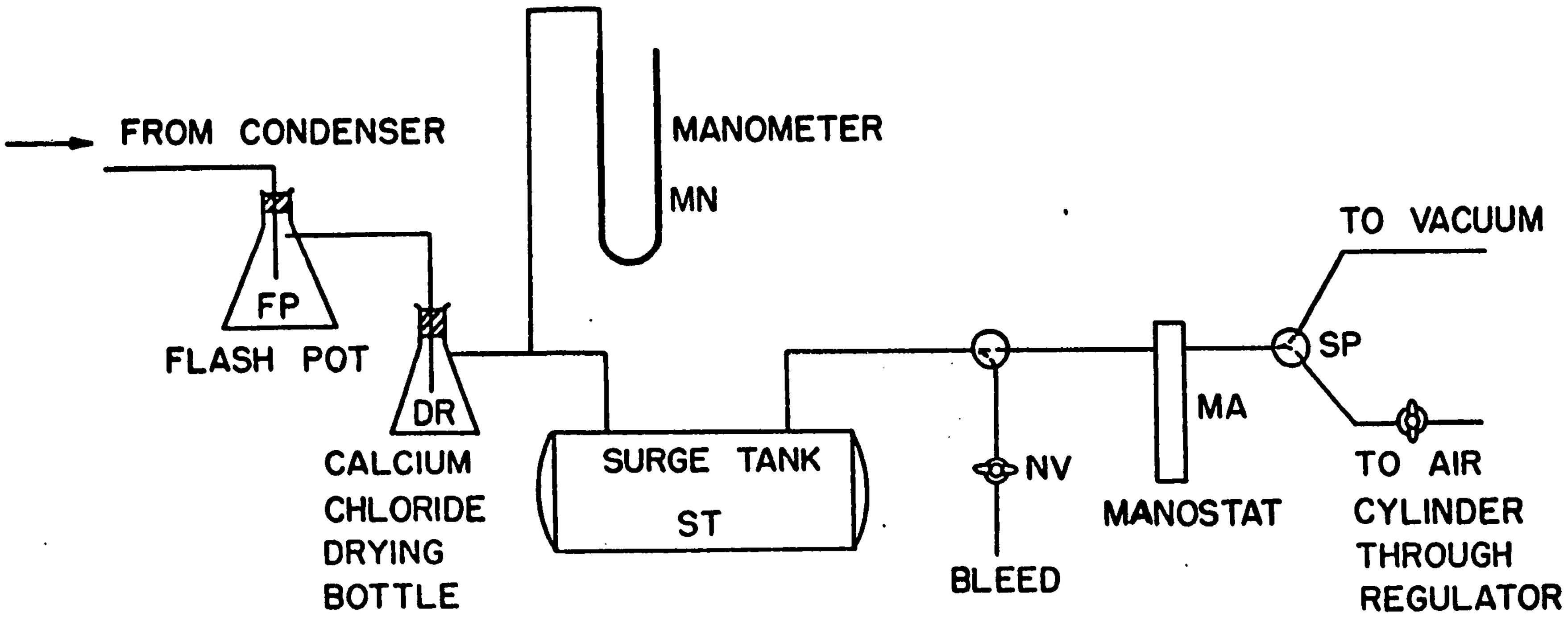

FIGURE 4.2 Pressure Measurement and Control System

5. TESTING OF THE STILL

5.1 Introduction

The present version of the Gillespie still is the first of its kind to be built in these laboratories to measure vapor-liquid equilibrium. Though the still retains the essential characteristics of the one described by Lu et al., an assessment of the performance of the equilibrium still is necessary. Such an assessment is generally accomplished by comparing the equilibrium data obtained using the apparatus under consideration with the results of other investigators using different experimental methods. Agreement of the data with previously published results represents a necessary condition of reliability, and the extent of agreement is a measure of the likelihood that the data are sound. The present still was tested using two binary test mixtures and the results obtained are compared with the literature data.

5.2 Test Mixtures

Isobaric vapor-liquid equilibrium data at 760 mm. Hg. were measured on two binaries: ethanol-benzene and methanol-water. Pure absolute alcohol from Gooderham and Worts Limited, and Baker-analysed spectrophotometric grade methyl alcohol were used without further purification. Reagent grade benzene supplied by Fisher Scientific Co. was redistilled in the packed column described earlier. The fraction employed in this work had a boiling point of 80.1°C (± 0.05). Refractive index, density and normal boiling point of the chemicals were also measured. Table 5.1 shows these properties and the corresponding literature values (1). They are in favourable agreement and generally within the variation of the published values.

5.3 Experimental Data

Several mixtures of ethanol-benzene and methanol-water systems were made up and their refractive indices at 25°C were measured. These calibration data are shown in Tables A-1 and A-2, and Figures A-1 and A-2, of Appendix A. The calibration chart for methanol-water system shows a maximum and equilibrium measurements in the region of doubtful accuracy in calibration were avoided. The still was run approximately one hour after steady state was reached, and the refractive indices of the condensed vapor and liquid samples were measured for composition analysis.

Tables 5.2 and 5.3 give the experimental vapor-liquid equilibrium data and activity coefficients computed by using Equation (2.17) and neglecting vapor phase solution nonideality. Volumetric data were taken from Timmerman (1) and virial coefficients were computed using Wohl's (4) equation. The correction factors are small and generally within experimental uncertainties. Vapor pressures at the temperatures under consideration were computed using Antoine's equation given by

$$\log P = A - \frac{B}{C + t} \qquad (5.1)$$

where A, B and C are constants and are given in Table 5.4.

Benzene-ethanol data are compared with those of Wehe and Coates (5), and Ellis (6). These are shown in Figures 5.1, 5.2 and 5.3 as x-y, x-y-t and x-logγ plots. Methanol-water data are compared with the smoothed equilibrium data given in Perry (7) and Figures 5.4 and 5.5 show a comparison between the present and literature data. Figure 5.6 shows the computed activity coefficients for this system.

5.4 Discussion

Comparison of the data indicates no systematic discrepancy between the present and literature values. In general, the comparison is favourable. At lower compositions of ethanol in ethanol-benzene system, literature data show a slightly higher value in y for a couple of points than the present data. A similar comparison of data in dilute zones for methanol-water system with literature data did not indicate the same trend and, in fact, the agreement is very good. Hence, it is felt that the discrepancy is only due to random errors in the measurements.

The general agreement in the above case is quite encouraging and it is not likely that the present apparatus suffers from any serious basic deficiencies.

Nomenclature

A	constant in Antoine's vapor pressure equation
B	constant in Antoine's vapor pressure equation
C	constant in Antoine's vapor pressure equation
^oC	degrees centigrade
P	pressure
R	gas constant
T	absolute temperature in ^oK
t	temperature in ^oC
x	mole fraction in liquid
y	mole fraction in vapor

Greek Letters:

β	second virial coefficient
γ	activity coefficient

Subscripts:

1	first component
2	second component
c	critical property

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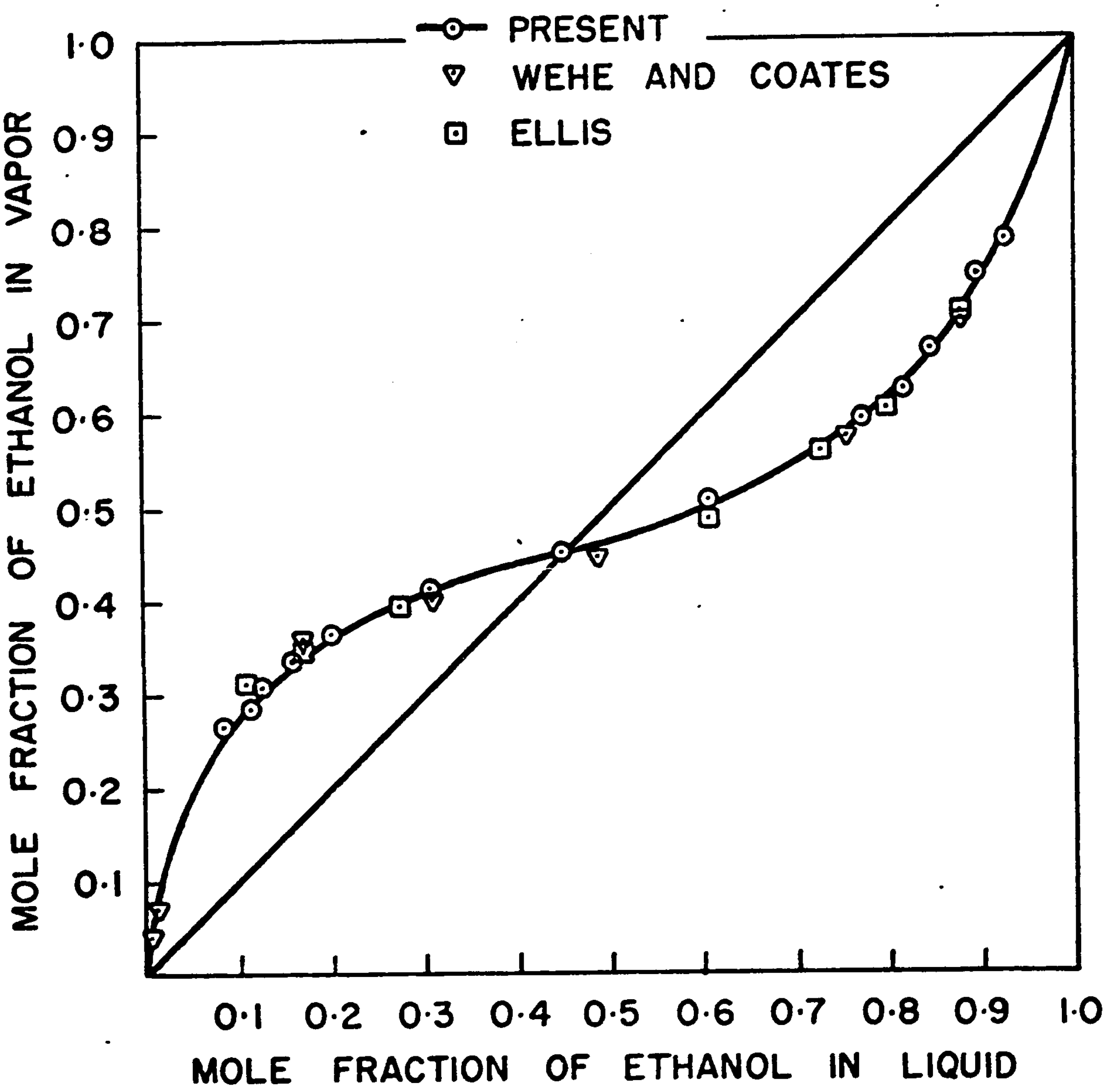

FIGURE 5.1 Vapor-Liquid Equilibrium (x-y) of Ethanol-Benzene Mixtures at 760 mm. Hg.

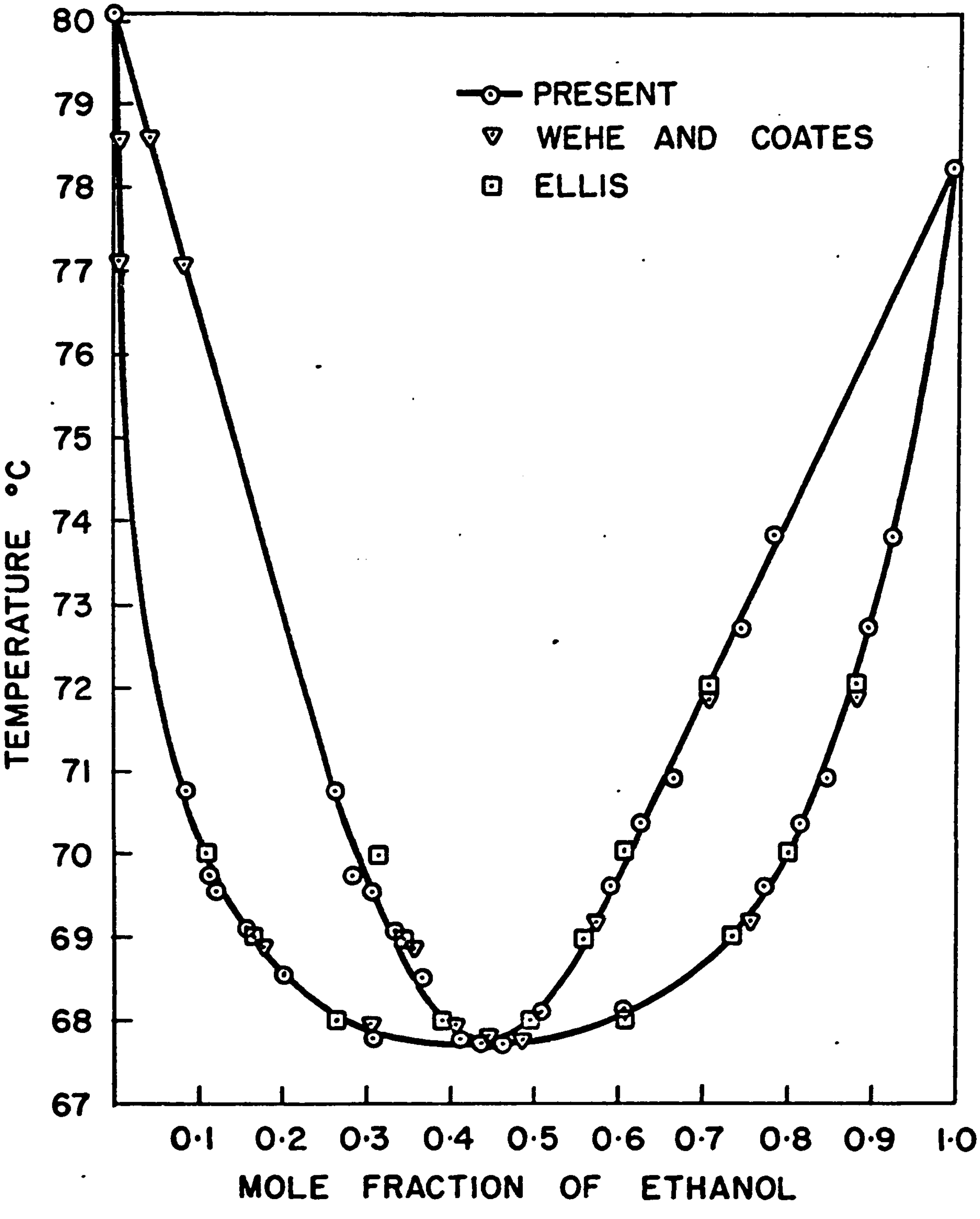

FIGURE 5.2 Vapor-Liquid Equilibrium (t-x-y) of Ethanol-Benzene Mixtures at 760 mm. Hg.

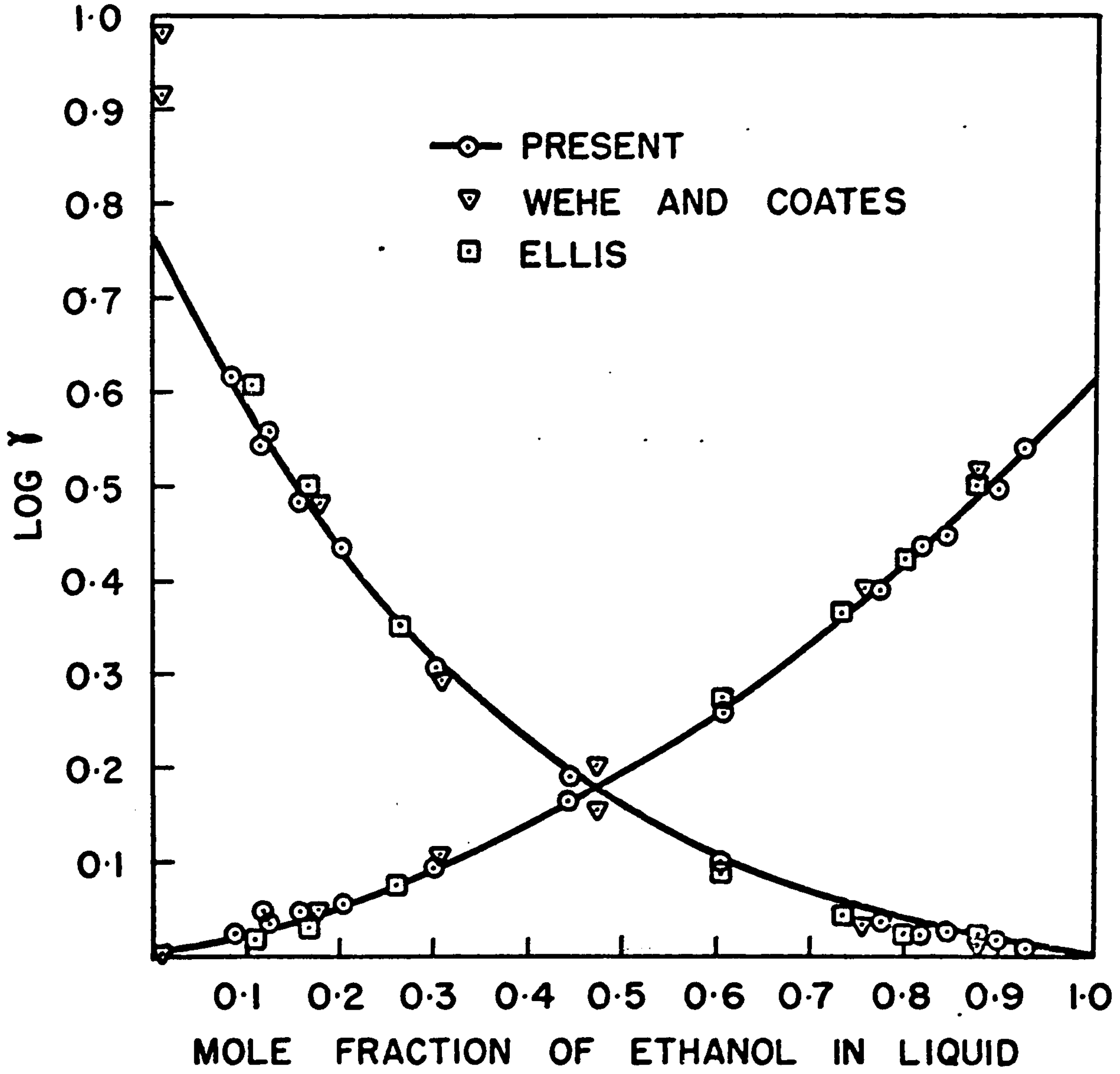

FIGURE 5.3 Activity Coefficients in Ethanol-Benzene Mixtures at 760 mm. Hg.

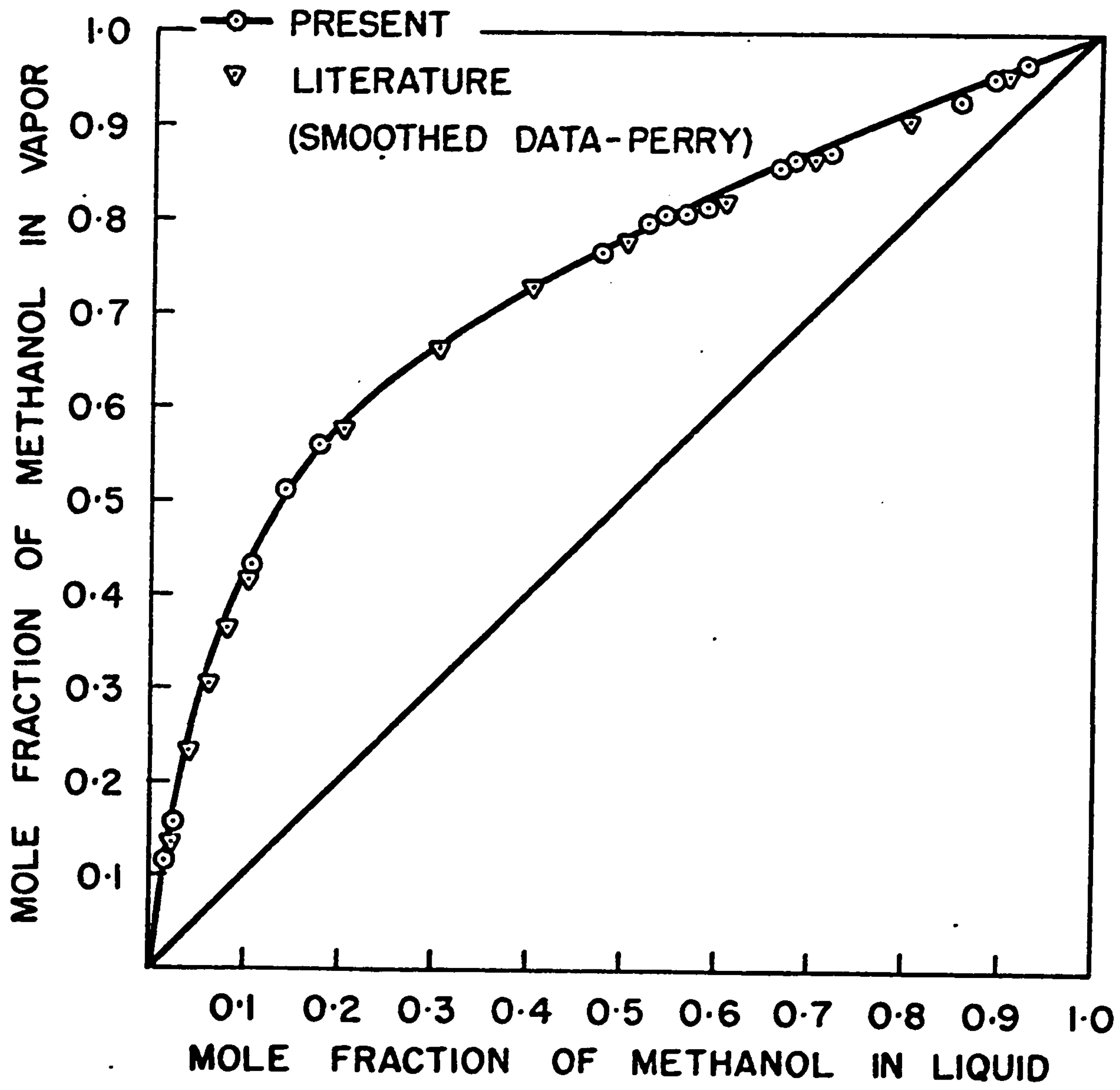

FIGURE 5.4 Vapor-Liquid Equilibrium (x-y) of Methanol-Water Mixtures at 760 mm. Hg.

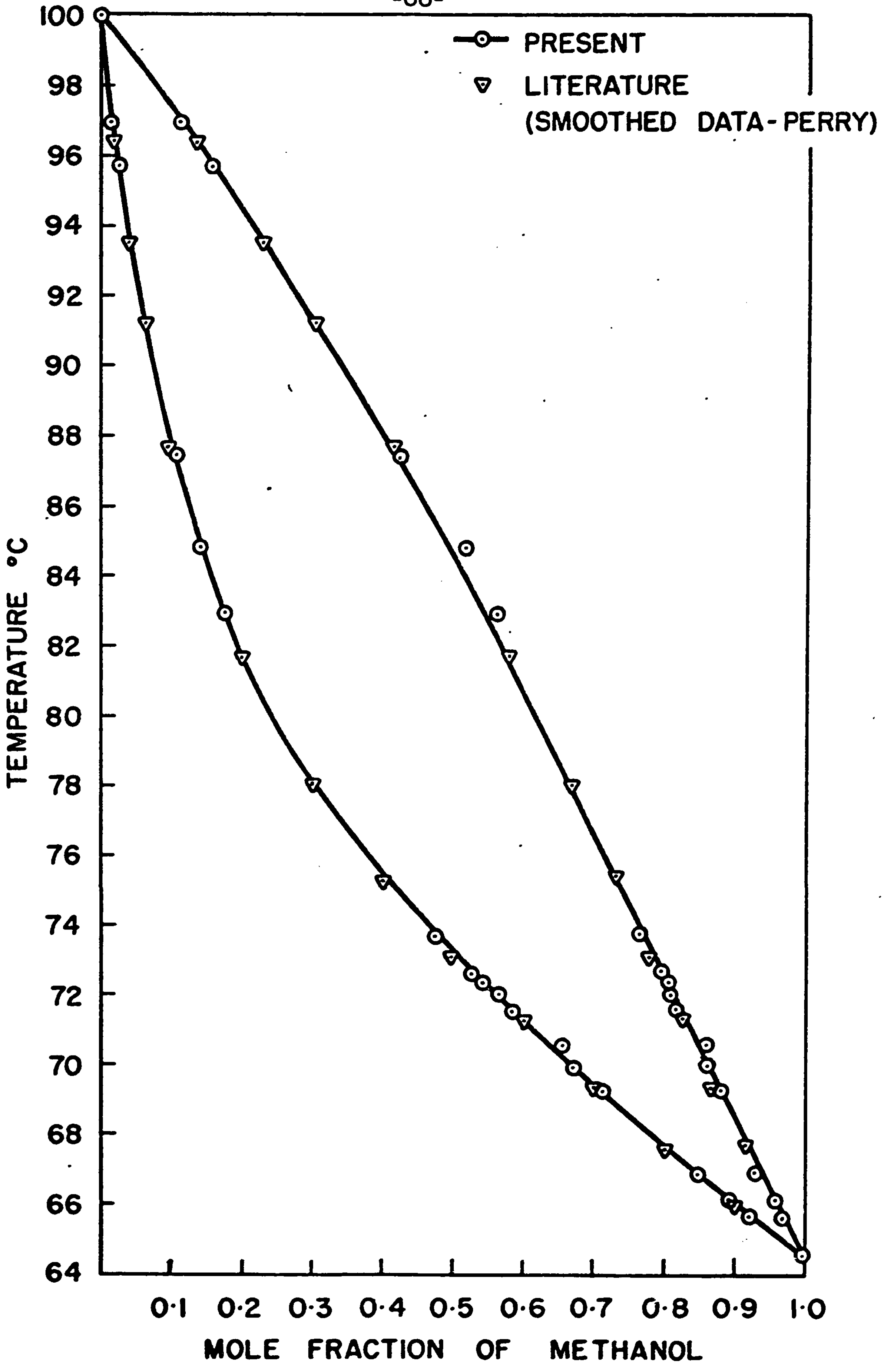

FIGURE 5.5 Vapor-Liquid Equilibrium (t-x-y) of Methanol-Water Mixtures at 760 mm. Hg.

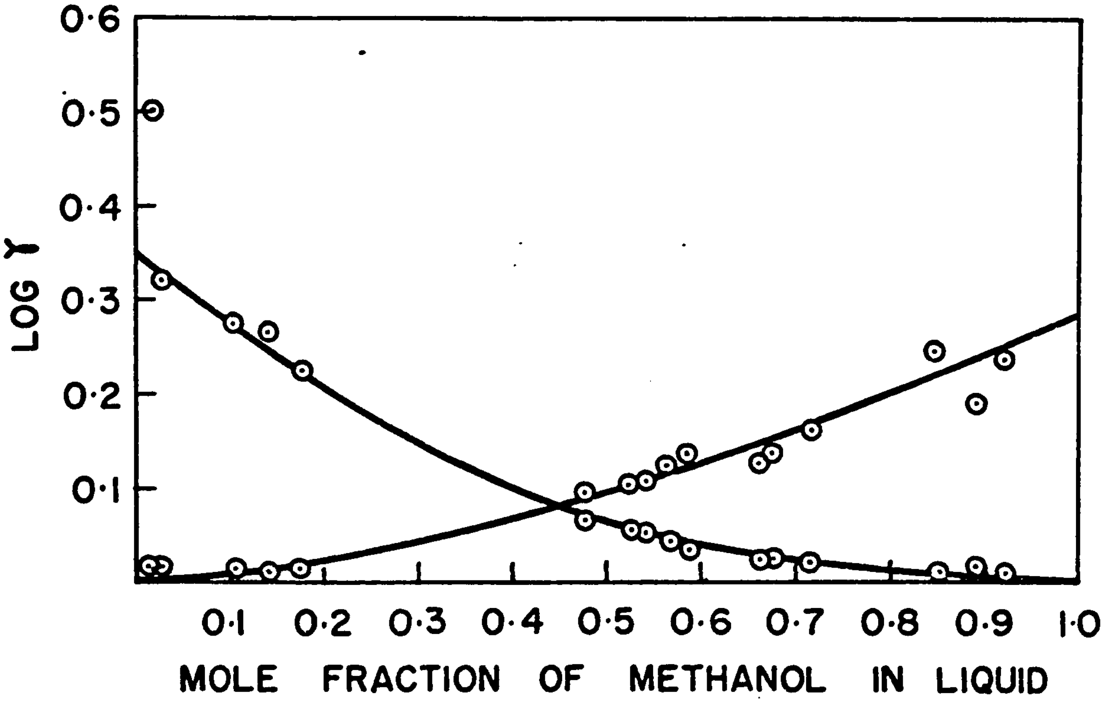

FIGURE 5.6 Activity Coefficients in Methanol-Water Mixtures at 760 mm. Hg.

TABLE 5.1

PHYSICAL CONSTANTS OF ETHANOL, METHANOL AND BENZENE

Chemical	Refractive Index at 25°C		Density at 25°C		Normal Boiling Point °C	
	Present	Lit.	Present	Lit.	Present	Lit.
Ethanol	1.3594	1.3595- 1.3596	0.7850	0.7851	78.2	78.2- 78.42
Methanol	1.3287 (at 20°C)	1.3287 (at 20°C)	0.7866	0.7866	64.6	64.5- 64.75
Benzene	1.4978	1.4979	0.8735	0.8734	80.1	80.1

TABLE 5.2

EXPERIMENTAL EQUILIBRIUM DATA
SYSTEM: BENZENE-ETHANOL

COMPONENT ONE IS ETHANOL
TOTAL PRESSURE = 760 mm. Hg.

x_1	y_1	T^oK	P_1	P_2	$\log\gamma_1$	$\log\gamma_2$	$\log\gamma_1/\gamma_2$
0.086	0.265	343.9	561.4	566.6	0.6174	0.0280	0.5894
0.112	0.282	342.9	538.4	548.2	0.5475	0.0441	0.5033
0.120	0.308	342.7	533.9	544.6	0.5594	0.0348	0.5246
0.158	0.335	342.2	522.8	535.7	0.4854	0.0437	0.4417
0.200	0.368	341.6	509.7	525.1	0.4346	0.0521	0.3824
0.308	0.410	340.8	493.4	511.8	0.3079	0.0960	0.2118
0.442	0.446	340.8	492.8	511.2	0.1881	0.1626	0.0255
0.604	0.505	341.2	501.2	518.1	0.0992	0.2570	-0.1578
0.770	0.590	342.7	534.4	545.0	0.0340	0.3900	-0.3560
0.815	0.628	343.5	550.9	558.3	0.0235	0.4322	-0.4087
0.841	0.665	344.0	563.7	568.5	0.0249	0.4449	-0.4200
0.898	0.744	345.8	607.2	602.8	0.0136	0.4964	-0.4828
0.924	0.782	346.9	635.2	624.6	0.0037	0.5395	-0.5359

TABLE 5.3

EXPERIMENTAL EQUILIBRIUM DATA
SYSTEM: METHANOL-WATER

COMPONENT ONE IS ETHANOL
TOTAL PRESSURE = 760 mm. Hg.

x_1	y_1	T^oK	P_1	P_2	$\log\gamma_1$	$\log\gamma_2$	$\log\gamma_1/\gamma_2$
0.012	0.114	370.0	2354.3	659.0	0.5006	0.0139	0.4867
0.026	0.157	368.8	2262.1	630.2	0.3205	0.0177	0.3028
0.102	0.430	360.6	1721.9	464.4	0.2788	0.0142	0.2646
0.140	0.514	357.9	1573.2	419.8	0.2568	0.0073	0.2495
0.175	0.560	356.0	1468.3	388.6	0.2261	0.0153	0.2108
0.473	0.765	346.8	1054.7	268.4	0.0697	0.0970	-0.0274
0.526	0.794	345.7	1012.6	256.4	0.0569	0.1055	-0.0485
0.540	0.801	345.5	1005.0	254.3	0.0525	0.1071	-0.0546
0.565	0.805	345.1	990.0	250.1	0.0414	0.1298	-0.0884
0.585	0.816	344.6	972.7	245.1	0.0397	0.1336	-0.0939
0.662	0.857	343.7	938.3	235.5	0.0226	0.1306	-0.1080
0.675	0.865	343.0	915.4	229.1	0.0287	0.1345	-0.1059
0.714	0.878	342.2	886.7	221.1	0.0242	0.1614	-0.1372
0.850	0.930	340.0	812.9	200.6	0.0104	0.2423	-0.2319
0.890	0.956	339.3	791.6	194.7	0.0137	0.1882	-0.1745
0.920	0.965	338.8	777.1	190.7	0.0112	0.2360	-0.2248

TABLE 5.4

ANTOINE CONSTANTS FOR ETHANOL, METHANOL, BENZENE AND WATER

Chemical	A	B	C	Reference
Ethanol	8.1122	1592.18	226.06	(2)
Methanol*	7.9295	1490.19	230.0	(1)
Benzene	6.9128	1214.56	221.16	(3)
Water*	7.9172	1666.88	230.0	(1)

* Computed from data in Reference (1) using C = 230.0

6. EXPERIMENTAL RESULTS

6.1 Introduction

Vapor-liquid equilibrium data are usually measured at constant pressure, perhaps because of their direct usefulness in the design of distillation columns. However, there are several benefits to be gained from making measurements at constant temperature, though they are more difficult than isobaric measurements.

1. As pointed out earlier, the activity coefficients are more sensitive to temperature than pressure. Isothermal data are, therefore, more meaningful to test any theory or predictive model.

2. The excess thermodynamic functions of enthalpy, free energy and entropy of solutions are easily evaluated if isothermal measurements are available at different temperatures.

Suitable experimental isothermal data are not available in the literature to test predictive models. In the present study, isothermal data on eight binary ketone-alkane systems and three ether-alkane systems were measured.

6.2 Systems Investigated

The data on ketone-alkane systems were measured at 65°C and the ether-alkane systems at 90°C. The systems investigated are listed below.

1. Ketone-Alkane Mixtures

   Acetone/n-Hexane
   Acetone/n-Heptane
   Acetone/n-Decane
   Methyl Ethyl Ketone/n-Hexane
   Methyl Ethyl Ketone/n-Octane
   Methyl Ethyl Ketone/n-Decane
   Diethyl Ketone/n-Hexane
   Dipropyl Ketone/n-Hexane

2. Ether-Alkane Systems

   n-Dipropyl Ether/n-Octane
   n-Dipropyl Ether/n-Nonane
   n-Dibutyl Ether/n-Heptane

6.3 Chemicals

Reagent grade ketones supplied by Matheson Coleman and Bell were redistilled and the fractions with physical properties (boiling point, refractive index and density) closely reproducing literature values were used. Research grade n-octane and n-nonane supplied by Phillips Petroleum Co., and the ethers from Aldrich Chemicals, were directly used. Heptane from Eastman Organic Chemicals, Fisher certified reagent grade hexane, and decane from Baker Chemical Co., were all redistilled for further purification. The physical properties of the chemicals used in the experimental vapor-liquid equilibrium determinations are given in Table 6.1. Available literature values (1,2,3,4) are also listed for comparison. The agreement is good.

6.4 Experimental Data

6.4.1 Analytical Method

Vapor-liquid equilibrium data were measured using the modified Gillespie still. Refractive index and gas chromatography were employed as the analytical techniques. The method used for analysis of the phases in each system is given below.

System	Analytical Technique
Acetone/n-Hexane	R.I.
Acetone/n-Heptane	R.I.
Acetone/n-Decane	G.C.
Methyl Ethyl Ketone/n-Hexane	G.C.
Methyl Ethyl Ketone/n-Octane	R.I.
Methyl Ethyl Ketone/n-Decane	G.C.
Diethyl Ketone/n-Hexane	G.C.
Dipropyl Ketone/n-Hexane	G.C.
Dipropyl Ether/n-Octane	R.I.
Dipropyl Ether/n-Nonane	R.I.
Dibutyl Ether/n-Heptane	R.I.

The calibration data are presented in Appendix A.

6.4.2 Experimental Accuracy

Compositions were read from the calibration charts and it was possible to read the charts to an accuracy of 0.5 mole percent or better. Calibration charts for acetone-decane and M.E.K.-decane systems show a scatter of the order of one percent in the mid-composition zone from the line drawn to be visually best. Temperature could be measured with an accuracy of $0.02^{\circ}C$ and the present measurements are believed to be within $\pm$ $0.05^{\circ}C$. Pressure could be measured to within a fraction of a millimeter but the accuracy achieved by the manostat is ± 0.2 percent of the still pressure.

6.4.3 Activity Coefficient Data

Activity coefficients were calculated from experimental data using the following equations.

$$\ell n \gamma_1 = \ell n \frac{\pi \; y_1}{x_1 P_1^o} + \frac{(\beta_1 - v_1^L)(\pi - P_1^o)}{RT} \qquad (6.1)$$

$$\ell n \gamma_2 = \ell n \frac{\pi \; y_2}{x_2 P_2^o} + \frac{(\beta_2 - v_2^L)(\pi - P_1^o)}{RT} \qquad (6.2)$$

where γ = activity coefficient

π = total pressure

x = mole fraction in liquid

y = mole fraction in vapor

P^o = pure component vapor pressure

β = second virial coefficient

v = liquid molal volume

R = gas constant

T = temperature.

Second virial coefficients were computed using Wohl's (5) equation given by

$$\beta = \frac{R\,T_c}{P_c}\left[0.197 - 0.012\,T_R - \frac{0.4}{T_R} - \frac{0.146}{T_R^{3.27}}\right] \qquad (6.3)$$

where T_c = critical temperature

T_R = reduced temperature

P_c = critical pressure.

Critical constant data and volumetric information were taken from the literature. Critical constant data for dipropyl ketone, dipropyl and dibutyl ethers were not available in the literature. They were, therefore, estimated using Lydersen's (6) correlations. All the supplementary data used in the calculation of activity coefficients are listed in Appendix B. Activity coefficient correction factors are significant (about 10 percent in γ) for systems involving acetone. For other systems, the correction factors are much less.

6.5 Results and Discussion

6.5.1 Ketone-Alkane Mixtures

Experimental data for these mixtures are presented in Tables 6.2-6.9. Vapor-liquid equilibrium curves and activity coefficient composition diagrams are shown in Figures 7.1-7.3 and

7.7-7.20. These mixtures show considerable nonideality.

Acetone/n-hexane and M.E.K./n-hexane show azeotropes having a composition of 0.69 and 0.32 mole fraction of the ketone, respectively. Acetone/n-heptane and M.E.K./n-octane systems, as is evident from the total pressures, show the existence of an azeotrope at very high concentrations of the ketone. However, the composition of the azeotropes is not clearly established in the experiments because of analytical uncertainty in the very dilute zones.

There was considerable difficulty in the measurement of the data on systems containing n-decane, particularly acetone/n-decane. At lower concentrations of the ketone, the condensed vapor sample started to flash severely when it joined the liquid sample in the return line. Therefore, experiments in the dilute concentrations with respect to acetone and M.E.K. could not be conducted. The recirculation method appears unsuitable for systems with high relative volatility and hence large differences in vapor-liquid compositions. Static methods should prove to be better alternatives.

Mixtures of M.E.K. and the alkanes studied exhibited peculiar behaviour in the still. These solutions creep on the glass surface. The reason for such a behaviour could not be established. However, no contamination of the samples was experienced. It was also difficult to hold the solutions containing M.E.K. with stopcocks. Data that were of a suspicious nature were rejected. At lower pressures the stopcocks were sealed externally with plasticine to avoid leaks.

6.5.2 Ether-Alkane Mixtures

Experimental equilibrium data for the ether/alkane systems are presented in Tables 6.10-6.12.

During the experimental determination some difficulties were experienced in establishing the equilibrium pressure. Though the apparent pressure could be read accurately, pressure changes of 10-15 mm. Hg. showed no effect on temperature within the accuracy of temperature measurement. This was particularly true for the systems containing dipropyl ether.

Activity coefficient data for these systems show their numerical value to be close to unity. There is a considerable scatter in the data and this could be partly attributed to the uncertainty in pressure. In view of the activity coefficients being close to unity, the equilibrium data were compared with ideal values (computed using Raoult and Dalton's Laws). In a binary,

$$y_1 = \frac{P_1^o x_1}{(P_1^o x_1 + P_2^o x_2)} \tag{6.4}$$

The comparison between the experimental and calculated values of y is shown in Tables 6.13-6.15 and Figures 6.1-6.3.

The assumption of ideal solution behaviour predicts the data reasonably well, and within experimental uncertainty these systems can be regarded as nearly ideal.

Nomenclature

P	pressure
P^o	pure component vapor pressure
R	gas constant
T	temperature
v	molal volume
x	mole fraction in liquid
y	mole fraction in vapor

Greek Letters:

β	second virial coefficient
γ	activity coefficient
π	total pressure

Subscripts:

1 & 2	components 1 and 2
c	critical property
R	reduced property

Superscript:

L	liquid

References

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5. Wohl, K., Z. Phy. Chem. B2, 77 (1929).

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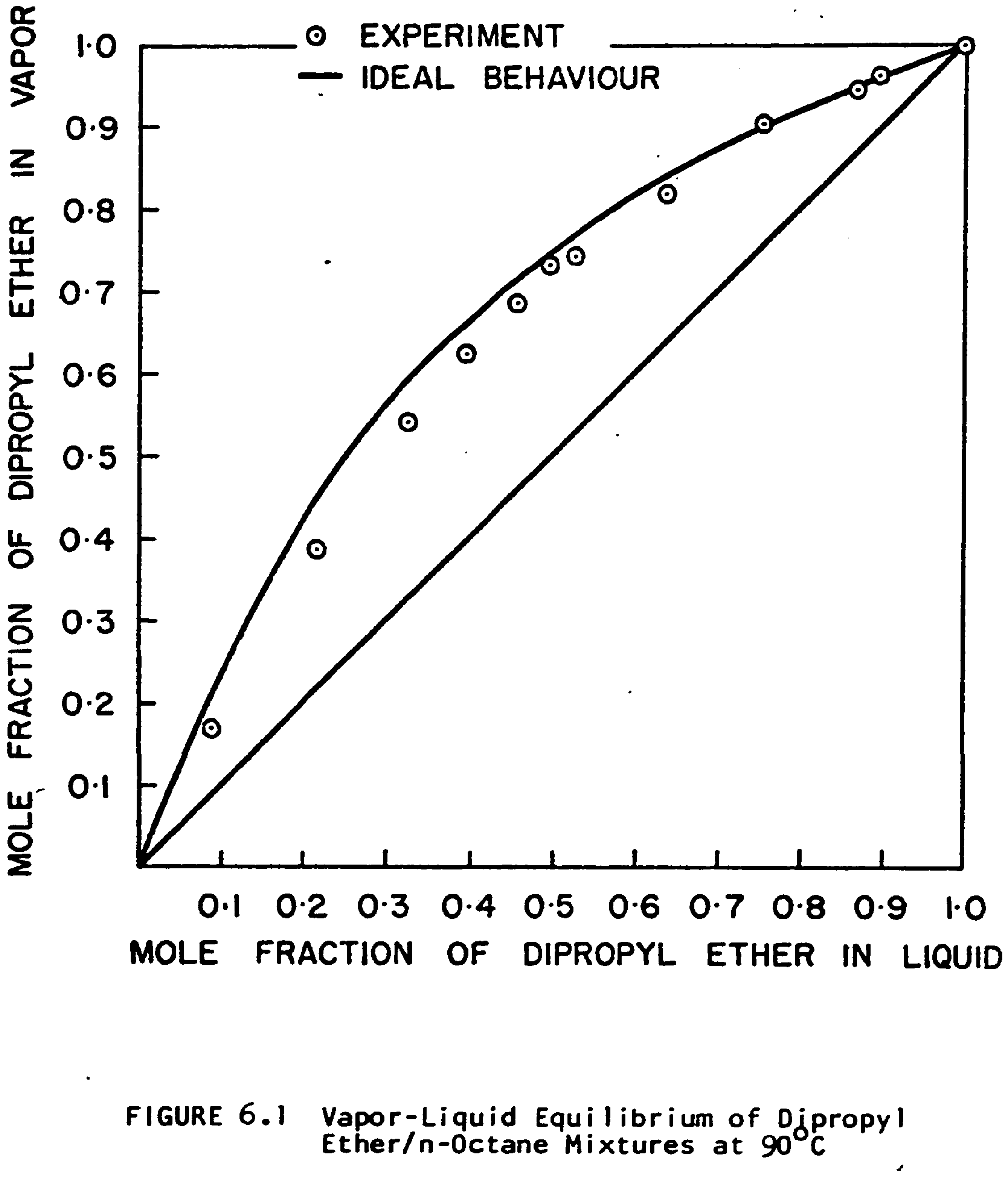

FIGURE 6.1 Vapor-Liquid Equilibrium of Dipropyl Ether/n-Octane Mixtures at 90°C

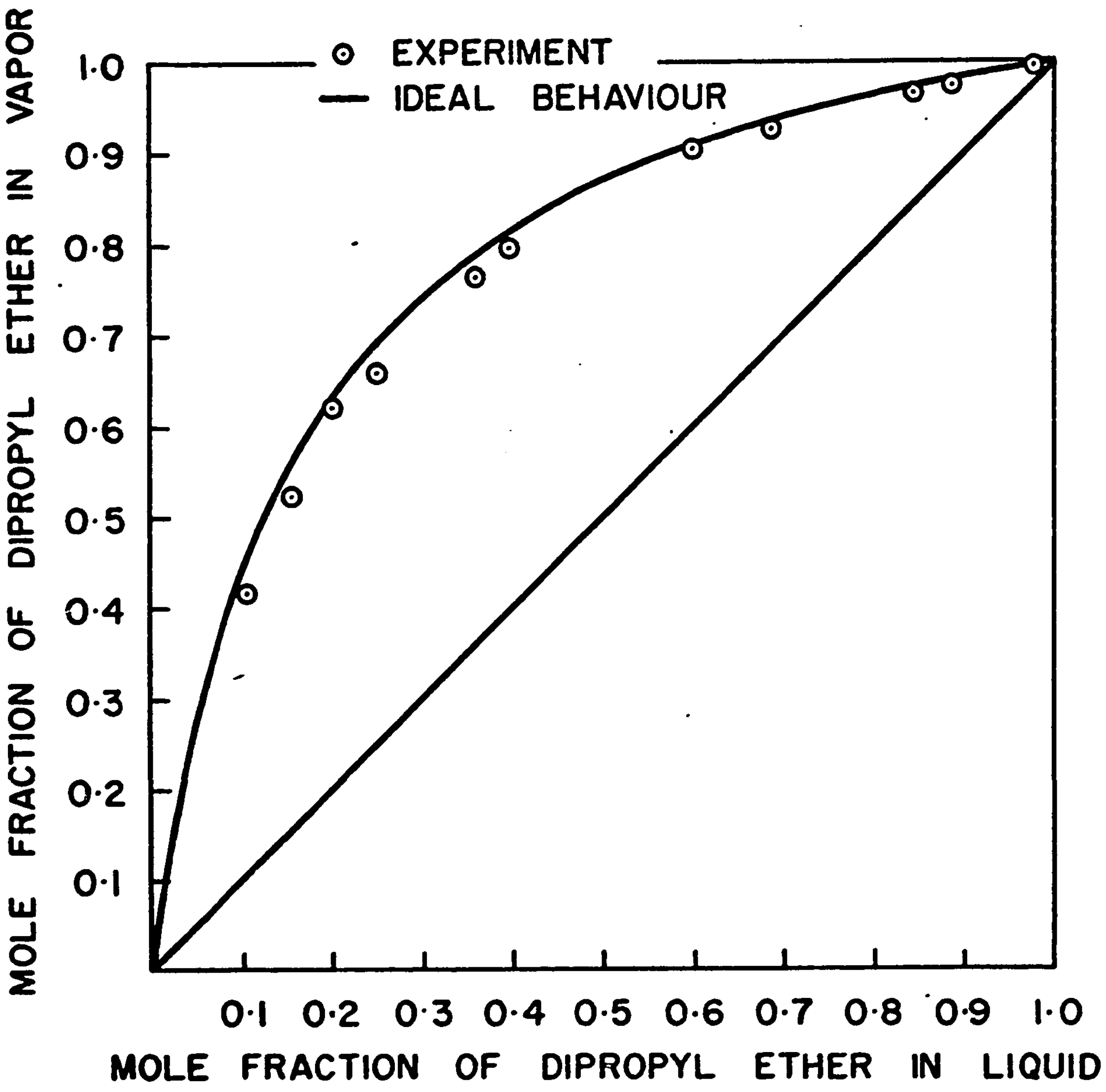

FIGURE 6.2 Vapor-Liquid Equilibrium of Dipropyl Ether/n-Nonane Mixtures at 90°C

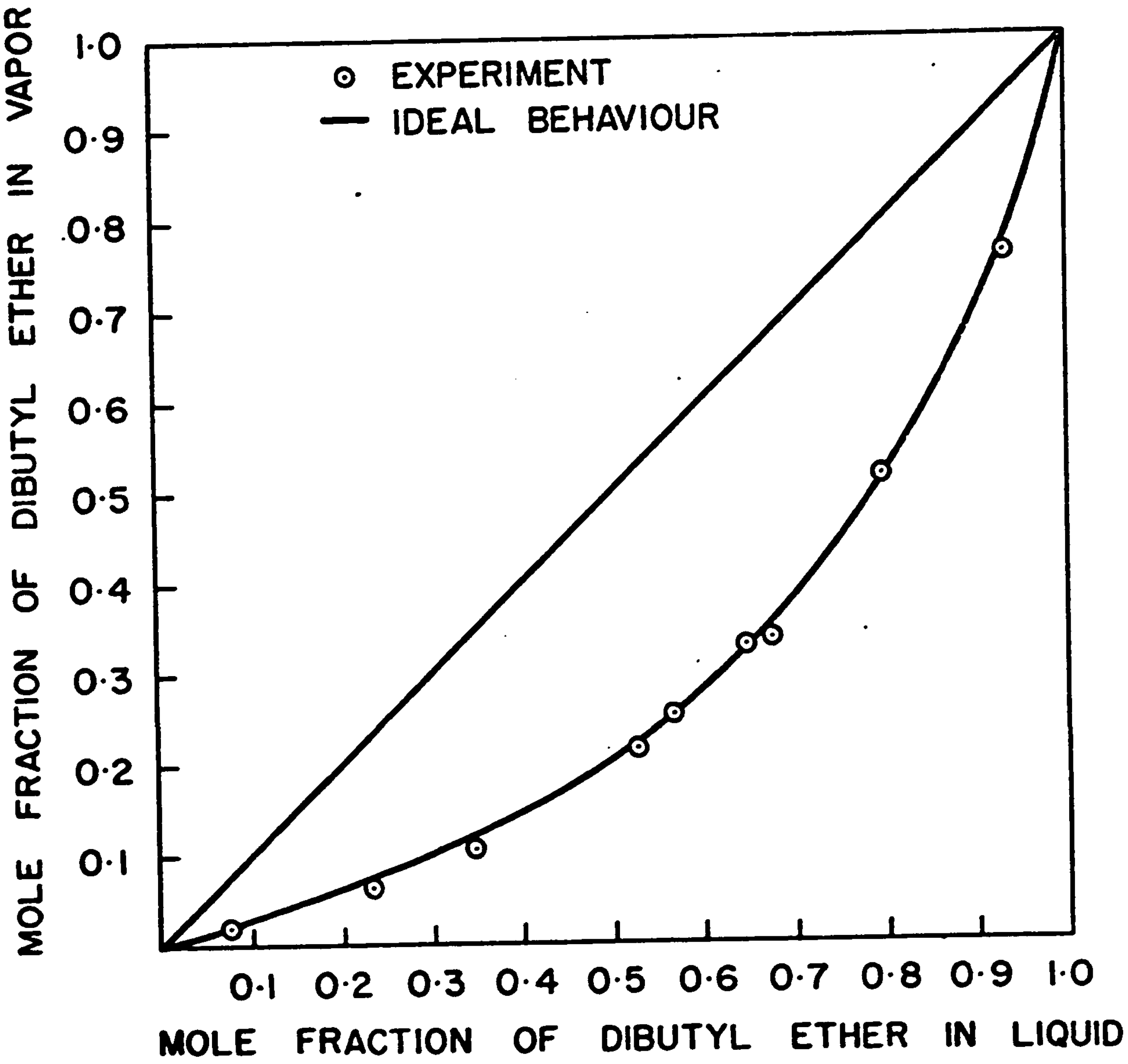

FIGURE 6.3 Vapor-Liquid Equilibrium of Dibutyl Ether/n-Heptane Mixtures at 90°C

TABLE 6.1

PHYSICAL PROPERTIES[I] OF PURE COMPOUNDS

Compound[II]	Refractive Index		Density		Normal Boiling Point (°C)	
	Present	Literature	Present	Literature	Present	Lit.
Acetone (2,2,2)	1.3586/20°C	1.3588/20°C	0.7848	0.7850	56.2	56.8
M.E.K. (2,2,2)	1.3762	1.3761	0.7998	0.7995	79.6	79.58
Diethyl Ketone (2,2,2)	1.3904	1.3900	0.8092	0.8095	102.5	102.7
Dipropyl Ketone (2,2,2)	1.4070/20°C	1.4073/20°C	0.8178/20°C	0.8174/20°C	143.2	143.5
n-Hexane (1,1,1)	1.3778	1.3723	0.6550	0.6548	68.6	68.67
n-Heptane (1,1,1)	1.3850	1.3851	0.6792	0.6795	98.4	98.4
n-Octane (1,1,1)	1.3949	1.3950	0.6982	0.6982	125.4	125.6
n-Nonane (1,1,1)	1.4028	1.4030	0.7132	0.7138	51.0	
n-Decane (1,1,1)	1.4092	1.4097	0.7259	0.7263	173.8	174.1
Dipropyl Ether (*,3,4)	1.3775	III	0.7375/30°C	0.7373/30°C	91.0	90.7
Dibutyl Ether (*,3,4)	1.3960	III	0.7600/30°C	0.7597/30°C	141.5	

I. Measured at 25°C.

II. Numbers in parentheses give references (at the end of Chapter 6) to literature values of refractive index, density and normal boiling point.

III. Not available at suitable temperature.

TABLE - 6.2

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: ACETONE - N-HEXANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 55°C

COMPONENT ONE IS KETONE

x_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.268	0.528	1145.9	0.3439	0.0242	0.3197
0.375	0.570	1201.1	0.2506	0.0711	0.1795
0.495	0.613	1237.9	0.1740	0.1299	0.0441
0.648	0.675	1261.3	0.1066	0.2183	-0.1117
0.690	0.690	1256.4	0.0873	0.2514	-0.1641
0.768	0.740	1257.4	0.0715	0.3012	-0.2297
0.905	0.840	1167.9	0.0249	0.4488	-0.4239
0.975	0.940	1106.5	0.0191	0.5810	-0.5619

TABLE - 6.3

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: ACETONE - N-HEPTANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

x_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I / γ_2)
0.118	0.595	581.3	0.4683	0.0153	0.4530
0.238	0.691	714.4	0.3155	0.0454	0.2702
0.413	0.768	867.5	0.2034	0.1122	0.0912
0.490	0.788	901.9	0.1565	0.1496	0.0069
0.578	0.798	954.1	0.1137	0.2332	-0.1195
0.710	0.838	999.0	0.0647	0.3184	-0.2537
0.753	0.856	1024.9	0.0590	0.3470	-0.2879
0.867	0.894	1031.0	0.0191	0.4851	-0.4660

TABLE - 6.4

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: ACETONE - N-DECANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.345	0.980	638.8	0.2589	0.0699	0.1890
0.415	0.984	693.2	0.2151	0.0393	0.1759
0.474	0.985	752.0	0.1917	0.1102	0.0815
0.564	0.988	807.8	0.1475	0.1269	0.0206
0.730	0.989	872.5	0.0684	0.2990	-0.2306
0.841	0.991	916.0	0.0280	0.4615	-0.4335
0.888	0.992	947.8	0.0191	0.5679	-0.5488
0.926	0.994	966.1	0.0095	0.6605	-0.6510
0.985	0.998	1006.5	0.0015	0.8979	-0.8965

TABLE -6.5

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: METHYL ETHYL KETONE - N-HEXANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 65 °C

COMPONENT ONE IS KETONE

x_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.215	0.260	765.0	0.2984	0.0252	0.2732
0.286	0.301	770.9	0.2413	0.0448	0.1964
0.392	0.354	771.7	0.1752	0.0808	0.0944
0.585	0.439	743.3	0.0793	0.1700	-0.0907
0.630	0.475	723.8	0.0703	0.1801	-0.1098
0.684	0.502	701.8	0.0457	0.2129	-0.1672
0.818	0.595	641.1	0.0041	0.3253	-0.3212
0.880	0.685	594.9	0.0023	0.3660	-0.3637
0.945	0.825	523.4	-0.0016	0.3961	-0.3977

TABLE -6.6

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: METHYL ETHYL KETONE - N-OCTANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.058	0.472	169.1	0.4864	-0.0130	0.4995
0.148	0.655	245.5	0.3818	0.0036	0.3782
0.265	0.765	318.5	0.3074	0.0102	0.2973
0.376	0.814	361.9	0.2368	0.0329	0.2039
0.382	0.816	359.5	0.2281	0.0296	0.1985
0.562	0.847	403.9	0.1261	0.1472	-0.0211
0.576	0.845	388.3	0.0977	0.1507	-0.0530
0.636	0.855	431.5	0.1044	0.2315	-0.1270
0.730	0.870	441.5	0.0618	0.3232	-0.2614
0.810	0.880	450.8	0.0304	0.4496	-0.4192
0.970	0.968	456.7	-0.0010	0.6825	-0.6835

TABLE -6.7

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: METHYL ETHYL KETONE - N-DECANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 65 °C

COMPONENT ONE IS KETONE

X_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.264	0.937	204.3	0.2073	0.0589	0.1483
0.520	0.972	325.1	0.1274	0.0840	0.0434
0.538	0.969	292.8	0.0667	0.1021	-0.0354
0.550	0.974	343.7	0.1276	0.1025	0.0251
0.555	0.975	320.1	0.0938	0.0614	0.0325
0.570	0.974	349.2	0.1188	0.1286	-0.0098
0.648	0.977	365.4	0.0838	0.1807	-0.0969

TABLE - 6.8

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: DIETHYL KETONE - N-HEXANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

x_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.063	0.049	688.4	0.3752	0.0138	0.3613
0.248	0.131	660.1	0.1899	0.0528	0.1370
0.372	0.182	612.6	0.1258	0.0738	0.0519
0.443	0.215	591.7	0.1079	0.0936	0.0143
0.508	0.248	576.2	0.0995	0.1178	-0.0183
0.561	0.268	550.5	0.0711	0.1366	-0.0654
0.640	0.316	498.4	0.0440	0.1517	-0.1076
0.702	0.368	472.2	0.0475	0.1768	-0.1293
0.763	0.412	432.8	0.0239	0.2082	-0.1844
0.834	0.490	376.2	0.0016	0.2419	-0.2404
0.874	0.570	342.8	0.0077	0.2482	-0.2405

TABLE -6.9

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: DIPROPYL KETONE - N-HEXANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_1/γ_2)
0.072	0.012	660.4	0.3396	0.0174	0.3222
0.210	0.025	567.7	0.1328	0.0187	0.1140
0.420	0.048	470.6	0.0387	0.0640	-0.0253
0.470	0.038	406.0	0.0114	0.0364	-0.0250
0.618	0.094	341.9	0.0310	0.0891	-0.0581
0.745	0.136	258.3	-0.0071	0.1247	-0.1318

TABLE - 6.10

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: DIPROPYL ETHER - N-OCTANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 90°C

COMPONENT ONE IS ETHER

X_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.084	0.168	297.5	-0.0966	0.0292	-0.1258
0.214	0.388	363.2	-0.0544	0.0462	-0.1006
0.327	0.542	405.1	-0.0472	0.0334	-0.0805
0.393	0.621	475.7	-0.0001	0.0628	-0.0629
0.454	0.685	512.2	0.0109	0.0590	-0.0481
0.492	0.732	509.1	0.0023	0.0177	-0.0154
0.525	0.742	533.9	-0.0001	0.0499	-0.0500
0.633	0.819	612.9	0.0192	0.0646	-0.0454
0.750	0.902	682.0	0.0320	0.0084	0.0236
0.867	0.948	735.2	0.0217	0.0376	-0.0159
0.895	0.965	759.5	0.0291	-0.0186	0.0477

TABLE -6.II

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: DIPROPYL ETHER - N-NONANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 90 °C

COMPONENT ONE IS ETHER

X_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.106	0.415	166.8	-0.0525	-0.0068	-0.0457
0.155	0.525	178.3	-0.0868	-0.0444	-0.0423
0.200	0.620	207.4	-0.0604	-0.0535	-0.0069
0.250	0.658	253.2	-0.0461	0.0130	-0.0591
0.356	0.761	313.2	-0.0458	0.0127	-0.0585
0.391	0.799	348.5	-0.0200	0.0062	-0.0262
0.594	0.905	466.8	-0.0239	-0.0225	-0.0014
0.685	0.922	546.6	-0.0114	0.0663	-0.0778
0.843	0.968	646.7	-0.0102	0.0495	-0.0597
0.886	0.972	694.9	-0.0002	0.1591	-0.1593
0.973	0.992	747.2	-0.0020	0.2693	-0.2713

TABLE - 6.I2

EXPERIMENTAL EQUILIBRIUM DATA

SYSTEM: DIBUTYL ETHER - N-HEPTANE

VAPOR PHASE IMPERFECTIONS ACCOUNTED

TEMPERATURE = 90°C

COMPONENT ONE IS ETHER

X_I	Y_I	π (MM)	LOG γ_I	LOG γ_2	LOG (γ_I/γ_2)
0.075	0.020	580.6	-0.0253	0.0214	-0.0467
0.230	0.062	513.2	-0.0711	0.0306	-0.1017
0.345	0.105	471.8	-0.0530	0.0453	-0.0983
0.522	0.213	393.8	-0.0006	0.0504	-0.0509
0.566	0.250	364.0	0.0010	0.0382	-0.0371
0.645	0.327	323.6	0.0117	0.0286	-0.0169
0.672	0.337	324.4	0.0080	0.0575	-0.0495
0.795	0.513	260.1	0.0245	0.0338	-0.0093
0.930	0.760	198.4	0.0123	0.0776	-0.0652

TABLE- 6.I3

SYSTEM: DIPROPYL ETHER - N-OCTANE

TEMPERATURE = 90°C

COMPONENT ONE IS ETHER

X_I	Y_I-IDEAL	Y_I-EXP	Y_I-DIFF(ABS)
0.084	0.218	0.168	0.050
0.214	0.453	0.388	0.065
0.327	0.597	0.542	0.055
0.393	0.664	0.621	0.043
0.454	0.717	0.685	0.032
0.492	0.747	0.732	0.015
0.525	0.771	0.742	0.029
0.633	0.840	0.819	0.021
0.750	0.901	0.902	0.001
0.867	0.952	0.948	0.004
0.895	0.963	0.965	0.002

R.M.S DEVIATION IN Y_I IS 0.0359

TABLE-6.14

SYSTEM: DIPROPYL ETHER - N-NONANE

TEMPERATURE = 90 °C

COMPONENT ONE IS ETHER

X_I	Y_I-IDEAL	Y_I-EXP	Y_I-DIFF(ABS)
0.106	0.452	0.415	0.037
0.155	0.561	0.525	0.036
0.200	0.635	0.620	0.015
0.250	0.699	0.658	0.041
0.356	0.794	0.761	0.033
0.391	0.817	0.799	0.018
0.594	0.911	0.905	0.006
0.685	0.938	0.922	0.016
0.843	0.974	0.968	0.006
0.886	0.982	0.972	0.010
0.973	0.996	0.992	0.004

R.M.S DEVIATION IN Y_I IS 0.0241

TABLE- 6.15

SYSTEM: DIBUTYL ETHER - N-HEPTANE

TEMPERATURE = 90°C

COMPONENT ONE IS ETHER

X_I	Y_I-IDEAL	Y_I-EXP	Y_I-DIFF(ABS)
0.075	0.021	0.020	0.001
0.230	0.074	0.062	0.012
0.345	0.124	0.105	0.019
0.522	0.226	0.213	0.013
0.566	0.259	0.250	0.009
0.645	0.327	0.327	0.000
0.672	0.354	0.337	0.017
0.795	0.509	0.513	0.004
0.930	0.781	0.760	0.021

R.M.S DEVIATION IN Y_I IS 0.0129

7. PREDICTIVE METHOD

7.1 Introduction

Group contribution models for the prediction of mixture properties have a wide range of applicability requiring only a minimum of experimental data. The group solution model of Ratcliff and Chao (1) was used previously with success to predict vapor-liquid equilibrium data on paraffin-alcohol systems and extended recently to include other thermodynamic and transport properties (2,3,4). In the present work, the model is applied to predict the vapor-liquid equilibrium data on ketone-alkane and alcohol-aromatic hydrocarbon systems. The experimental data of the present study on ketone-alkane systems and literature data on alcohol-aromatic hydrocarbon systems are used for comparison.

The Redlich-Kister three-constant equation for the relative volatility deviation function ($\log\gamma_1/\gamma_2$) is used to smooth the data on the reference system by the weighted least squares method.

The method of calculating the weighting factors for the least squares method, the group solution model and a comparison between predicted and experimental data are presented in the following sections.

7.2 Smoothing of Experimental Data

The various sources of experimental error and the general relevance of applying Gibbs-Duhem equation to vapor-liquid equilibrium data are discussed exhaustively by Hala et al. (5). Systematic errors are generally due to faulty still design, which includes improper mixing, flash vaporization, superheating, entrainment and evaporation due to throttling of the equilibrium samples at the time of withdrawal. Taking for granted that these errors have been overcome, we shall focus our attention on random errors. These may be introduced in measuring liquid and vapor compositions, temperature, and pressure measurements. In general, errors in temperature and pressure measurements are small compared to those introduced in composition measurement. Equilibrium compositions are customarily determined graphically from calibration charts, and it could be safely assumed that the absolute error in composition measurement is constant. For a constant absolute error in composition, the reliability of activity coefficient data using Equations (6.1) and (6.2), rapidly diminishes as the pure components are approached. Thus for the method of least squares to be applicable when the data are fitted to any thermodynamic equation, each data point must be given a proper statistical weight. Gilmont, Zudkevitch and Othmer (6) have suggested a method applicable for this situation and it is described briefly as follows:

let e = absolute error in composition

then $\frac{e}{x_1}$ = relative error in x_1

and $\frac{e}{y_1}$ = relative error in y_1.

Relative volatility is defined as

$$\alpha_{12} = y_1 x_2 / x_1 y_2 \tag{7.1}$$

where α_{12} = relative volatility of component 1 with respect to 2

x = mole fraction in liquid

y = mole fraction in vapor.

The ideal relative volatility is given by

$$\alpha^{I}_{12} = P^{o}_{1} / P^{o}_{2} \tag{7.2}$$

where P^{o} = pure component vapor pressure.

The expression for activity coefficient ratio then becomes

$$\frac{\gamma_1}{\gamma_2} = \left(\frac{y_1}{y_2}\right)\left(\frac{x_2}{x_1}\right)\left(\frac{P^{o}_{2}}{P^{o}_{1}}\right) = \frac{\alpha_{12}}{\alpha^{I}_{12}} \tag{7.3}$$

It may be noted that vapor phase imperfections are ignored to reduce complexity. The absolute error in $\ell n\alpha_{12}$ is given by

$$\Delta\ \ell n\alpha_{12} = \frac{e}{x_1} + \frac{e}{x_2} + \frac{e}{y_1} + \frac{e}{y_2} \tag{7.4}$$

$$= \frac{e}{x_1 x_2} + \frac{e}{y_1 y_2} \tag{7.5}$$

Eliminating y_1 from Equation (7.4) yields

$$\Delta\ \ell n\alpha_{12} = \frac{e\ \alpha_{12} + (x_2 + \alpha_{12} x_1)^2}{\alpha_{12} x_1 x_2} \tag{7.6}$$

In accordance with the method of least squares, the weighting factor is inversely proportional to the square of the error. Therefore, the weighting factor, w, is given by

$$w \propto \left[\frac{1}{\Delta \ell n \alpha_{12}}\right]^2 \tag{7.7}$$

The proportionality constant may be obtained by letting w_o represent the weighting factor at a composition of $x_1 = x_2 = 0.5$ and $\ell n \alpha_{12} = 0$, which is the condition for maximizing the weighting factor. Since the method of least squares requires only relative weighting factors rather than absolute ones, we utilize a relative weighting factor defined as follows:

$$W = \left(\frac{w}{w_o}\right) \tag{7.8}$$

Combining Equations (7.6), (7.7) and (7.8) we get the relative weighting factor as a function of composition and relative volatility.

$$W = 64 \left(\frac{e_o}{e}\right)\left[\frac{x_1 x_2}{1 + \alpha_{21} (x_2 + \alpha_{12} x_1)^2}\right]^2 \tag{7.9}$$

Now, based on experience, the following assumptions are made.

1. The absolute error in the measurement of vapor and liquid composition does not vary with composition, i.e. $e = e_o$.

2. There is no error in ideal relative volatility and so the absolute error in the logarithm of the relative volatility deviation may be taken as that in the logarithm of the relative volatility.

3. The cause of all random errors is due to the measurement of composition and these errors may be expressed by the relative volatility function only.

The first assumption is based on the fact that in practically all analytical methods employed in vapor-liquid equilibria, the absolute error of measurement is a constant and the composition of vapor is determined by measurements on the corresponding condensed phase. The second assumption depends upon the error in ideal relative volatility being negligible in comparison with that in relative volatility itself. The third assumption is based on the usual procedure of applying the method of least squares to experimental data; namely, that the total random error is assumed to reside in the dependent variable.

The value of the weighting factor is thus given by

$$W = 64\left[\frac{x_1x_2}{1 + \alpha_{21}\ (x_2 + \alpha_{12}x_1)^2}\right]^2 \qquad (7.10)$$

The Redlich-Kister equation for relative volatility deviation function (in a binary solution) is given by

$$\log(\frac{\gamma_1}{\gamma_2}) = B(x_2-x_1) + C(6x_1x_2-1) + D(x_2-x_1)(1-8x_1x_2) \qquad (7.11)$$

The constants in the above equation are obtained by minimizing the sum of the weighted squares (weighting factor given by Equation (7.10)) of the dependent variable with respect to the three constants. Individual activity coefficients are obtained by combining Equation (7.11) with the Gibbs-Duhem equation. They are given by

$$\log\gamma_1 = x_1x_2 \quad B + C(x_1-x_2) + D(x_1-x_2)^2 \ + x_2\log(\frac{\gamma_1}{\gamma_2}) \qquad (7.12)$$

$$\log\gamma_2 = x_1x_2\left[B + C(x_1-x_2) + D(x_1-x_2)^2\right] - x_1\log\left(\frac{\gamma_1}{\gamma_2}\right) \quad (7.13)$$

7.3 The Group Solution Model

The group solution model proposed by Wilson and Deal (7) and modified by Ratcliff and Chao (1) is based on four postulates. They may be enumerated as follows.

Postulate I

The nonideal behaviour of a molecule, in terms of activity coefficient, may be regarded as consisting of two independent parts. The first part is associated with the overall 'skeleton' of the molecule and the other with the functional group interaction. Expressed mathematically

$$\log\gamma_i = \log\gamma_i^S + \log\gamma_i^G \quad (7.14)$$

where γ_i = molecular activity coefficient of component i.

The superscripts S and G represent the skeletal and group contribution terms, respectively. The skeletal contribution accounts for the deviation due to molecular size differences. The group interaction term represents the deviation due to the interactions between the functional groups of the molecule and those present in solution.

For the application of the model, the groups may be chosen arbitrarily. For example, an aliphatic ketone molecule could be regarded as made up of the groups 'carbonyl' and 'methylene'. It could also be regarded as made up of the groups 'acetone' and 'methylene'.

Postulate II

The skeletal contribution is given by Bronsted and Koefoed's (8) 'Theory of Congruence'.

$$\log\gamma_i^S = A\,(N_i - \sum_j x_j N_j)^2 \qquad (7.15)$$

where N_j = number of carbon atoms in molecular species j

x_j = mole fraction of component j in solution.

The summation in Equation (7.15) is over all the molecular species present in solution. The values of A are available in the literature (8,9) and are presented as a function of temperature by Ratcliff and Chao (1).

Postulate III

Each group in the molecules exists as an individual entity and acts independently in the solution of groups. The group contribution to $\log\gamma_i$ is given by the sum of the contributions of the individual groups present. Thus,

$$\log\gamma_i^G = \sum_k N_{ki}\,(\log\Gamma_k - \log\Gamma_k^*) \qquad (7.16)$$

where N_{ki} = number of groups of type k in molecular species i

Γ_k = activity coefficient of group k.

The superscript * denotes the standard state value.

The standard state may be any arbitrary composition of the 'solution of groups' at the solution temperature and pressure. Choosing the standard state to be that of the pure molecular species under consideration, as is conventional in classical thermodynamics, assures that the activity coefficient is unity for the pure compound. Thus, if aliphatic ketones are considered to be made up of methylene and carbonyl groups, then the standard state of carbonyl in acetone is its state in a solution containing 33.3 group percent carbonyl and 66.7 group percent methylene. The standard state of carbonyl in methyl ethyl ketone is that of a solution containing 25 percent carbonyl and 75 percent methylene.

The effect of pressure in the definition of standard state is not considered further since we are concerned here with condensed systems around atmospheric pressure and the effect of pressure on activity coefficient may be neglected.

Postulate IV

The final postulate of the model is that the group activity coefficients are functions only of the group composition, temperature and pressure.

$$\log \Gamma_k = f_k (X_1, X_2 \ldots X_k \ldots, T, P) \qquad (7.17)$$

The group fraction is computed from

$$X_k = \sum_j x_j N_{kj} / \sum_k \sum_j x_j N_{kj} \qquad (7.18)$$

This is analogous to the computation of mole fraction in solution.

Apart from the basic postulates, there are some assumptions inherent in the model. (1) The model assumes that the interactions of an isomeric molecule are similar to those of its normal counterpart, i.e. it doesn't distinguish between the shape of the molecules. However in many cases, mixtures of normal and isomeric molecules of the same species at normal pressures exhibit nearly ideal behaviour. Since we are dealing with highly nonideal systems, this assumption may not be serious. (2) The model assumes that the inter-molecular forces acting on a group and on a whole molecule are uniquely determined by the average group composition of the solution. Because of the dipole interactions and association effects, local composition may be different from the overall composition. However, we are using the model to predict data of one system from the known data on another system containing the same groups, and some cancellation of errors would be expected.

An important aspect in the application of the model is that the solution must not contain greater number of groups than molecular species.

7.4 Test of the Model

The model was tested on two classes of binary mixtures: ketone-alkane systems and alcohol-aromatic hydrocarbon systems.

7.4.1 Ketone-Alkane Systems

The systems for which the model was applied are acetone/n-heptane, acetone/n-hexane, acetone/n-decane, methyl ethyl ketone/n-hexane, methyl ethyl ketone/n-octane, methyl

ethyl ketone/n-decane, diethyl ketone/n-hexane, and dipropyl ketone/n-hexane. The experimental data for these systems are given earlier in Chapter 6 (Tables 6.3 to 6.11).

Acetone/n-heptane was chosen as the reference system from which the group contributions were computed as functions of carbonyl group fraction. Experimental vapor-liquid equilibrium data for this reference system are shown in Figure 7.1. The corresponding activity coefficients, given in Table 6.3, were fitted to the three-constant Redlich-Kister equation for $\log(\gamma_1/\gamma_2)$, given by Equation (7.11). The method of weighted least squares was used in fitting the data. The weighting factor used for each experimental point was calculated by using Equation (7.10). The constants thus obtained are given in Table 7.1. The smoothed activity coefficient data were generated from the Redlich-Kister constants by using Equations (7.12) and (7.13). The smoothed $\log(\gamma_1/\gamma_2)$ data and activity coefficients are shown in Figures 7.2 and 7.3.

To maintain simplicity, no distinction is made between CH_3 and CH_2 groups. Acetone is thus regarded as two methylene and one carbonyl. Heptane is considered to be consisting of seven methylene groups. The group fractions are computed using Equation (7.18).

The activity coefficients of methylene (Γ_{CH_2}) and carbonyl (Γ_{CO}) were determined by applying Equations (7.14) and (7.16). The skeletal contribution is insignificant (constant A is of the order of -5×10^{-4} to -6×10^{-4} between

$25^{o}C$ and $100^{o}C$) compared to group contributions and are, henceforth, neglected. Since the standard state activity coefficient of methylene $\Gamma^{*}_{CH_2}$ in n-heptane is unity, the group activity coefficient Γ_{CH_2} is given by

$$\log\Gamma_{CH_2} = \frac{1}{7}\log\gamma_H \qquad (7.19)$$

Computed values of log Γ_{CH_2} are shown in Figure 7.4 as a function of carbonyl group fraction.

The smoothing of the activity coefficient data by fitting them to the Redlich-Kister equation permitted extrapolation to limiting values. We thereby obtain the limiting value of Γ_{CH_2} at $X_{CO} = 1/3$. This is the standard state value of Γ_{CH_2} in acetone, i.e. for acetone $\log\Gamma^{*}_{CH_2} = 0.0842$.

For the group carbonyl, the relation corresponding to Equation (7.19) is

$$\log\left(\frac{\Gamma_{CO}}{\Gamma^{*}_{CO}}\right) = \log\gamma_A - 2\log\left(\frac{\Gamma_{CH_2}}{\Gamma^{*}_{CH_2}}\right) \qquad (7.20)$$

All quantities on the right-hand side of Equation (7.20) are known, and hence $\log(\Gamma_{CO}/\Gamma^{*}_{CO})$ may be calculated as a function of carbonyl group fraction. It is shown in Figure 7.5. Knowledge of Γ^{*}_{CO} is not necessary for predicting activity coefficients over the range of concentration of Figures 7.4 and 7.5, since we are only concerned with differences in values of $\log(\Gamma_{CO}/\Gamma^{*}_{CO})$, and Γ^{*}_{CO} therefore cancels out.

If the group solution model is satisfactory for mixtures containing alkanes and aliphatic ketones, Figures

7.4 and 7.5 should represent the nonideal behaviour of all mixtures of these compounds (binary or multicomponent) at 65°C. The computed values of $\log \Gamma_{CH_2}$ and $\log(\Gamma_{CO}/\Gamma^*_{CO})$ were fitted by power series, shown in Table 7.2, for calculation purposes.

7.4.1.1 Results and Discussion

The model was first checked by seeing how consistently it correlated the experimental data on the acetone/n-heptane system used to determine the group activity coefficients. The results are given in Figure 7.1, and show good agreement. The root mean square deviation between experimental and correlated vapor mole fractions is 0.007. The correlated and experimental activity coefficient and composition data are shown in Tables 7.3 and 7.4.

The model was then tested by using it to predict the behaviour of the seven other ketone/alkane systems. The procedures followed in applying the model are summarized in Figure 7.6. The results are plotted in Figures 7.7-7.13, and show good agreement between experiments and prediction. Figures 7.14-7.20 show the activity coefficient data. Tables 7.5-7.11 give the experimental and predicted x-y data, and 7.12-7.18 the activity coefficient data. The predictions are made solely from the parameters in Table 7.2, without using any experimental data for the system in question. Table 7.19 shows the root mean square deviations between experimental and predicted vapor mole fractions. The agreement, in general, is satisfactory.

7.4.2 Alcohol-Aromatic Hydrocarbon Systems

Successful extension of the group solution model to include aromatic compounds of varying shapes would open a new avenue in the prediction of mixture properties. As mentioned earlier, the group solution model in its present form does not allow for the effect of shape of the constituent species. Further, no distinction is made between a methylene group in an aliphatic molecule and that in an aromatic ring. However, we are predicting data of one system from the other and this similarity criterion should result in some cancellation of errors. To determine the seriousness of an error of this type, free energy data on a number of aliphatic and aromatic hydrocarbon mixtures were examined. The systems studied and the comments of the investigators are given below.

System	Remarks	Reference
Benzene-Toluene Toluene-Xylene	Mixtures form nearly ideal solutions at atmospheric pressure	(10)
Toluene-Ethyl Benzene	Solution ideal at atmospheric pressure	(11)
Heptane-Methyl Cyclohexane	Isothermal data at 97.2°C show the system to be ideal	(11)
Heptane-Toluene Octane-Toluene	Systems ideal within 5% of total pressure	(12)

System	Remarks	Reference
Benzene-Toluene Benzene-Ethyl Benzene Benzene-Propyl Benzene	Isobaric data at one atmosphere show ideality within experimental error	(13)
Ethyl Cyclohexane/n-Octane	Isobaric data between 50-760 mm. Hg. pressure show ideality	(14)
Benzene/n-Octane Benzene/n-Heptane	Isobaric data at 760 mm. Hg. show γ^o values to be about 1.2	(15)
Hexane-Hexene	Ideal within experimental error at 760 mm. Hg.	(16)

Data of Myers (17) on benzene-alkane systems are in considerable discrepancy with those of Ellis (15). The former indicate considerably higher values (1.3 to 1.7) for γ^o. However, as a first approximation, assuming that CH_3, CH_2 and CH groups in these mixtures interact similarly may not introduce serious error. Shape effects might also be neglected.

Literature data on alcohol-aromatic hydrocarbon systems were used to test the model. Isothermal data at 45°C of Brown et al. on ethanol-benzene (18), n-propanol-benzene (19), isopropanol-benzene (20), and n-butanol-benzene (19) were used. Data of Kretschmer et al. (21) on ethanol-toluene system at 35°C and the data of Ellis et al. (22) on n-butanol-ethyl benzene system at 100 mm. Hg. pressure were also employed. The temperatures in the measurements of these systems are the closest available to the set of data of Brown et al.

Ethanol-benzene was taken as the reference binary and the group contribution functions were derived in a similar manner to that described earlier. CH_3, CH_2, CH, and C groups were all considered identical in evaluating these functions. As in the case of ketone/alkane systems, skeletal contribution was neglected. These reference plots are shown in Figures 7.21 and 7.22. They relate $\log\Gamma_{CH_2}$ and $\log(\Gamma_{OH}/\Gamma^*_{OH})$ as functions of X_{CH_2}. $\mathrm{Log}\,\Gamma_{CH_2}$ curve was extrapolated to $X_{CH_2} = 2/3$ to get $\log\Gamma^*_{CH_2}$ value. Calculated values of the group contributions are also given in Table 7.20.

7.4.2.1 Results and Discussion

The model was tested by using it to predict data on the remaining five alcohol-aromatic hydrocarbon binaries. The procedure of prediction is similar to the previous case except that the vapor phase imperfections were insignificant and hence neglected. Calculation of x-y data from predicted activity coefficients for isothermal systems is straightforward. Isobaric data of n-butanol-ethyl benzene was calculated using the Antoine vapor pressure constants given in Reference (22).

Predicted and experimental x-y data for these systems are shown in Figures 7.23-7.28. The activity coefficient data are shown in Figures 7.29-7.34. Tables 7.21-7.25 and 7.27-7.32 also provide the predicted and experimental data. The agreement between the experiment and prediction in all the cases is very good. Table 7.33 shows the root mean square deviations of the predicted y values.

7.4.3 Prediction of Alcohol-Aromatic Hydrocarbon Data from Alcohol-Alkane Data

The model was fairly successful in predicting data on alcohol-aromatic hydrocarbons, implying that the carbon atom in an aromatic ring can be treated as CH_2 group of an alkane. It was, therefore, decided to explore the possibility of predicting aromatic hydrocarbon-alcohol data from that of aliphatic CH_2/OH systems.

Ratcliff and Chao's (1) data on aliphatic CH_2/OH systems is shown with the data on aromatic CH_2/OH systems in Figures 7.21 and 7.22. The agreement of the $\log \Gamma_{CH_2}/X_{CH_2}$ correlation between the two sets is reasonable except in high concentrations of alcohol where the aliphatic data show a higher value of $\log \Gamma_{CH_2}$. Similar agreement is also observed in the $\log(\Gamma_{OH}/\Gamma_{OH}^{*})/X_{CH_2}$ data when the two sets of data are set to match in the concentrated zone with respect to the hydrocarbon. Aliphatic $(\Gamma_{OH}/\Gamma_{OH}^{*})/X_{CH_2}$ data shown in Figure 7.22 could not be used in the predictions because of difficulties in extrapolating to the standard state values in mixtures containing ethanol. However, Ratcliff and Chao have made use of water-alcohol data to cover the complete group composition range in $\log\Gamma_{OH}/X_{CH_2}$ function. Their data are shown in Figure 7.22 (A) and were used in conjunction with data in Figure 7.21 to predict the activity coefficients and vapor-liquid equilibria. Predicted x-y data are shown in Figures 7.23-7.28 and Tables 7.34-7.39. Activity coefficient data are given in Tables 7.40-7.45 and Figures 7.29-7.34. The agreement in this case is as good as the data predicted from ethanol-benzene system. The root mean square deviations in y are given in Table 7.33.

7.5 Conclusions

The group solution model gives a good representation of the vapor-liquid equilibrium data of mixtures containing methylene and carbonyl at 65°C. Systems containing aromatic hydrocarbons and aliphatic alcohols are also amenable to a similar representation by the model and valuable predictions could be made. Data on aromatic hydrocarbon-alcohol systems can be reasonably predicted from data on aliphatic CH_2/OH systems. Predictions in the vicinity of the temperatures of the reference system should be satisfactory.

Nomenclature

A	constant in Equation (7.15)
B, C, D	constants in Redlich-Kister equations
e	absolute error in composition
N	total number of groups in a given molecular species

N_{ki}	number of groups of type k in molecular species i
P	pressure
T	temperature
w	weighting factor
W	relative weighting factor
x	mole fraction in liquid
X	group fraction in liquid
y	mole fraction in vapor

Greek Letters:

α	relative volatility
γ	molecular activity coefficient
Γ	group activity coefficient

Subscripts:

A	acetone
i	molecular species i
j	molecular species j
H	heptane
k	group species k
CH_2	methylene group
CO	carbonyl group
OH	hydroxyl group
1	component 1
2	component 2

Superscripts:

G	group contribution

I	ideal
o	pure component
S	skeletal contribution
*	standard state

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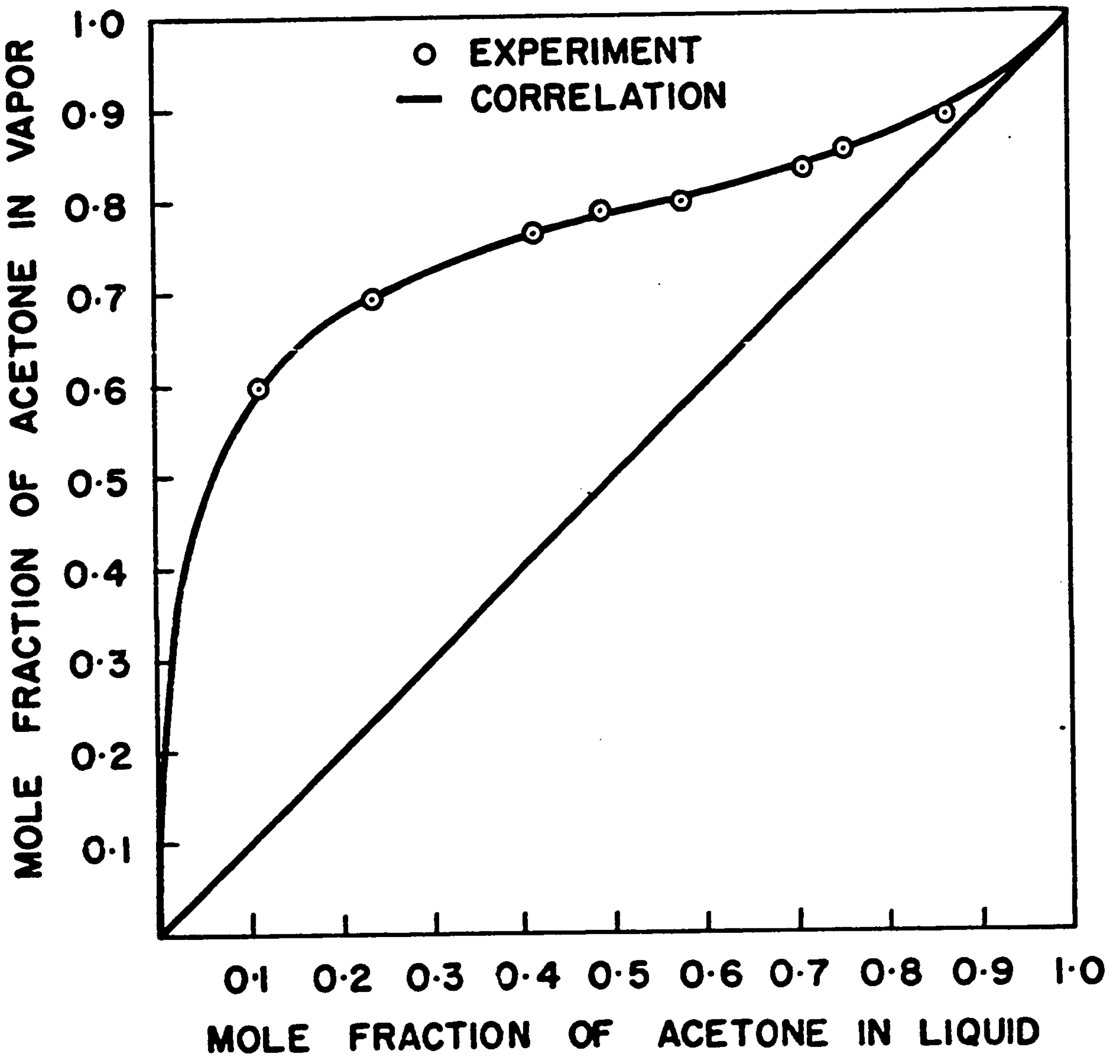


FIGURE 7.1 Vapor-Liquid Equilibrium of Acetone/n-Heptane Mixtures at 65°C

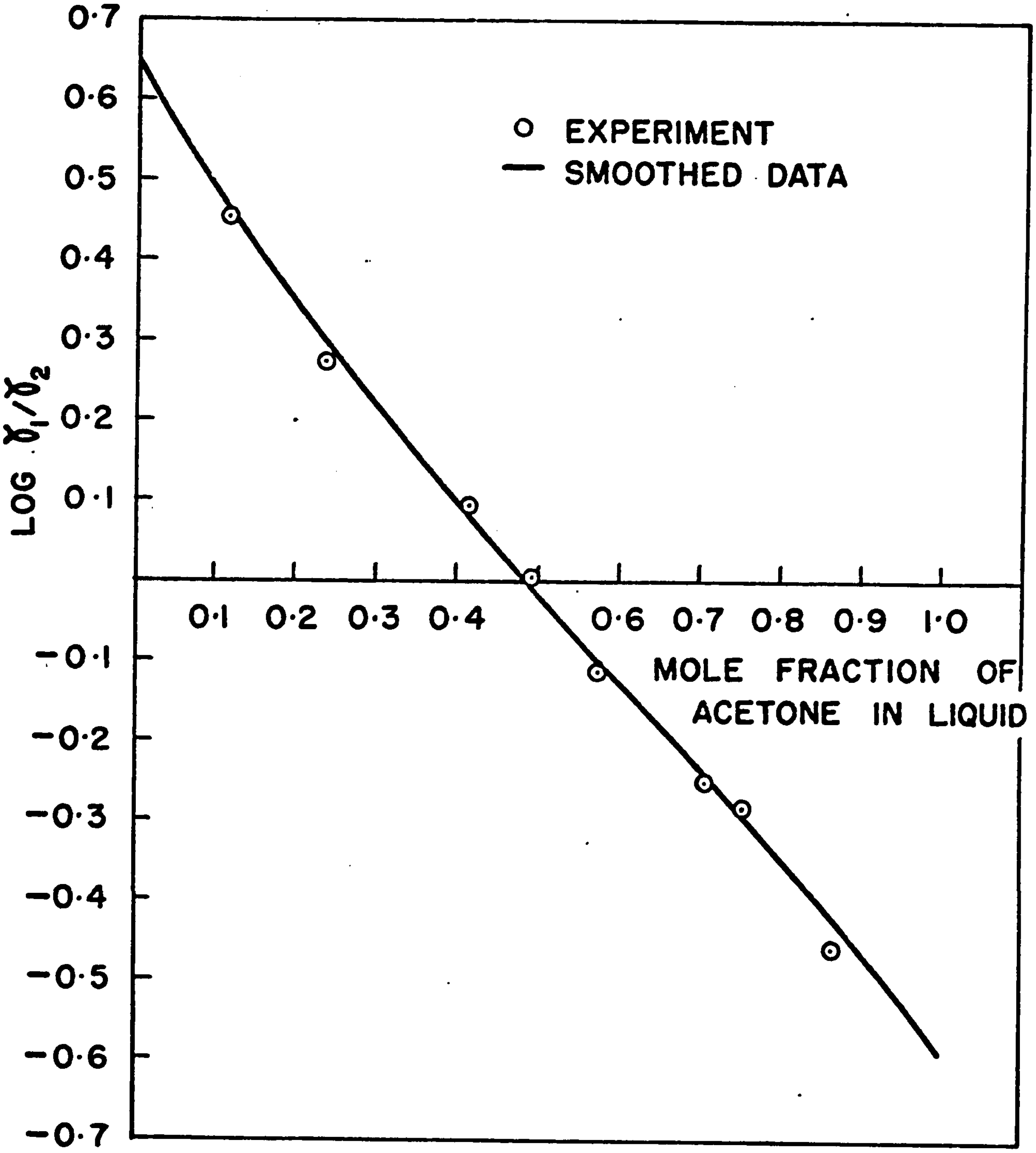


FIGURE 7.2 Relative Volatility Deviation in Acetone/ n-Heptane Mixtures at 65°C

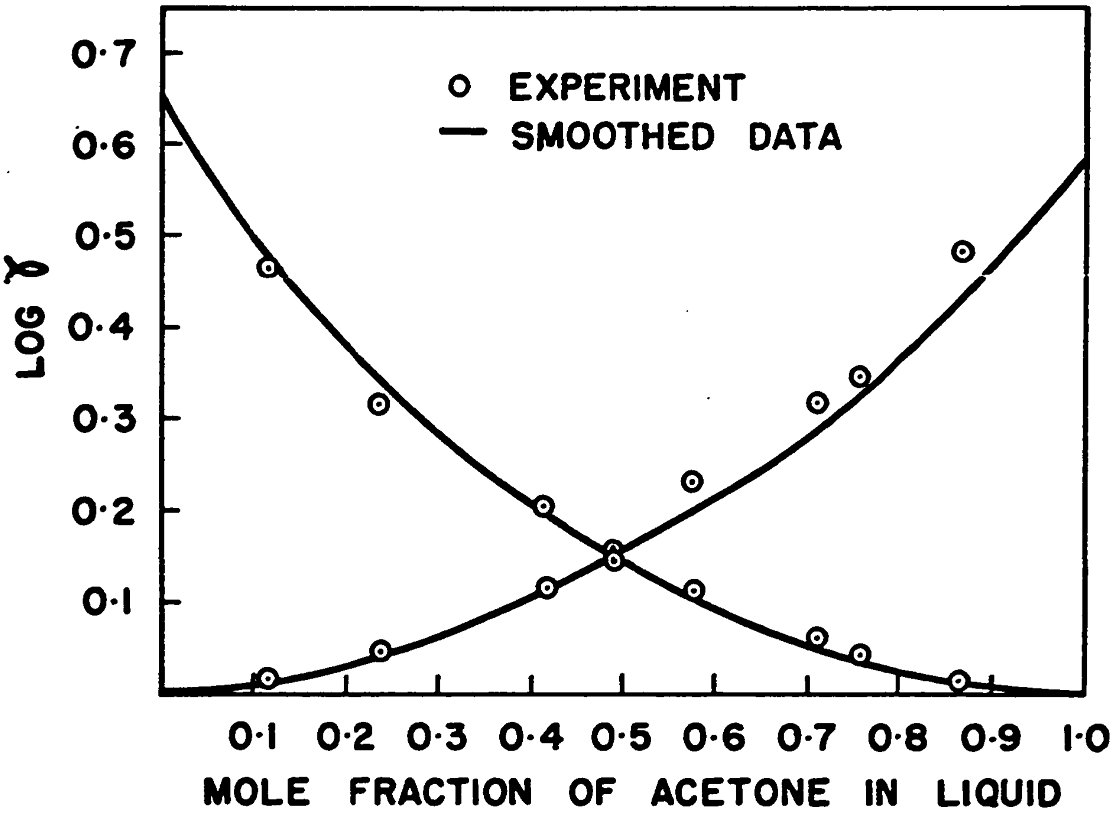


FIGURE 7.3 Activity Coefficients in Acetone/ n-Heptane Mixtures at 65°C

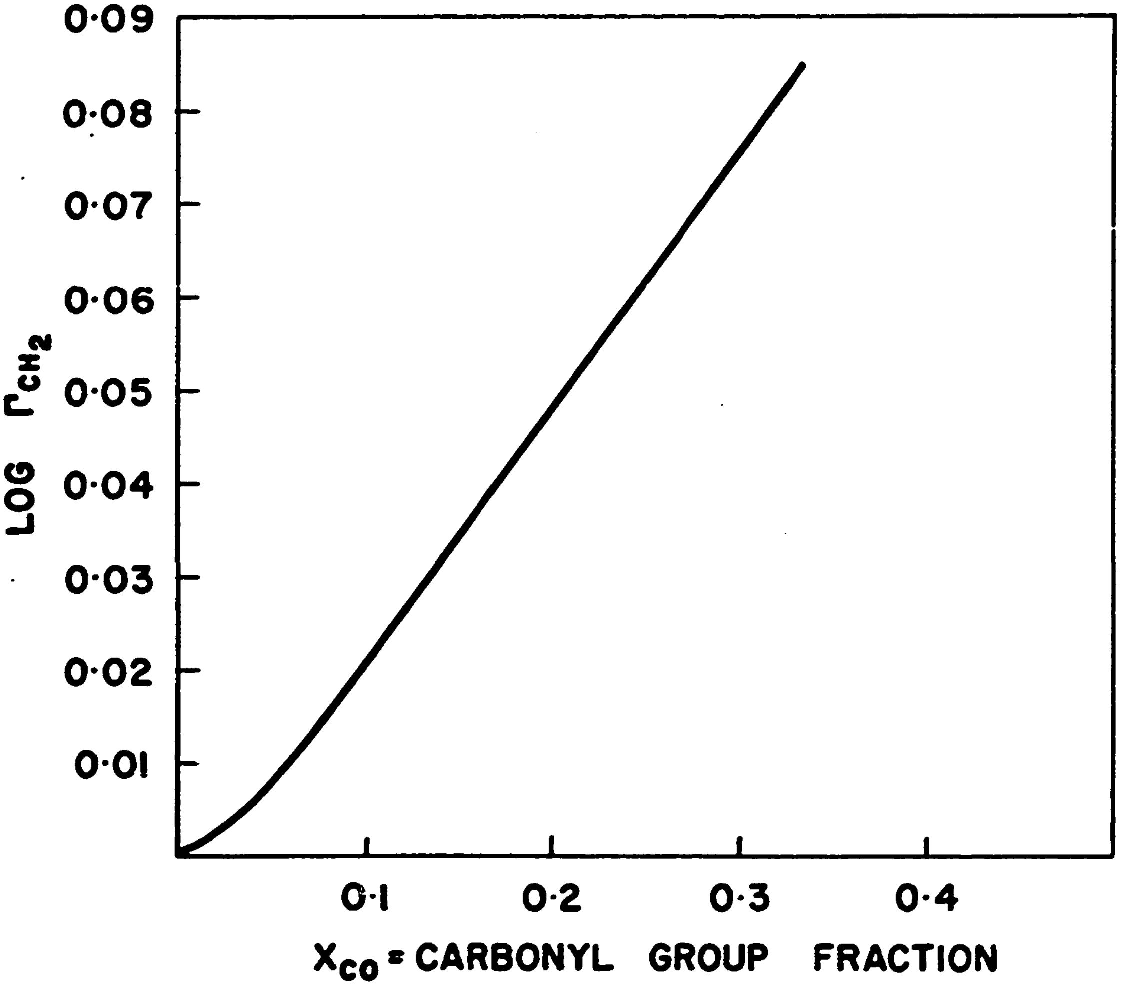


FIGURE 7.4 Group Activity Coefficient of Methylene in CH_2/CO Mixtures at 65°C

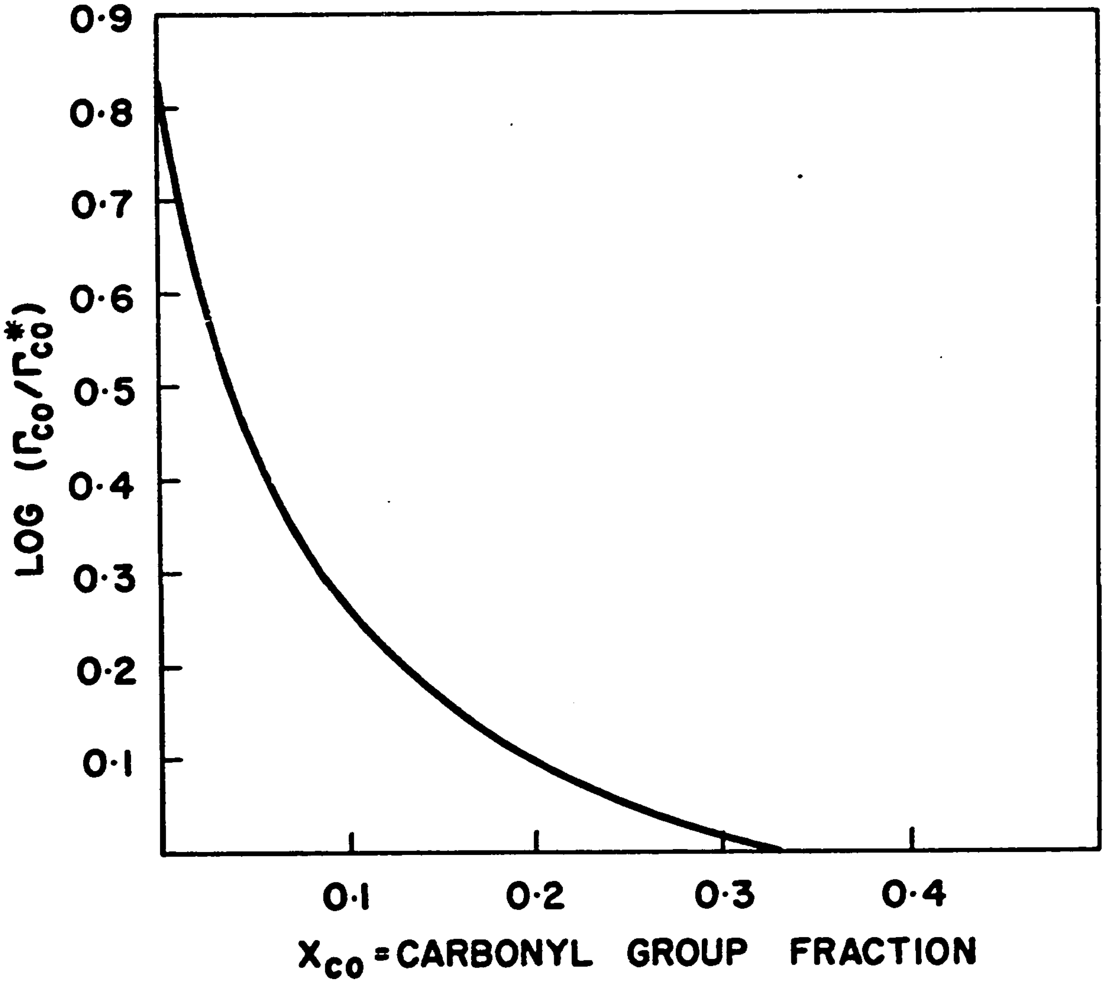
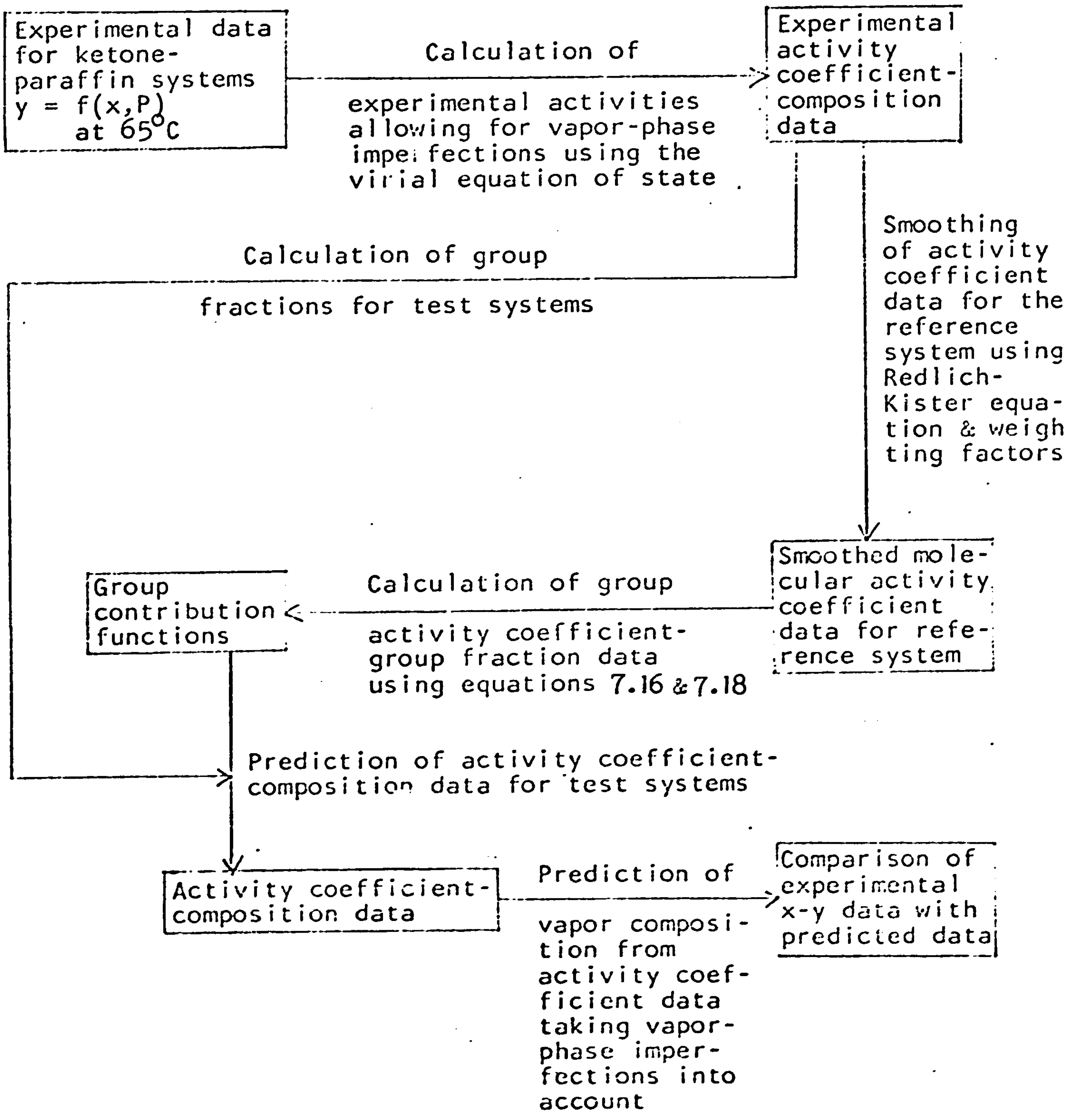


FIGURE 7.5 Group Activity Coefficient of Carbonyl in CH_2/CO Mixtures at 65°C

FIGURE 7.6

Application of Group Solution Model



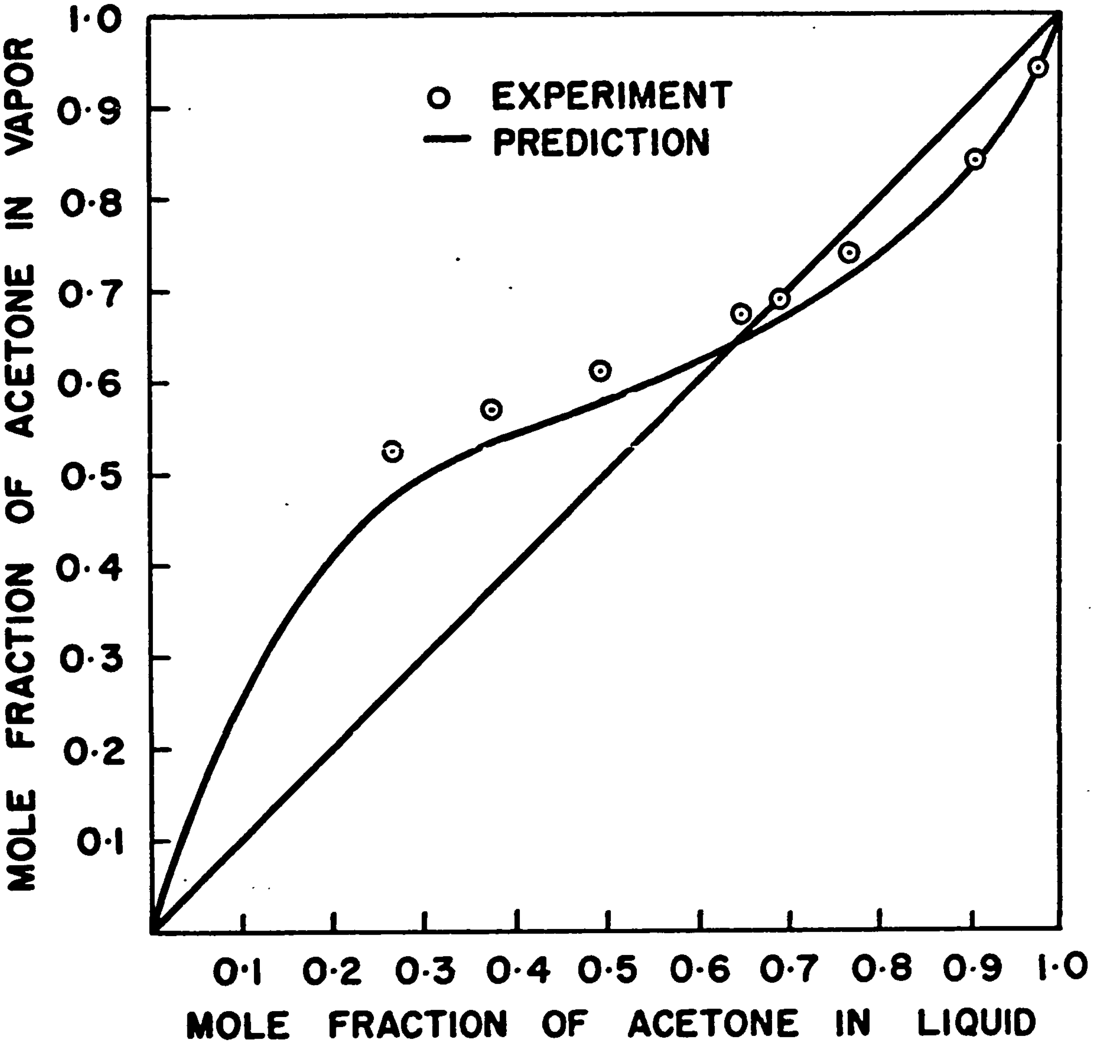


FIGURE 7.7 Vapor-Liquid Equilibrium of Acetone/n-Hexane Mixtures at 65°C

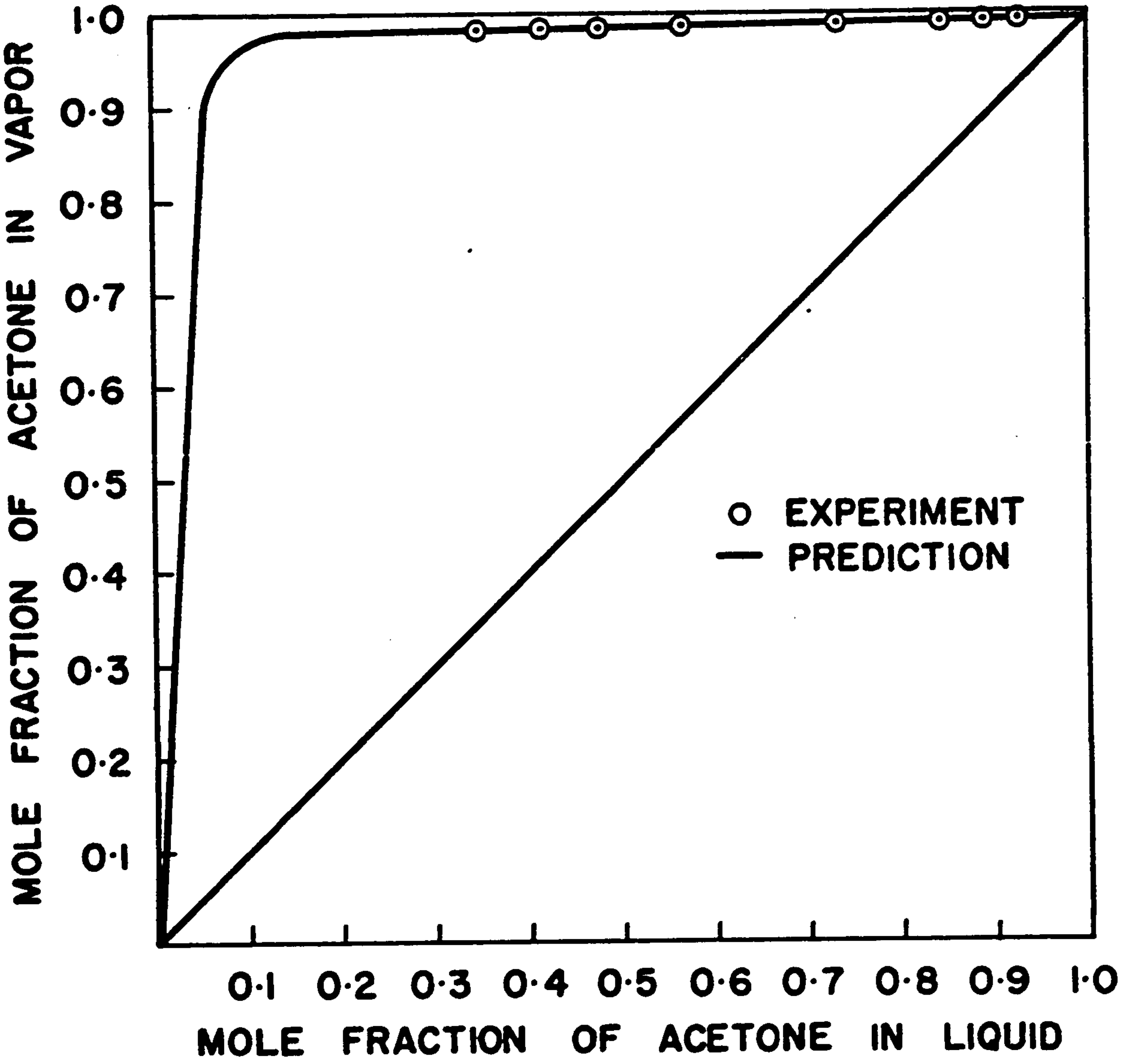


FIGURE 7.8 Vapor-Liquid Equilibrium of Acetone/ n-Decane Mixtures at 65°C

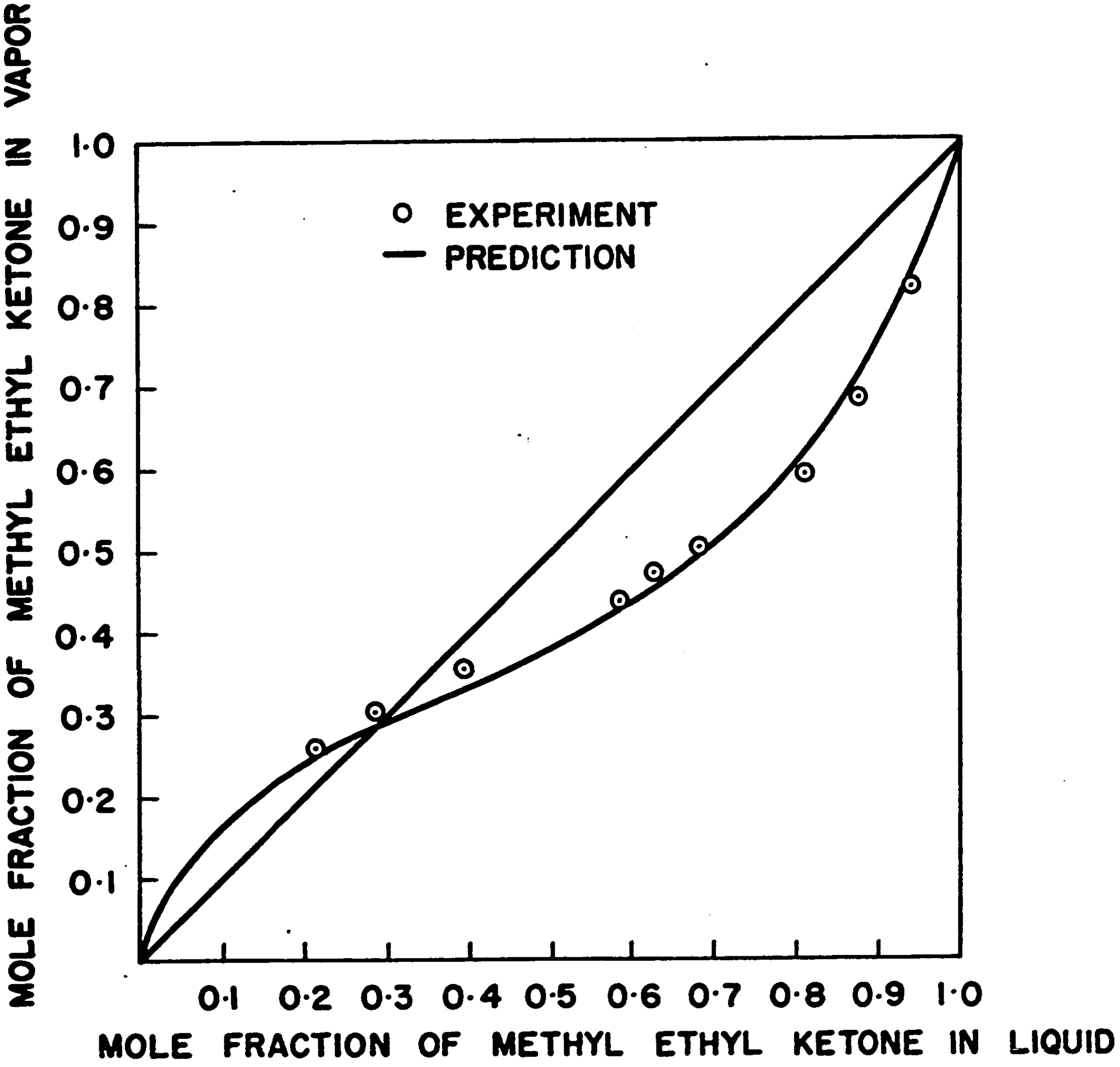


FIGURE 7.9 Vapor-Liquid Equilibrium of Methyl Ethyl Ketone/n-Hexane Mixtures at 65°C

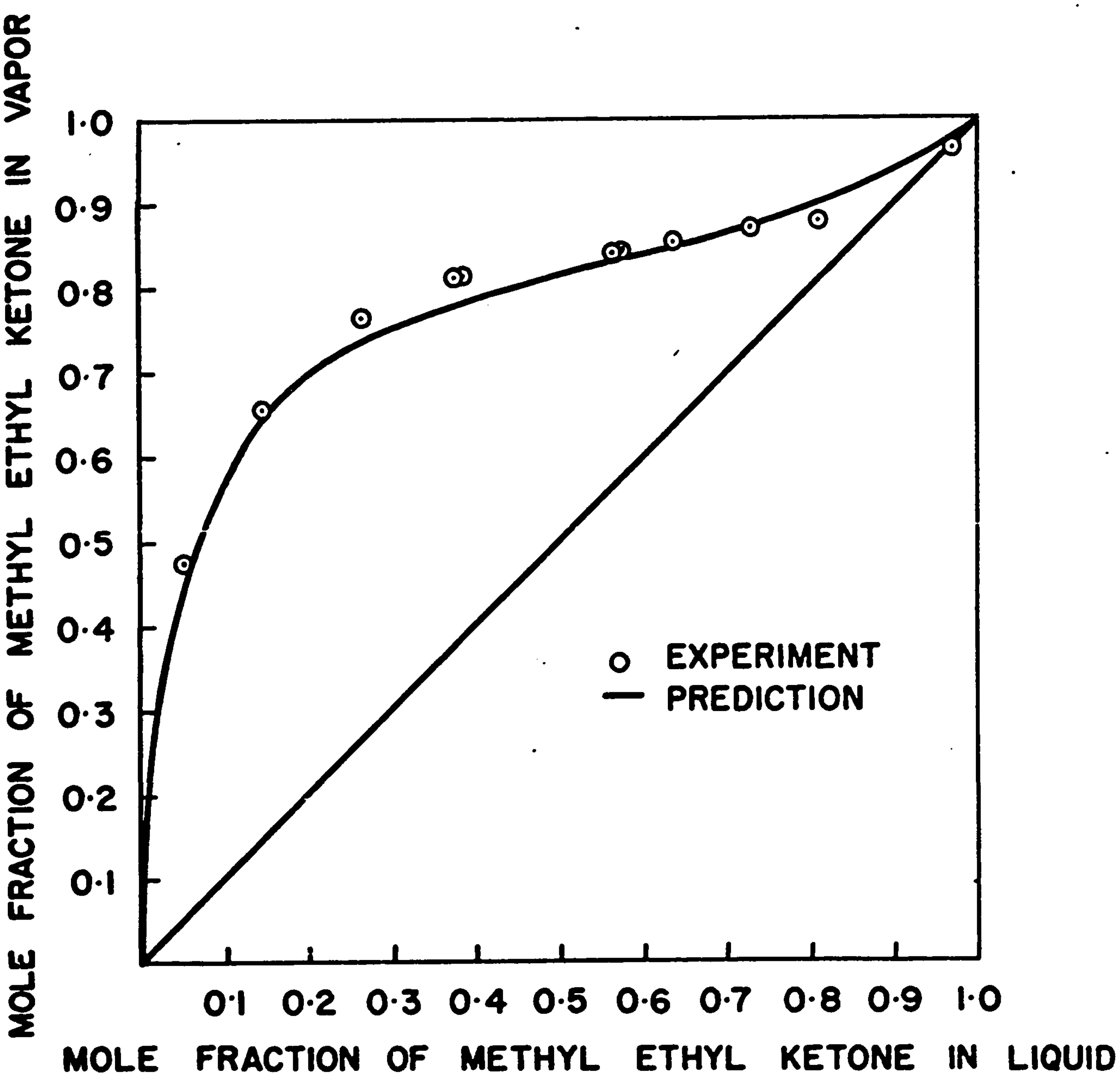


FIGURE 7.10 Vapor-Liquid Equilibrium of Methyl Ethyl Ketone/n-Octane Mixtures at 65°C

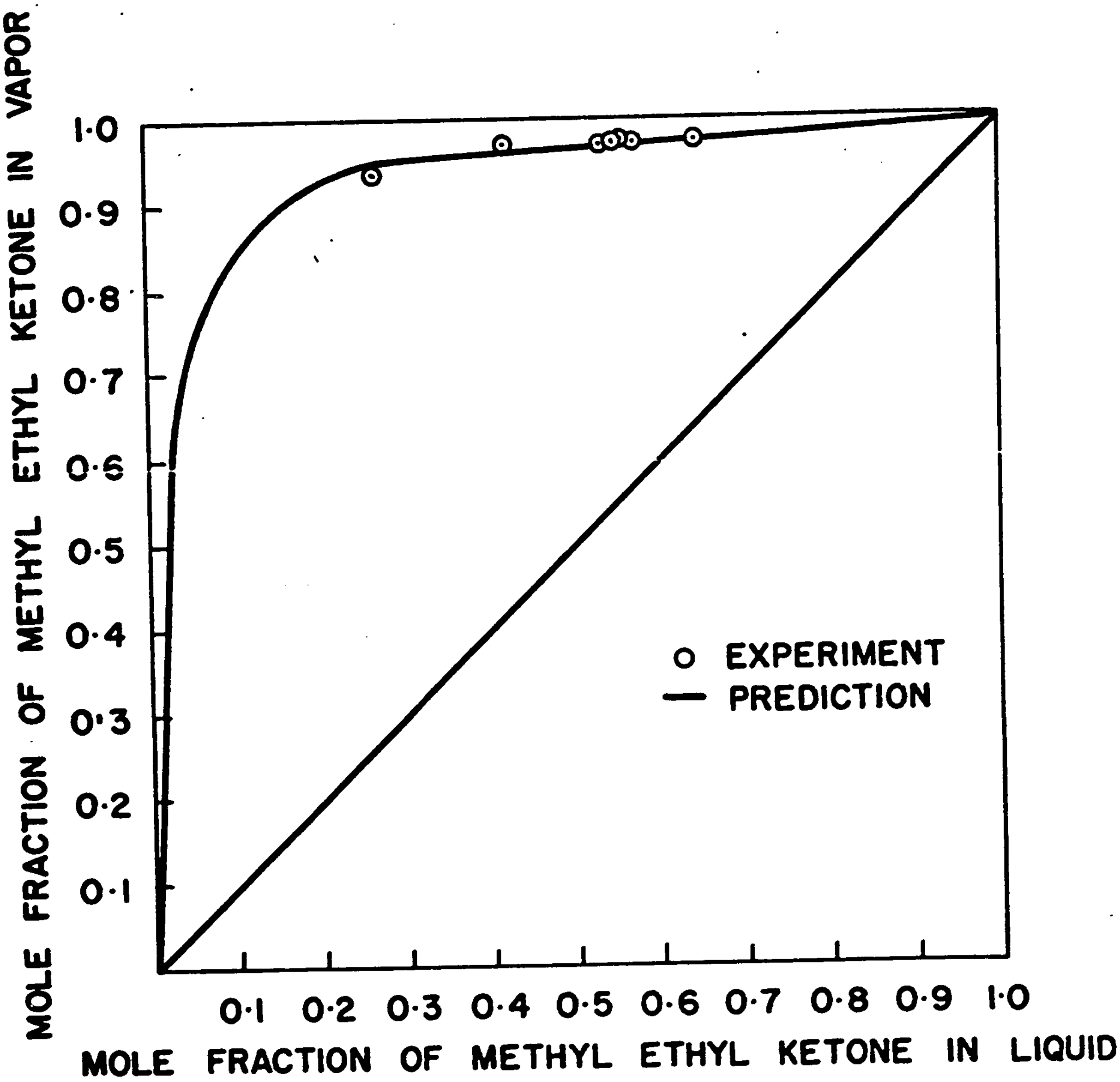


FIGURE 7.11 Vapor-Liquid Equilibrium of Methyl Ethyl Ketone/n-Decane Mixtures at 65°C

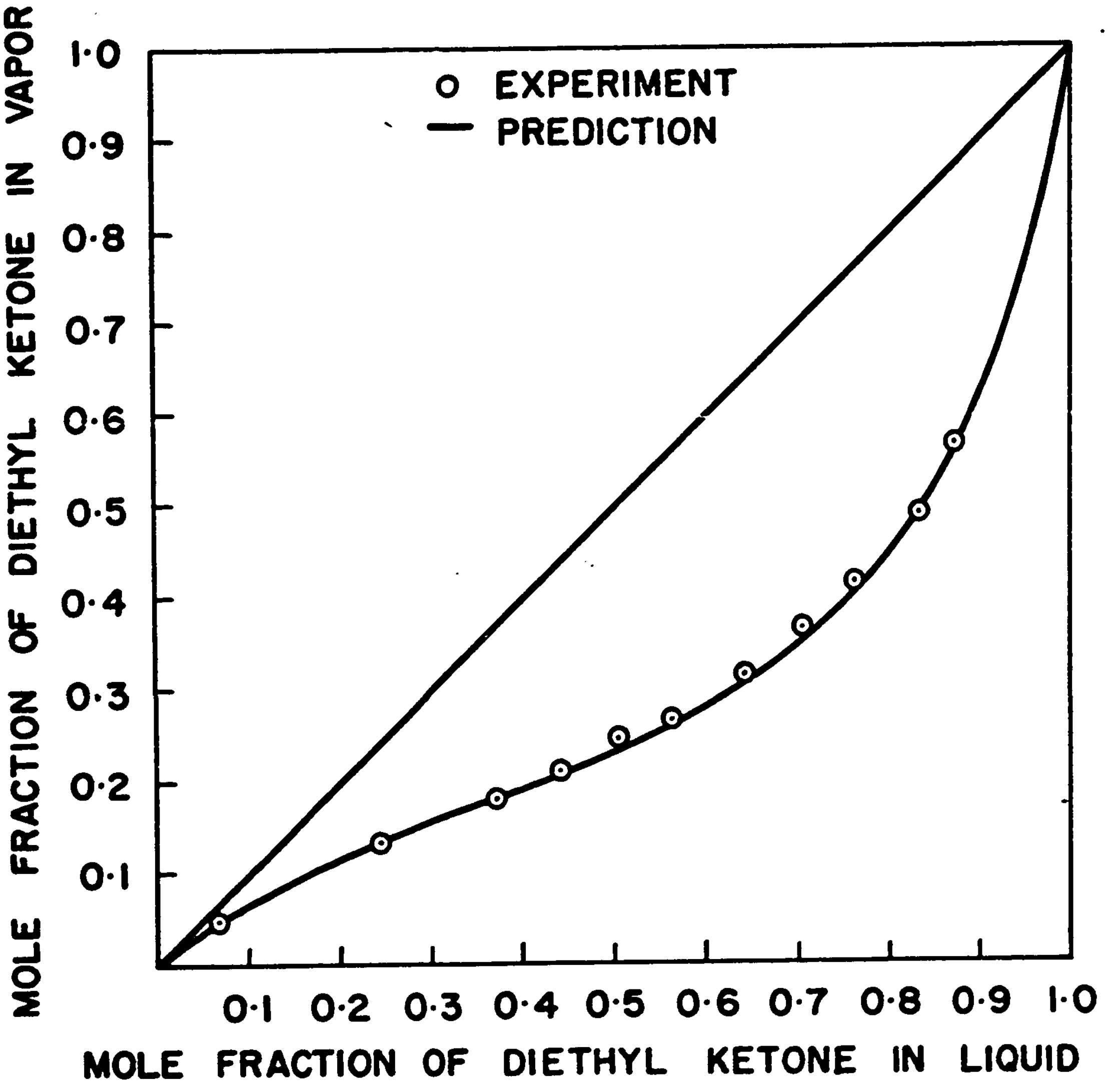


FIGURE 7.12 Vapor-Liquid Equilibrium of Diethyl Ketone/n-Hexane Mixtures at 65°C

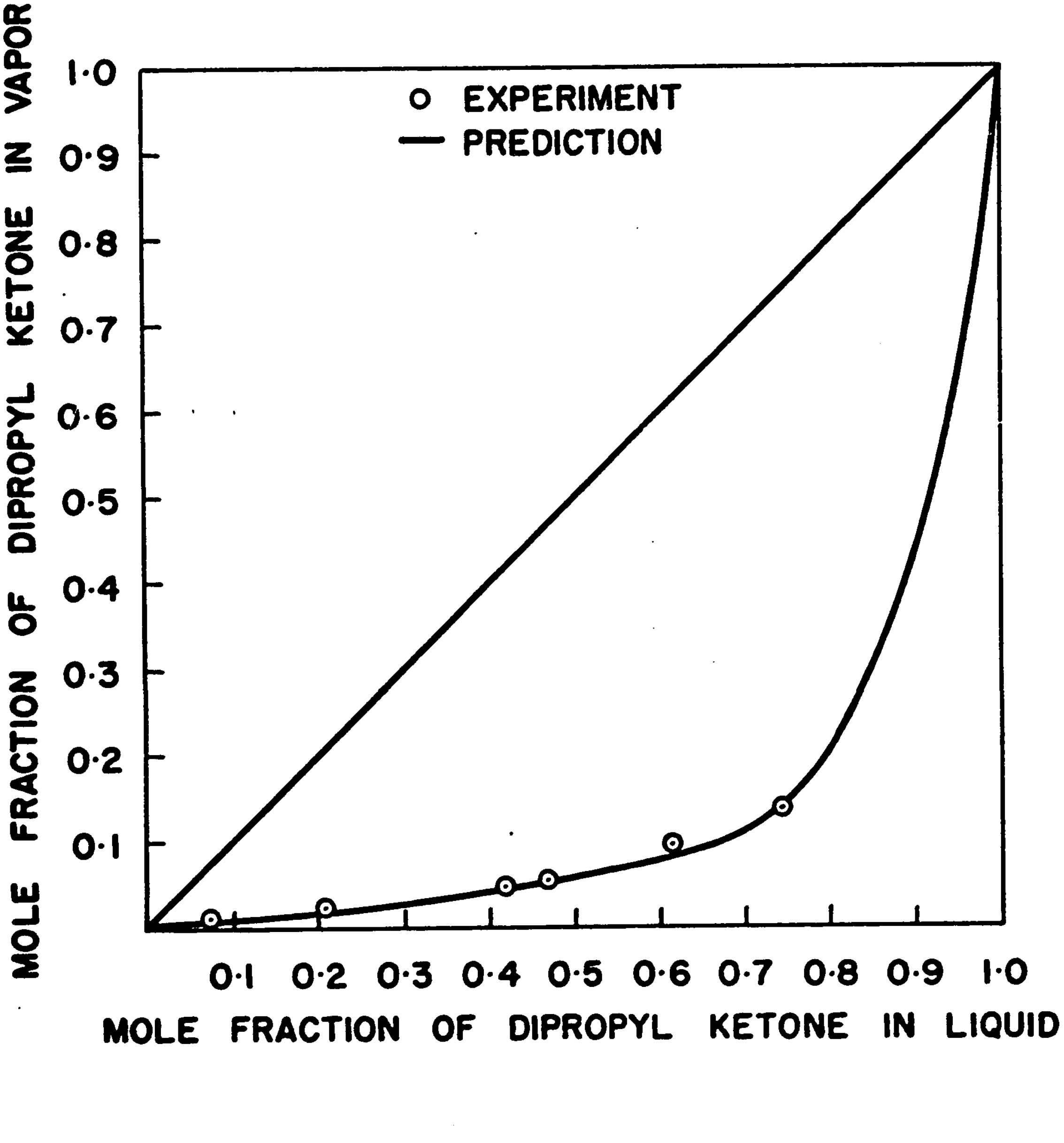


FIGURE 7.13 Vapor-Liquid Equilibrium of Dipropyl Ketone/n-Hexane Mixtures at 65°C

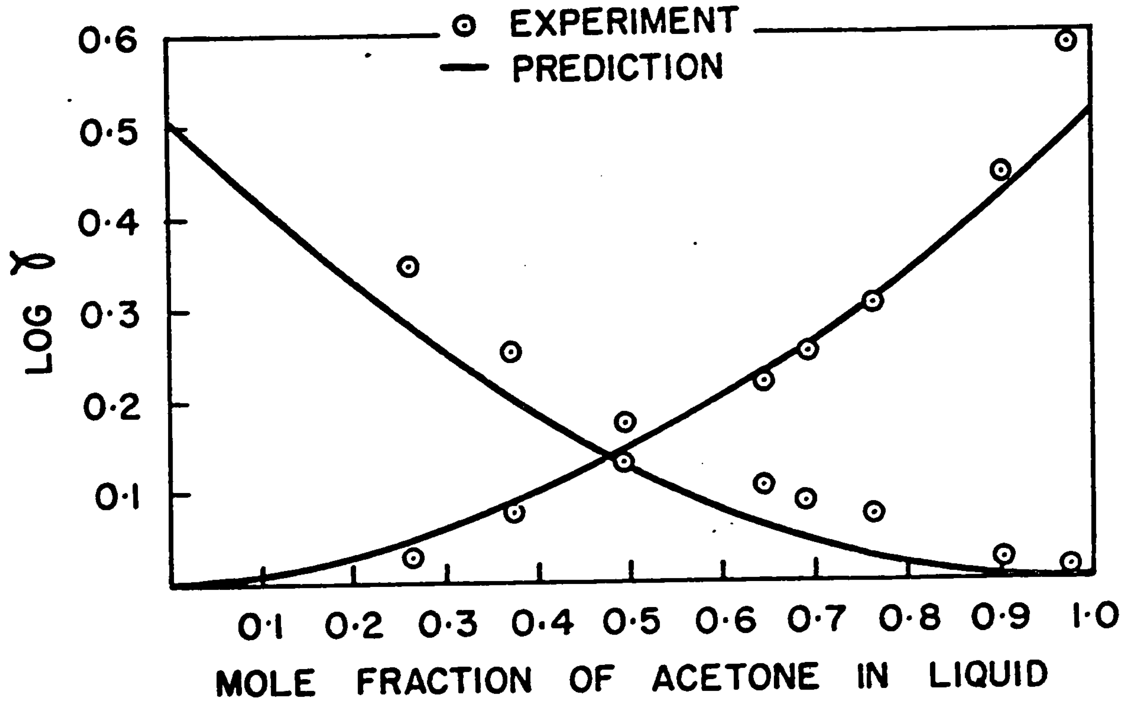


FIGURE 7.14 Activity Coefficients in Acetone/n-Hexane Mixtures at 65°C

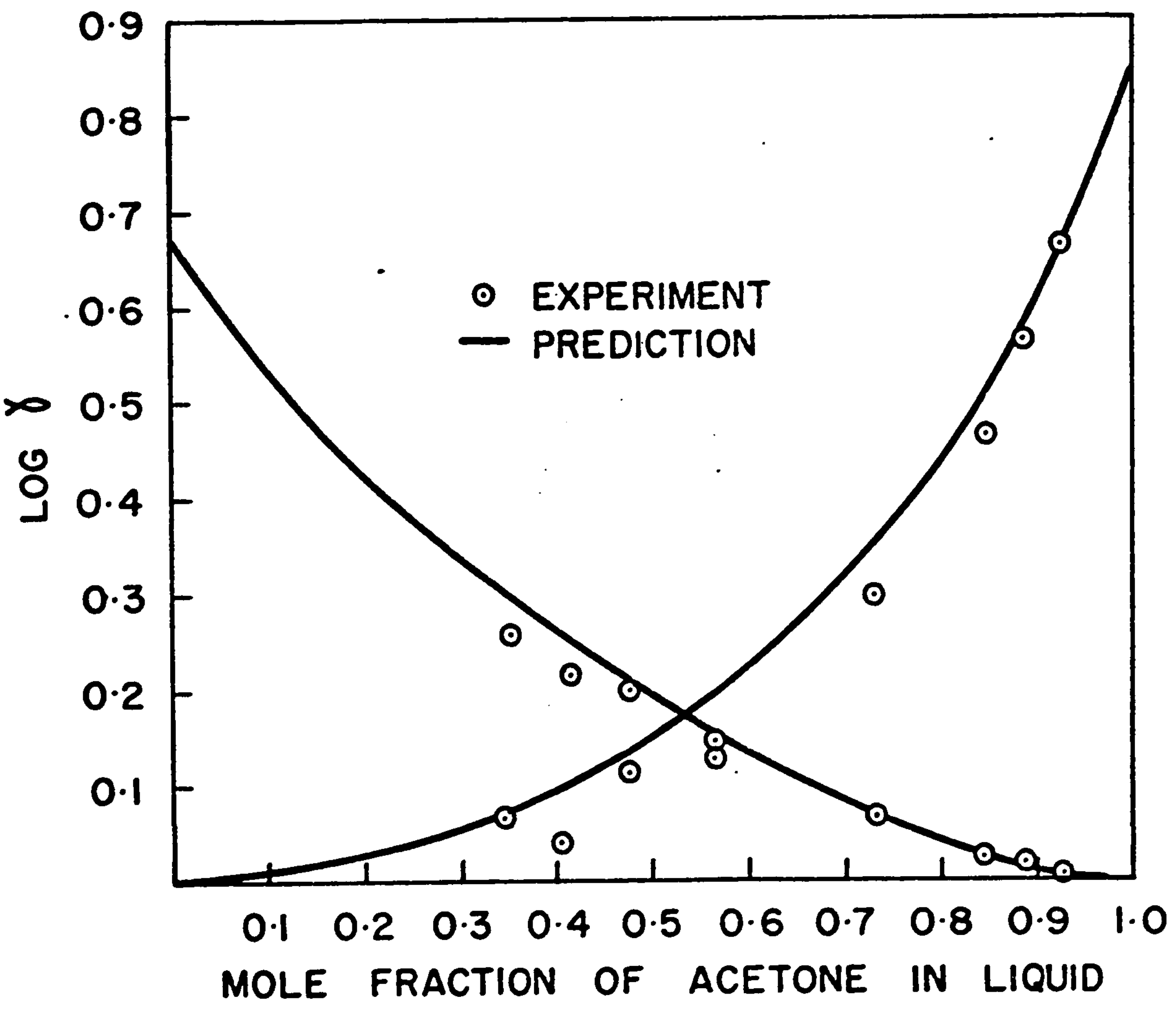


FIGURE 7.15 Activity Coefficients in Acetone/n-Decane Mixtures at 65°C

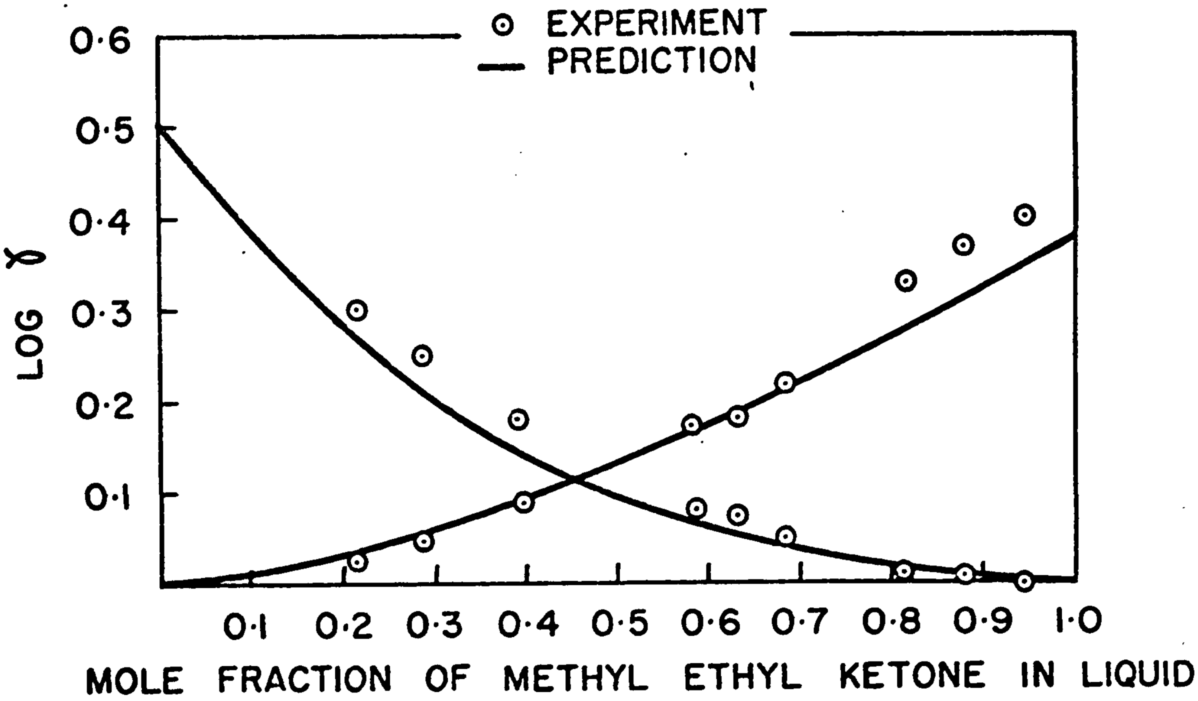


FIGURE 7.16 Activity Coefficients in Methyl Ethyl Ketone/n-Hexane Mixtures at 65°C

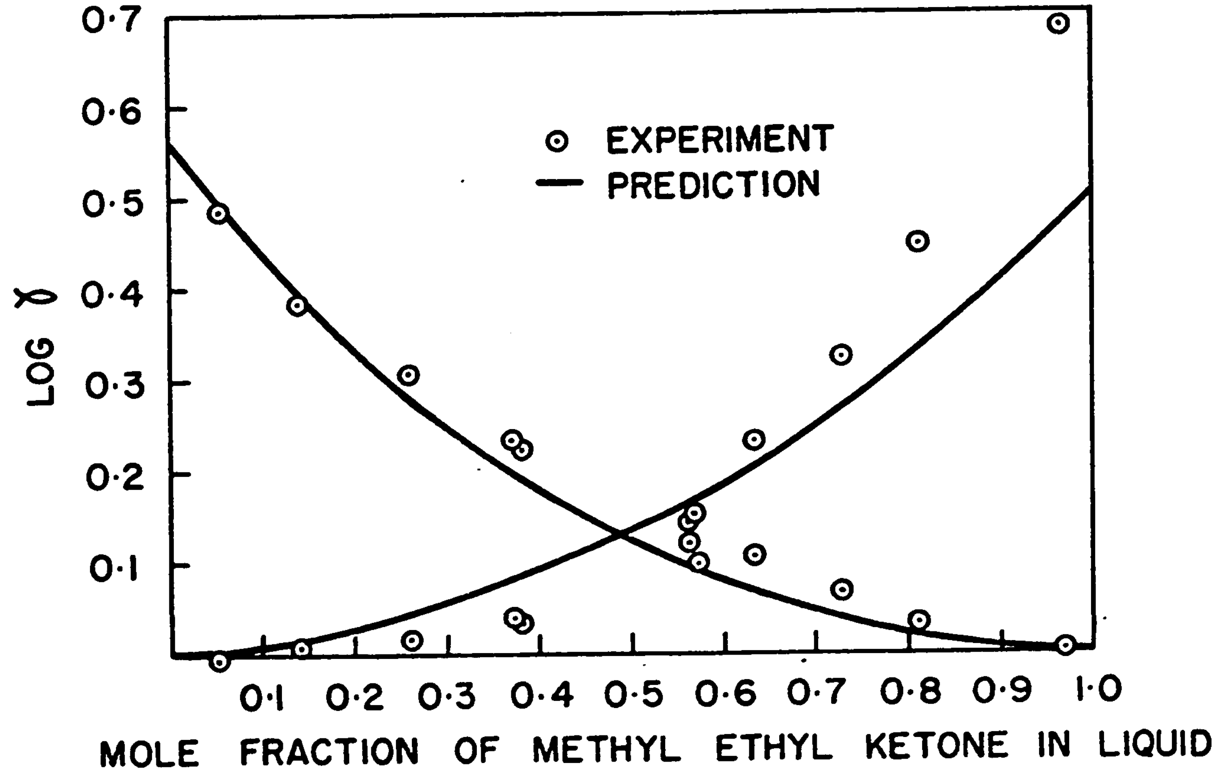


FIGURE 7.17 Activity Coefficients in Methyl Ethyl Ketone/n-Octane Mixtures at 65°C

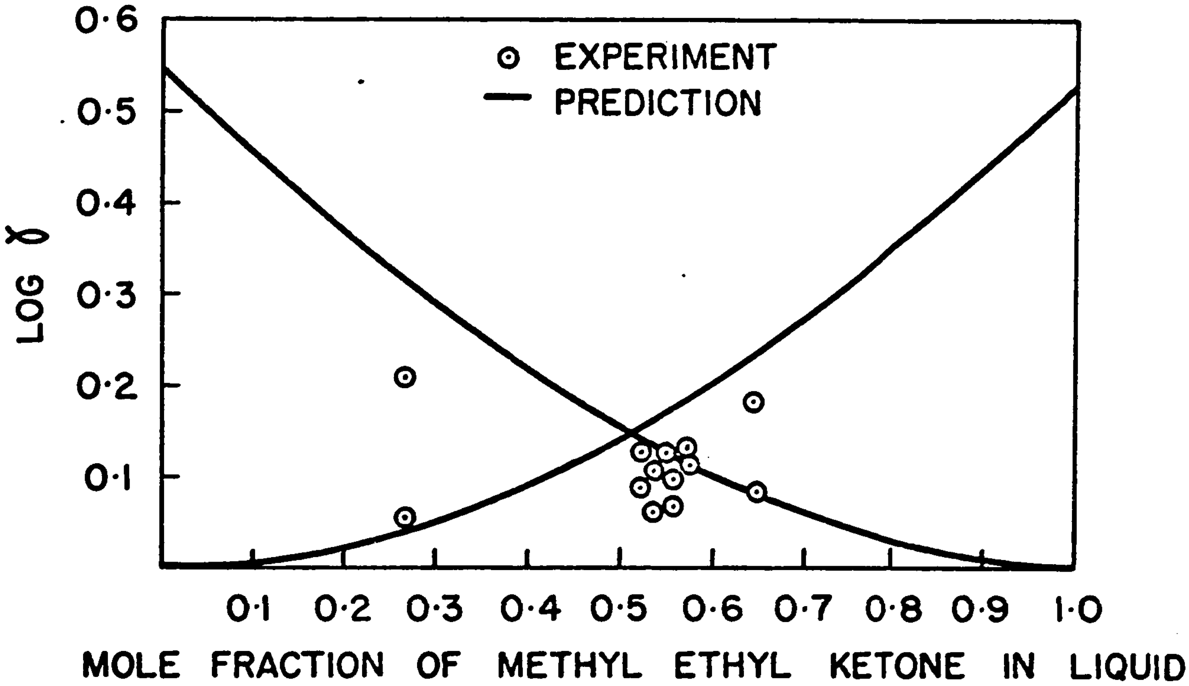


FIGURE 7.18 Activity Coefficients in Methyl Ethyl Ketone/n-Decane Mixtures at 65°C

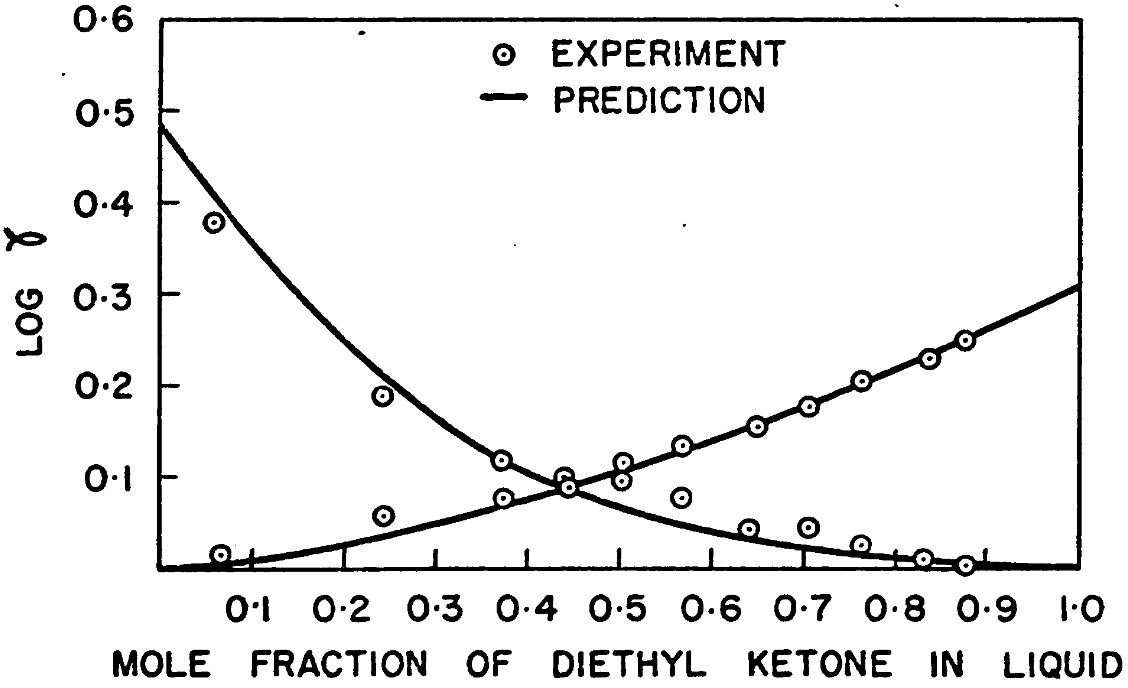


FIGURE 7.19 Activity Coefficients in Diethyl Ketone/ n-Hexane Mixtures at 65°C

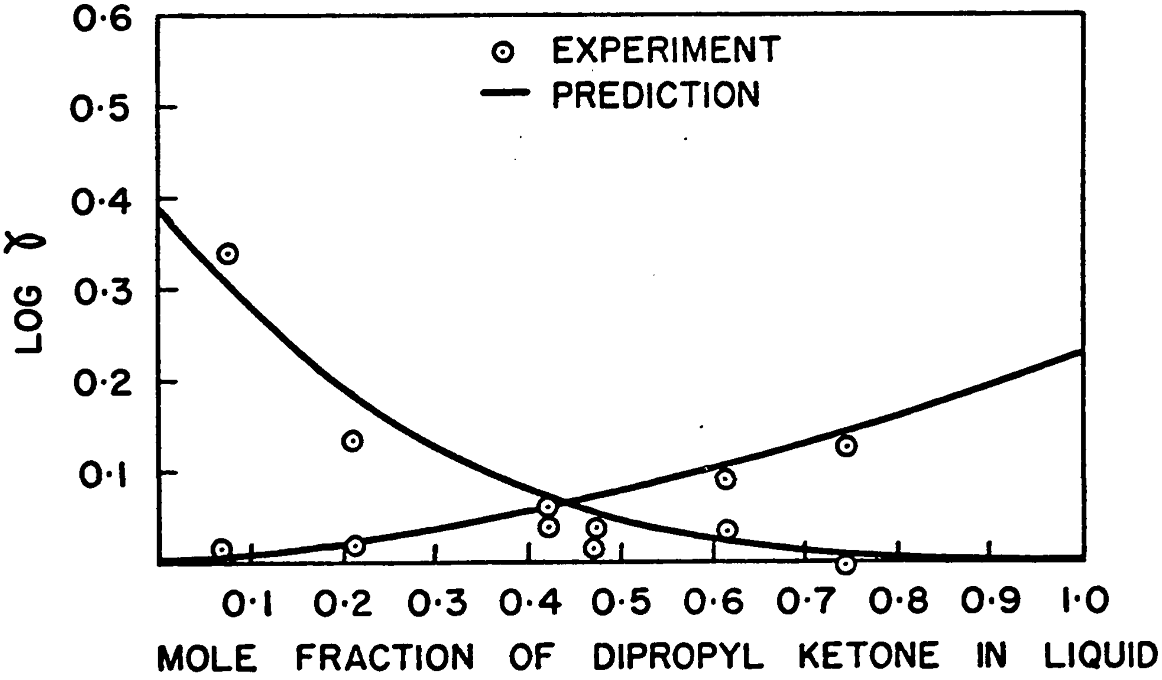


FIGURE 7.20 Activity Coefficients in Dipropyl Ketone/ n-Hexane Mixtures at 65°C

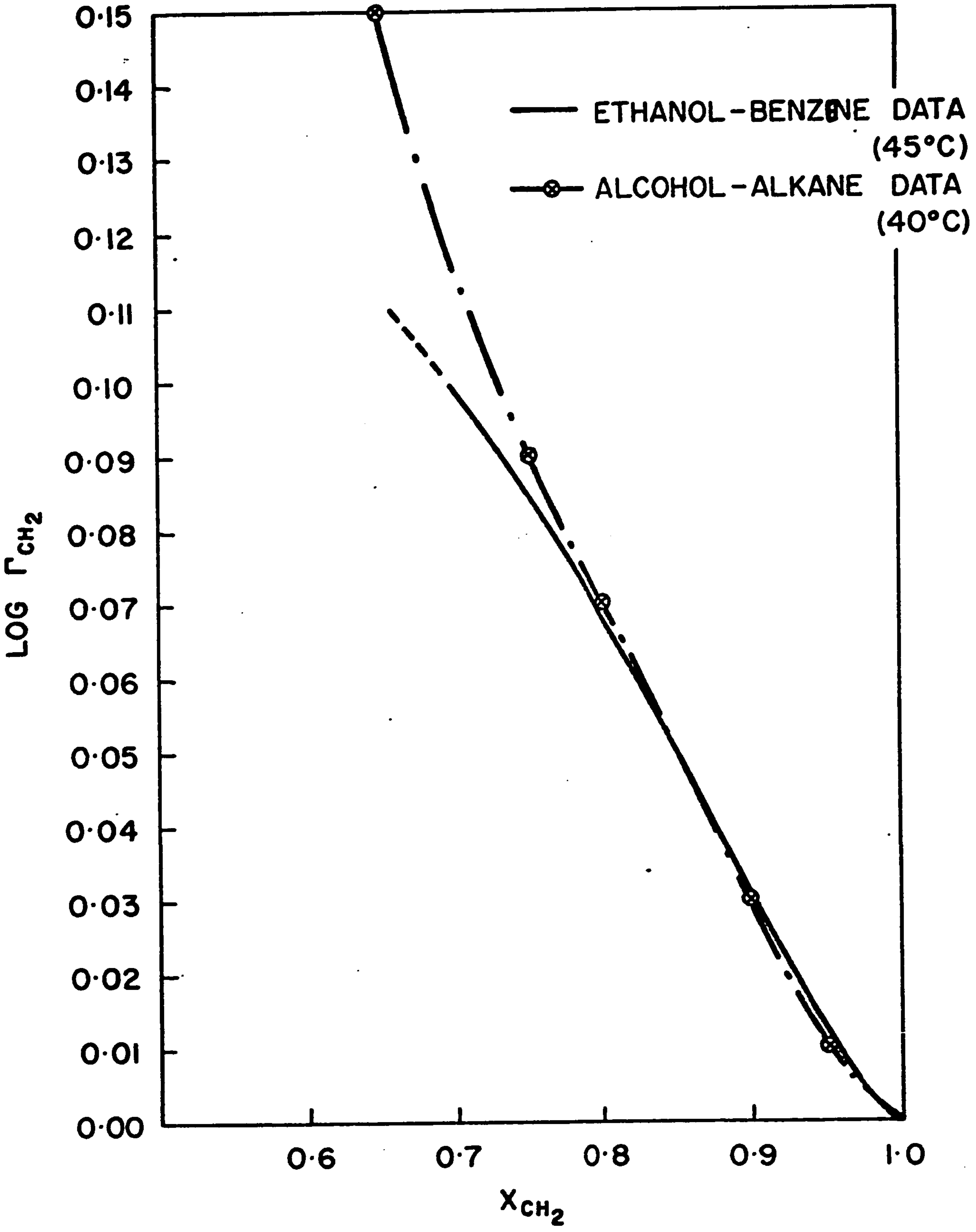


FIGURE 7.21 Group Activity Coefficient of Methylene in CH_2/[illegible] Mixtures at 45°C

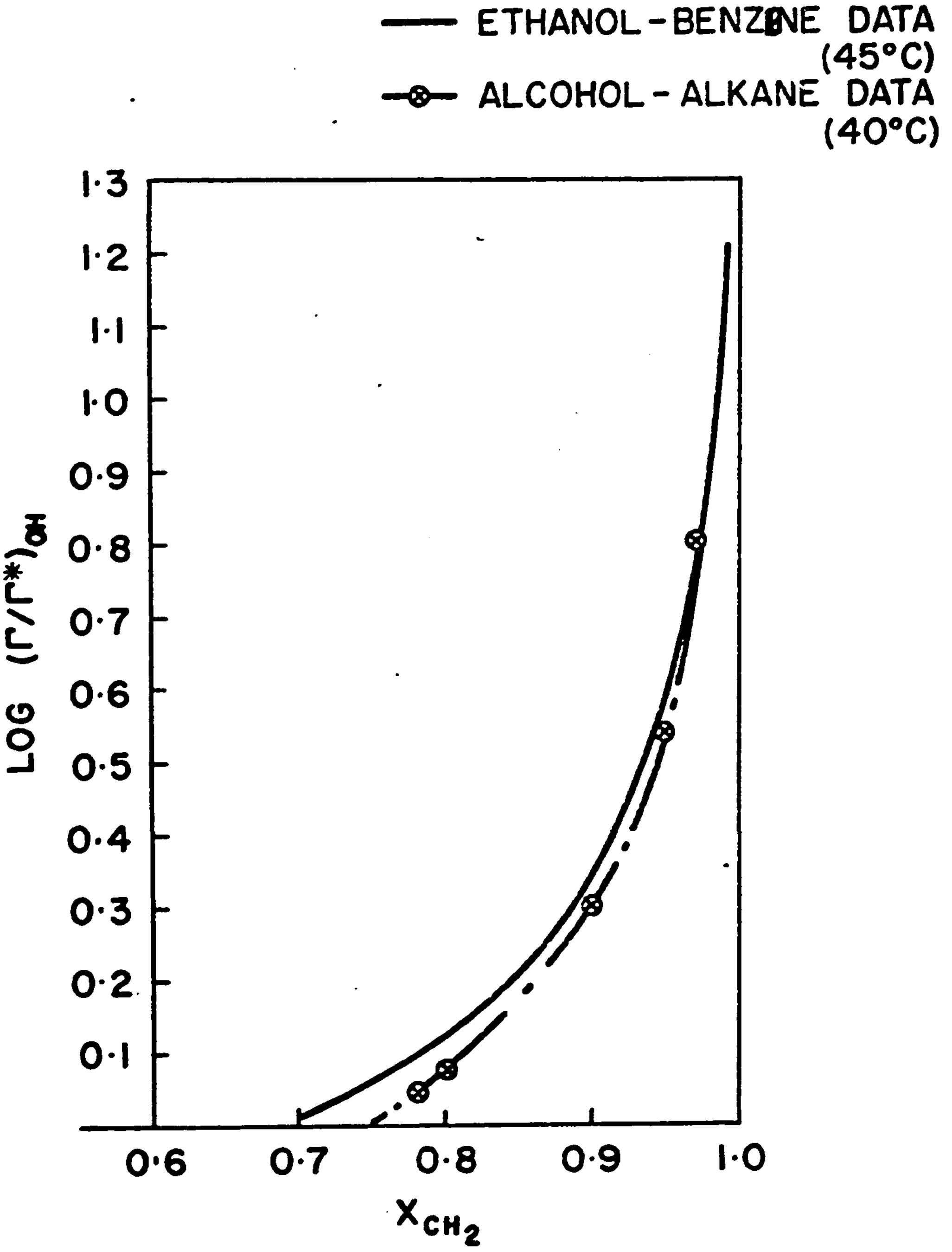


FIGURE 7.22 Group Activity Coefficient of Hydroxyl in CH_2/OH Mixtures at 45°C

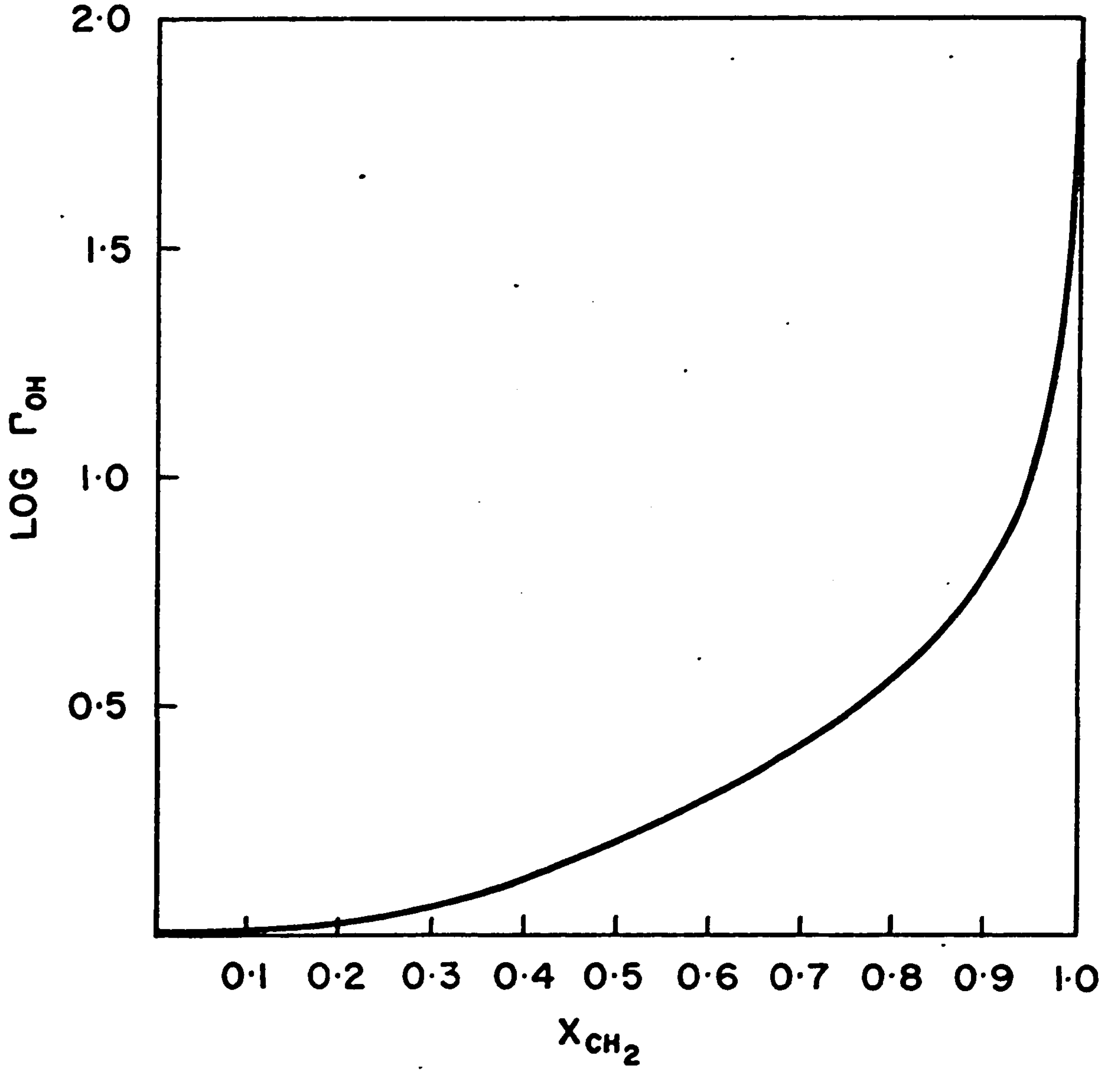


FIGURE 22(A) Group Activity Coefficient of Hydroxyl in Aliphatic CH /OH Mixtures at 40°C

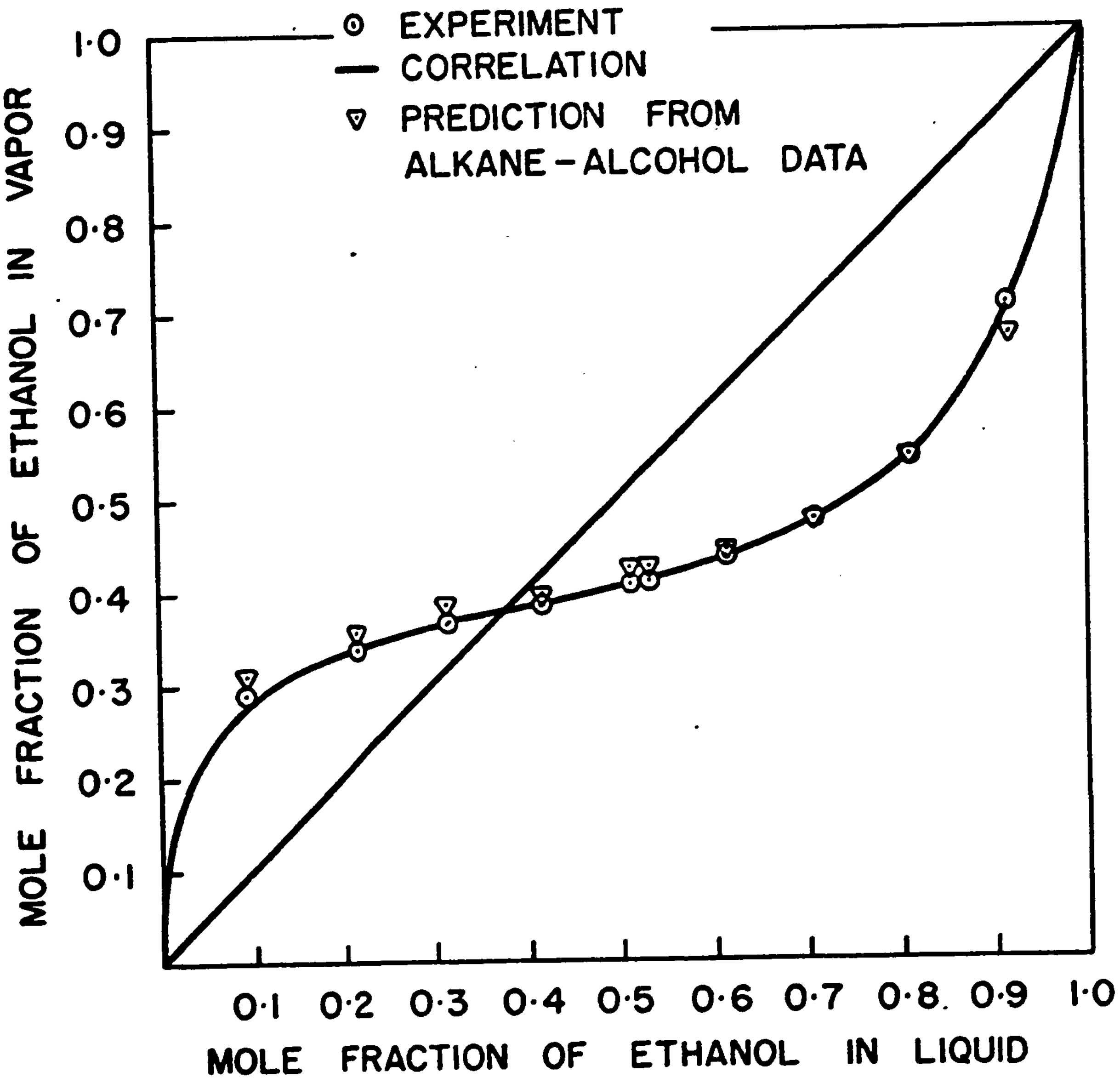


FIGURE 7.23 Vapor-Liquid Equilibrium of Ethanol-Benzene Mixtures at 45°C

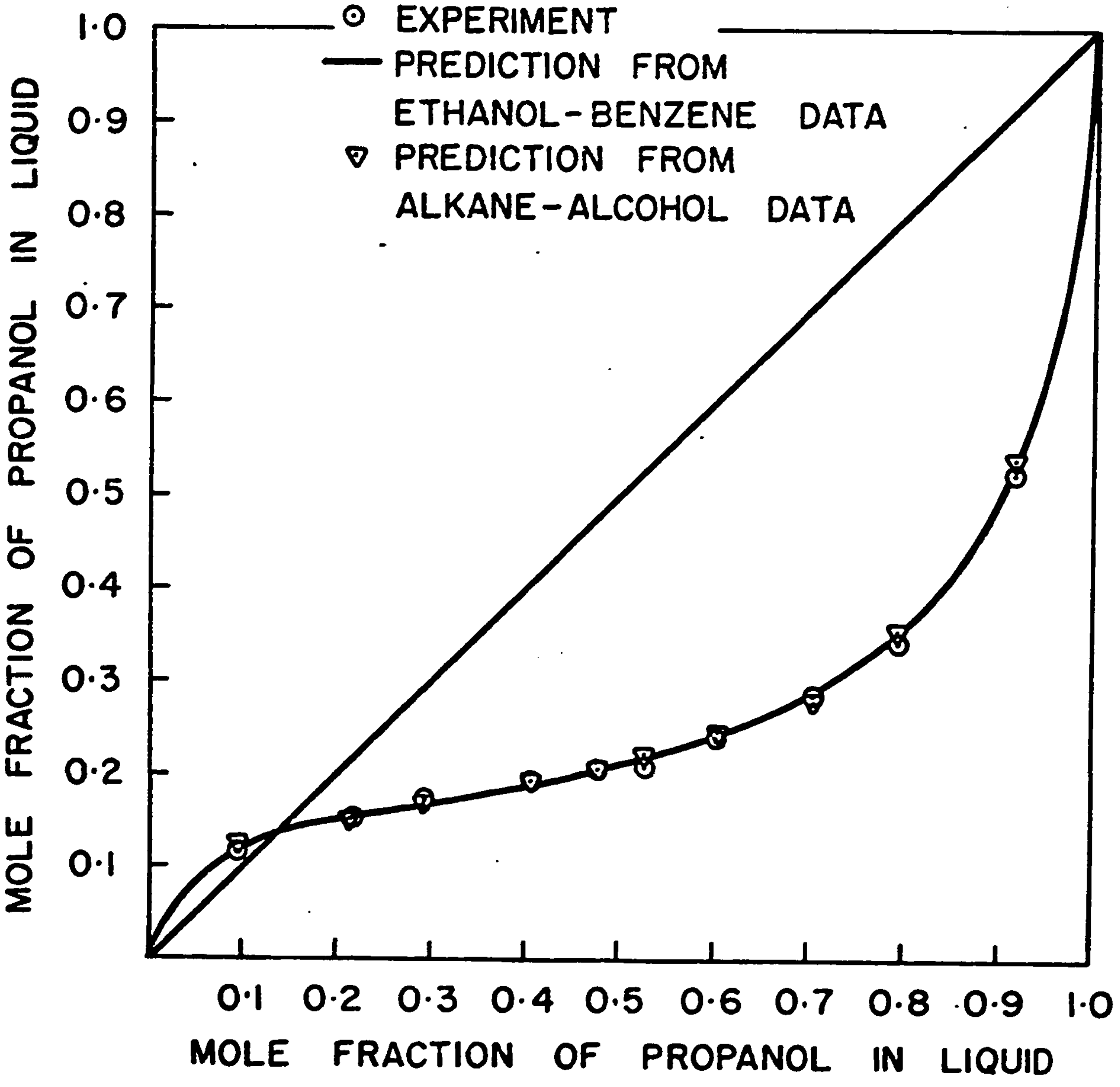


FIGURE 7.24 Vapor-Liquid Equilibrium of n-Propanol-Benzene Mixtures at 45°C

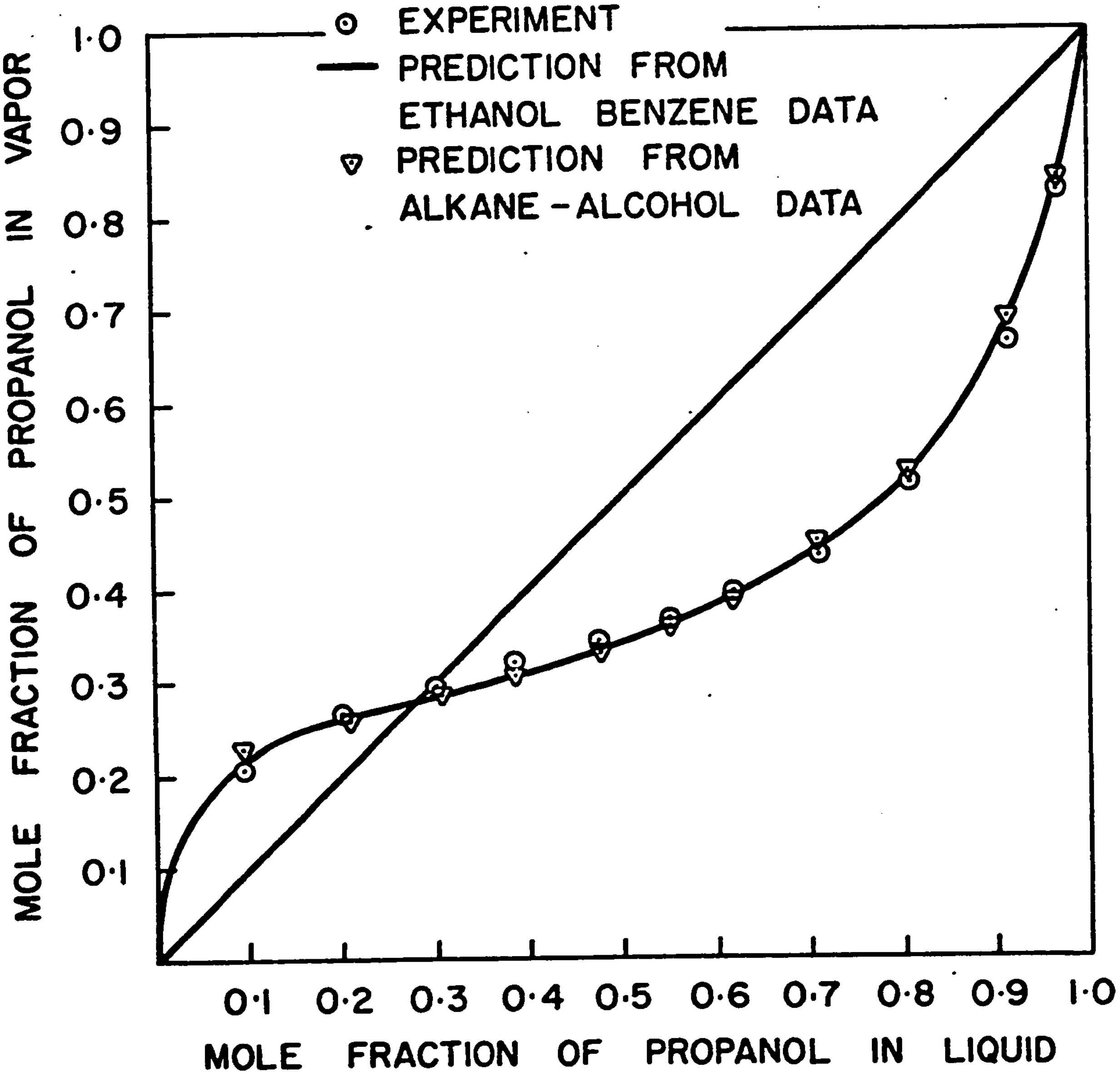


FIGURE 7.25 Vapor-Liquid Equilibrium of Isopropanol-Benzene Mixtures at 45°C

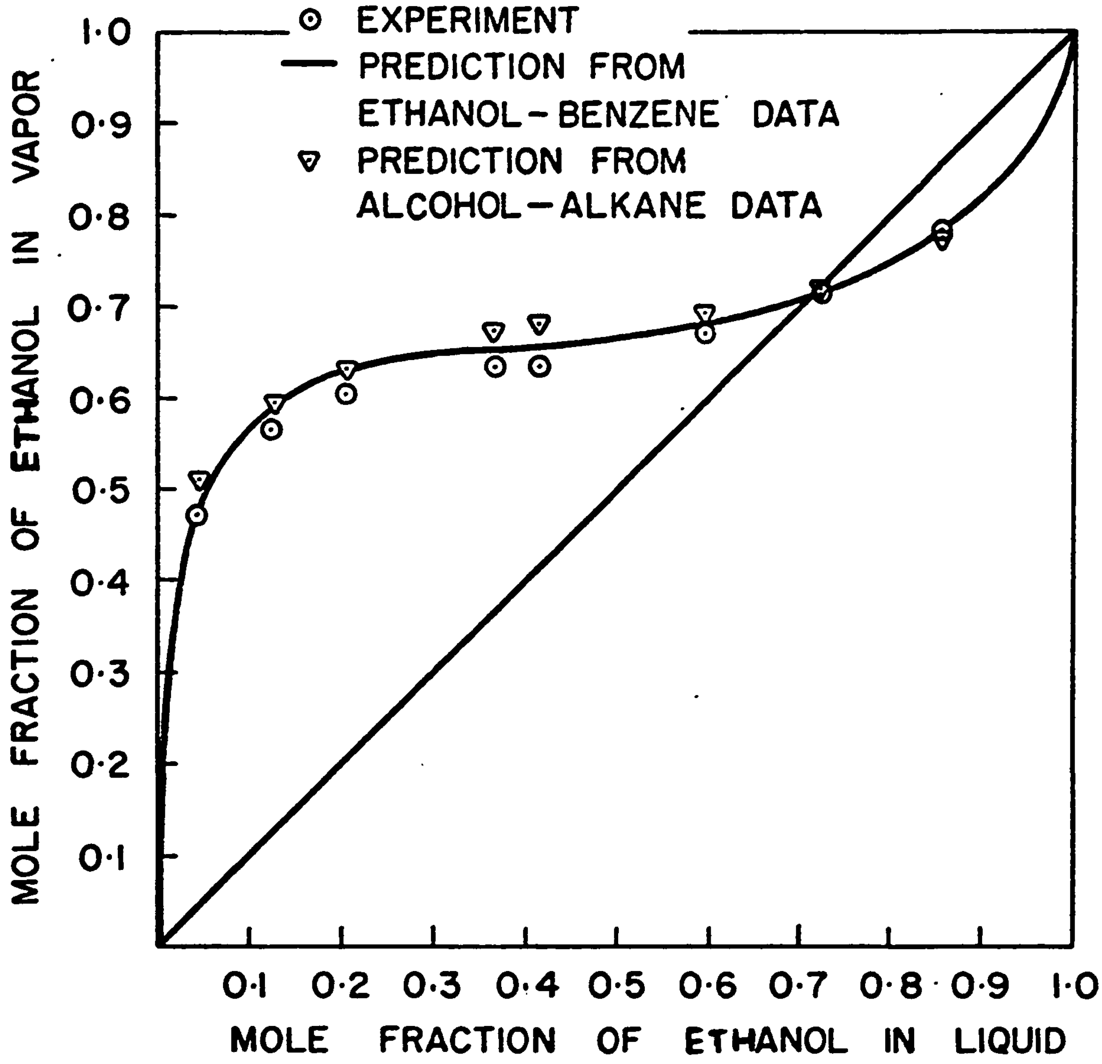


FIGURE 7.26 Vapor-Liquid Equilibrium of Ethanol-Toluene Mixtures at 35°C

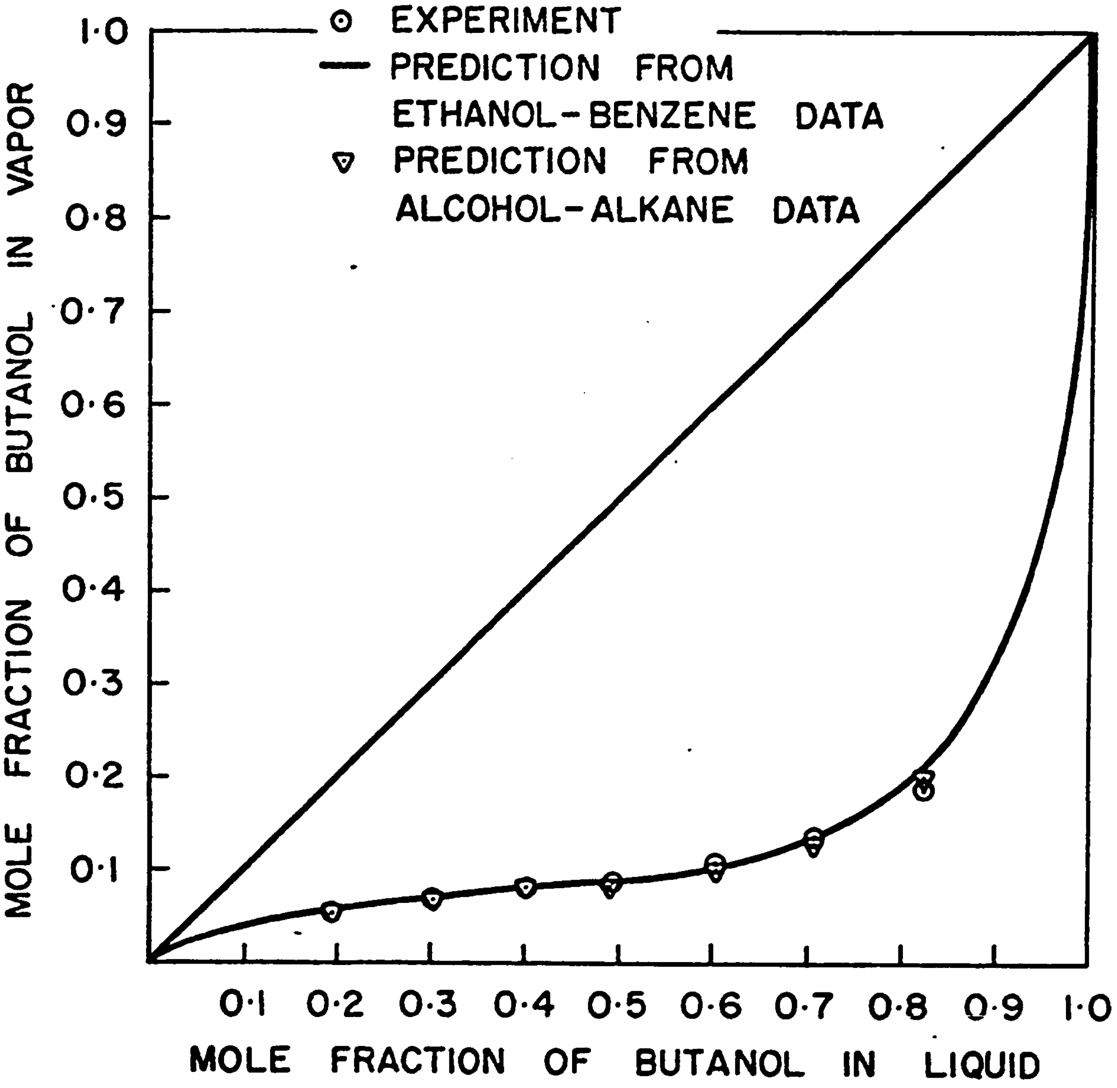


FIGURE 7.27 Vapor-Liquid Equilibrium of n-Butanol-Benzene Mixtures at 45°C

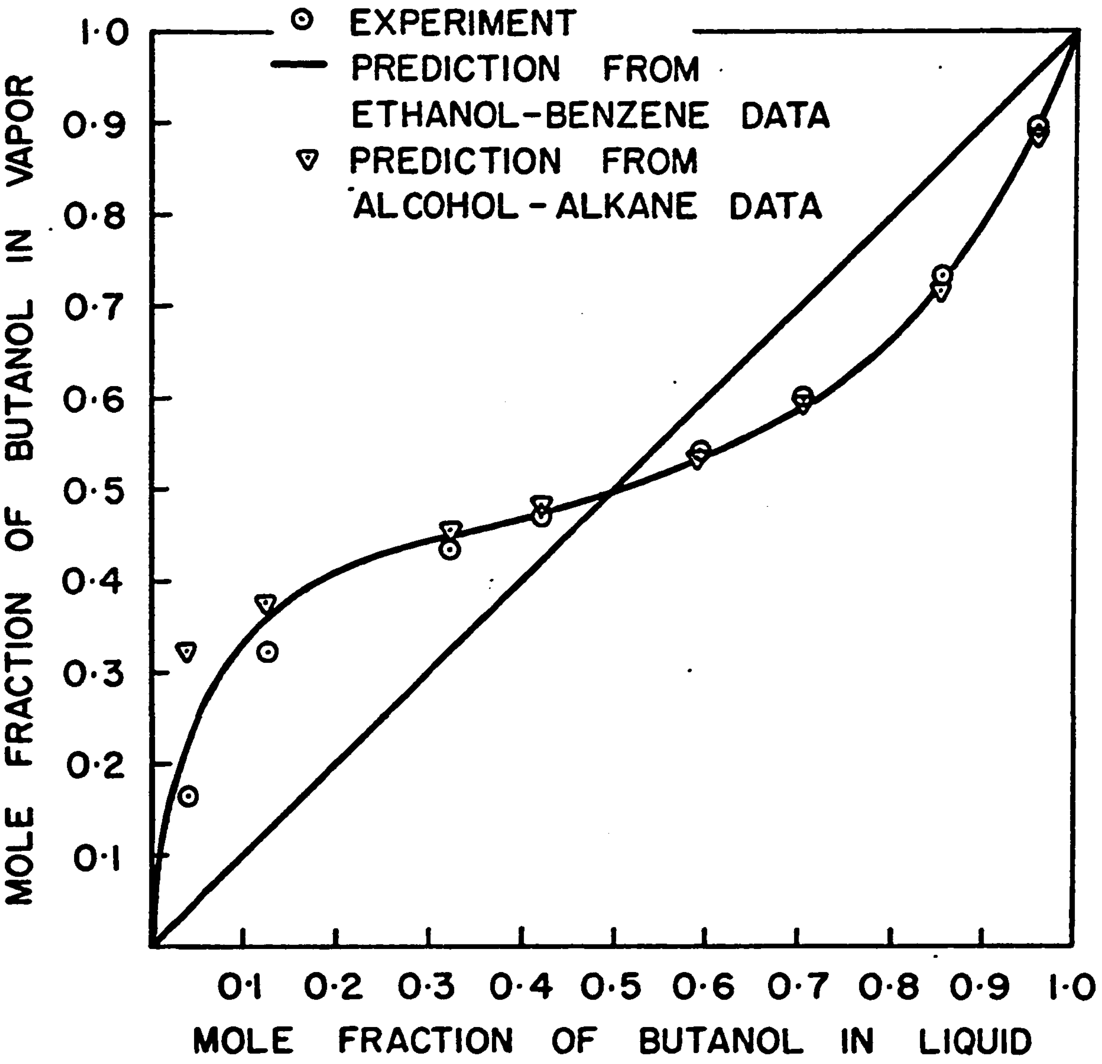


FIGURE 7.28 Vapor-Liquid Equilibrium of n-Butanol-Ethyl Benzene Mixtures at 100 mm. Hg.

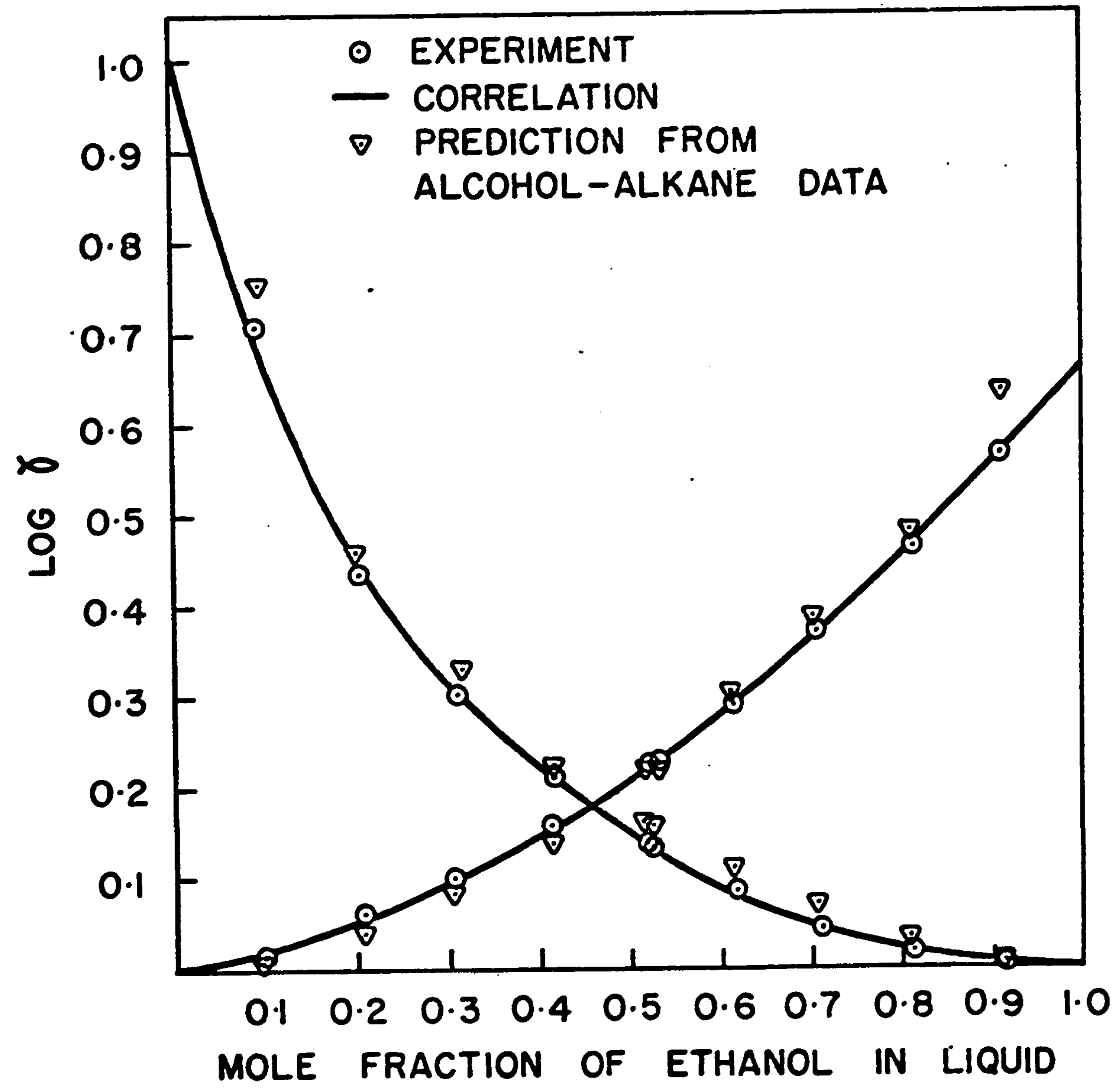


FIGURE 7.29 Activity Coefficients in Ethanol-Benzene Mixtures at 45°C

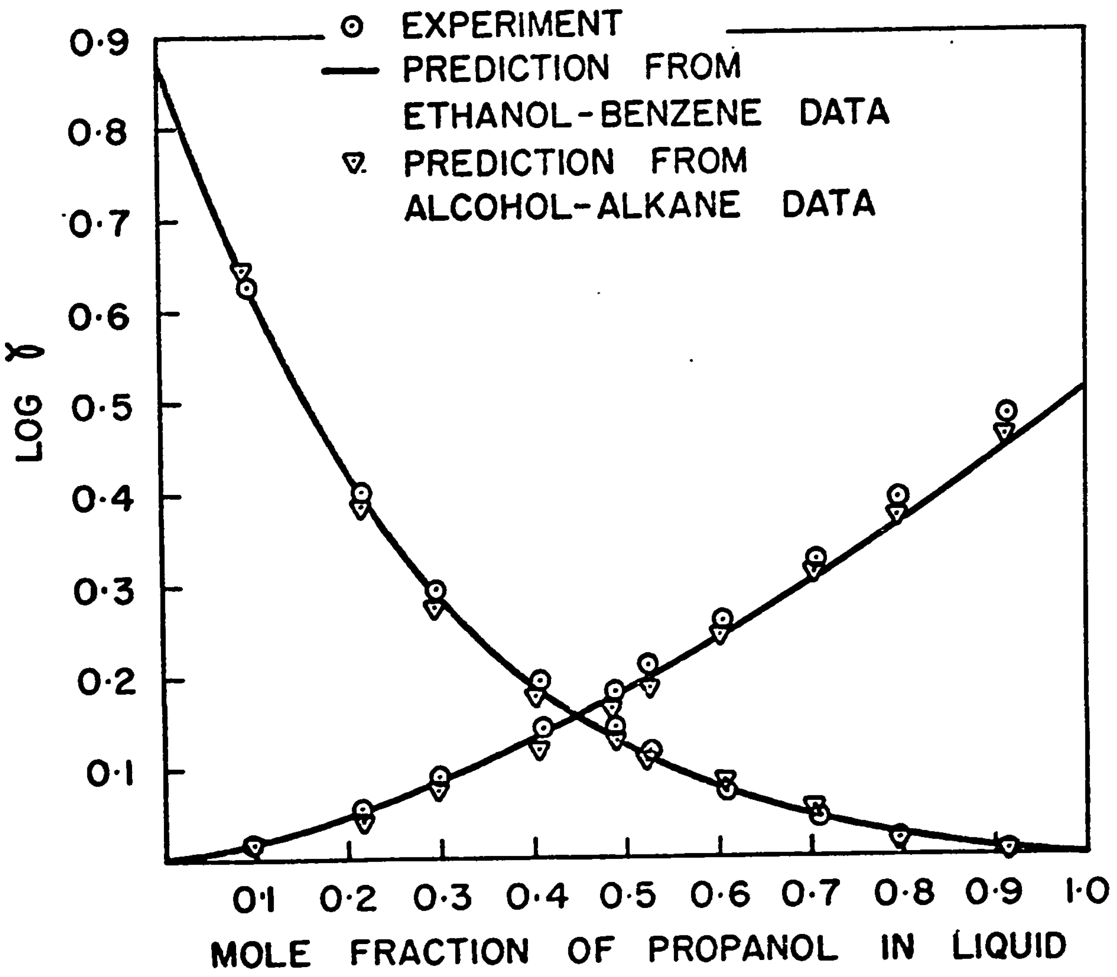


FIGURE 7.30 Activity Coefficients in n-Propanol-Benzene Mixtures at 45°C

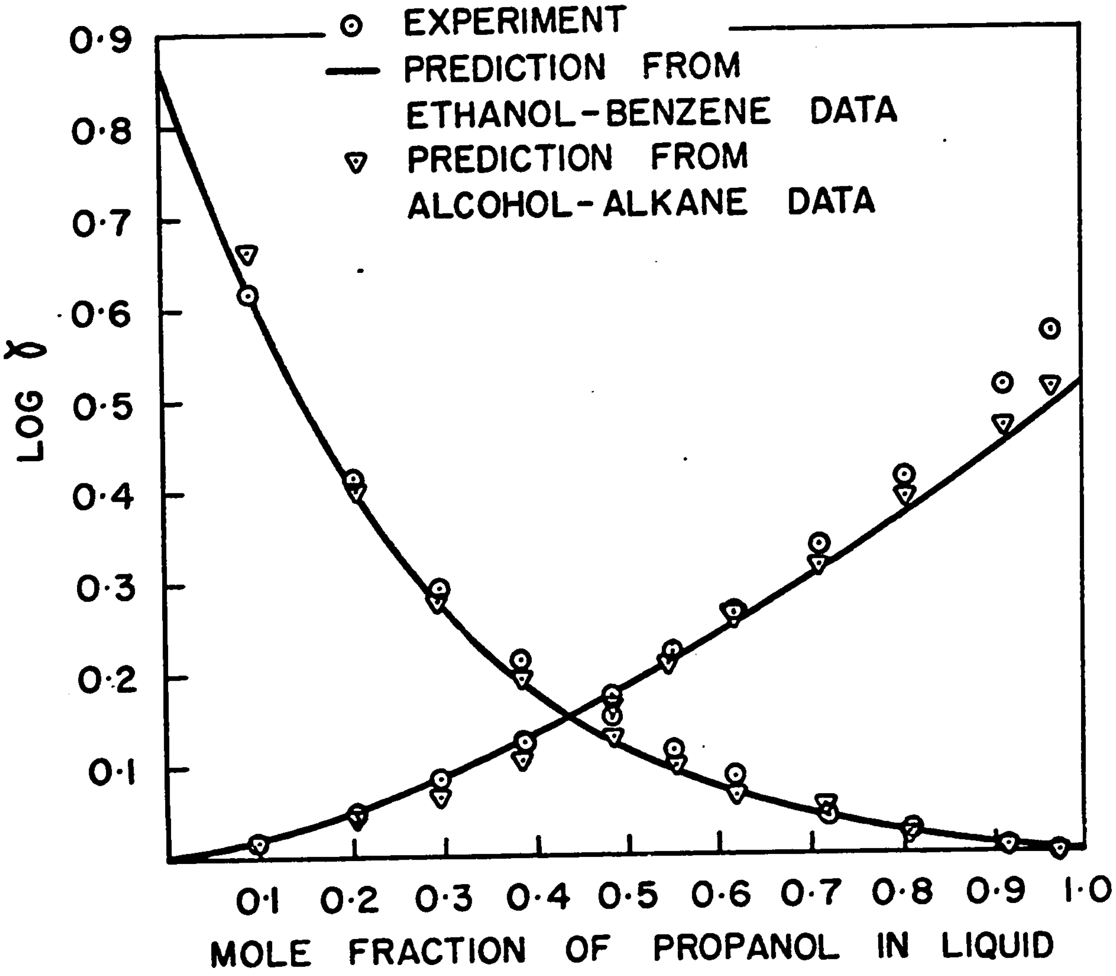


FIGURE 7.31 Activity Coefficients in Isopropanol-Benzene Mixtures at 45°C

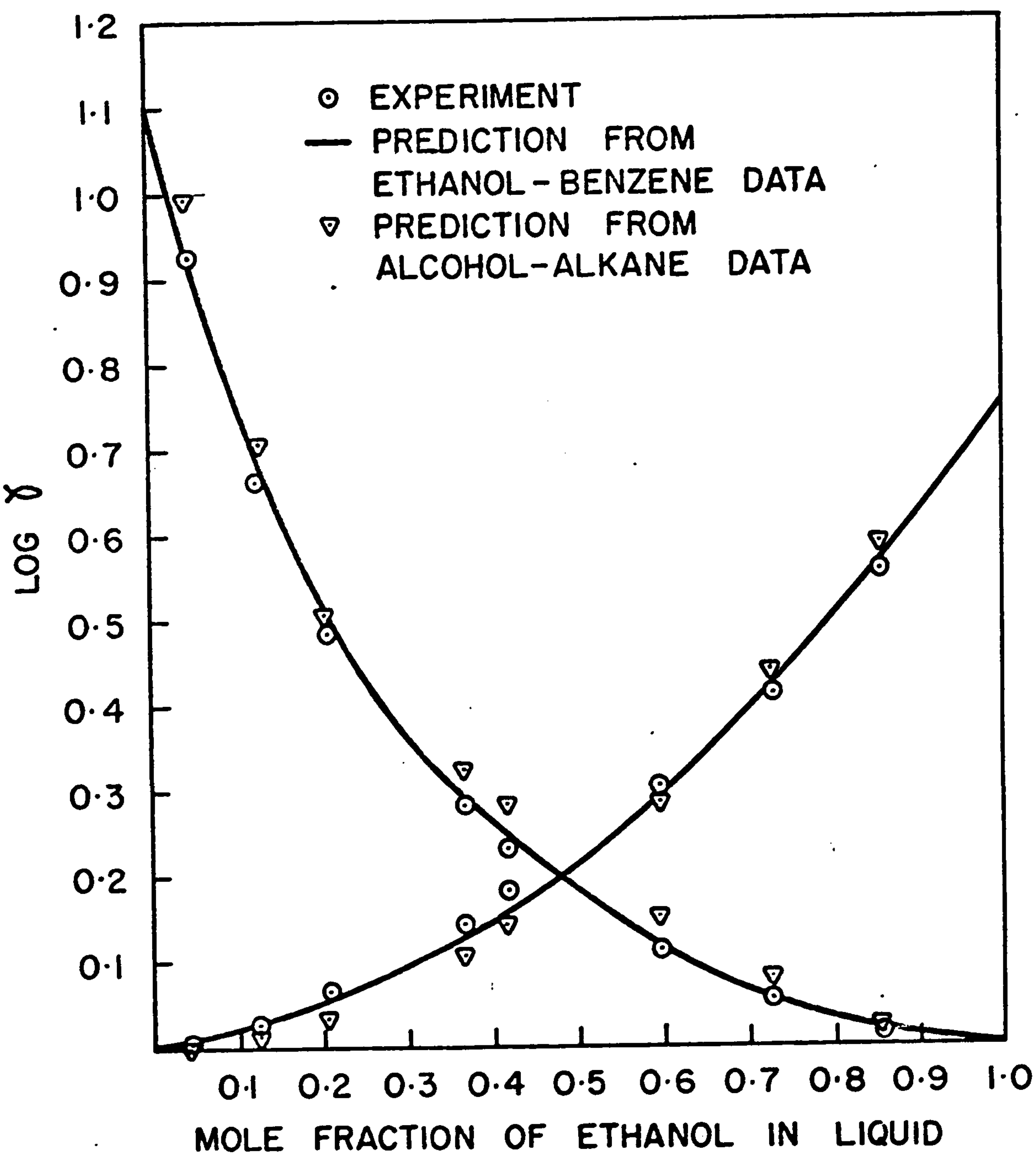


FIGURE 7.32 Activity Coefficients in Ethanol-Toluene Mixtures at 45°C

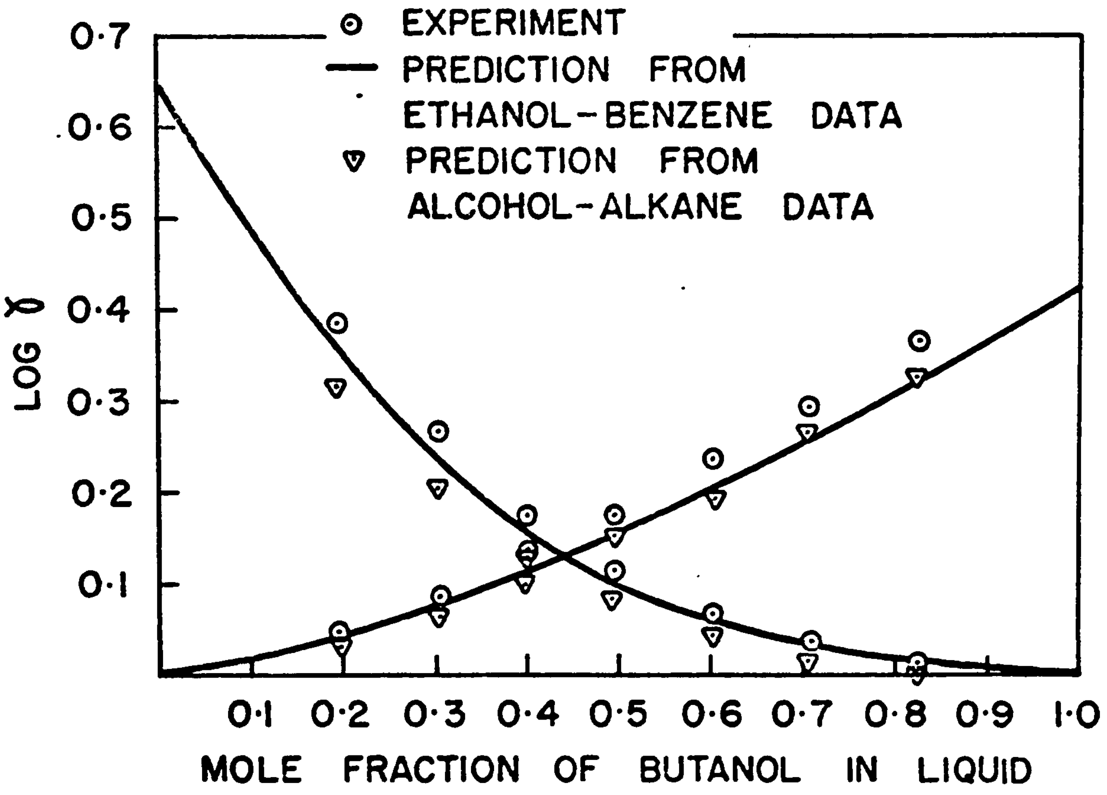


FIGURE 7.33 Activity Coefficients in n-Butanol-Benzene Mixtures at 45°C

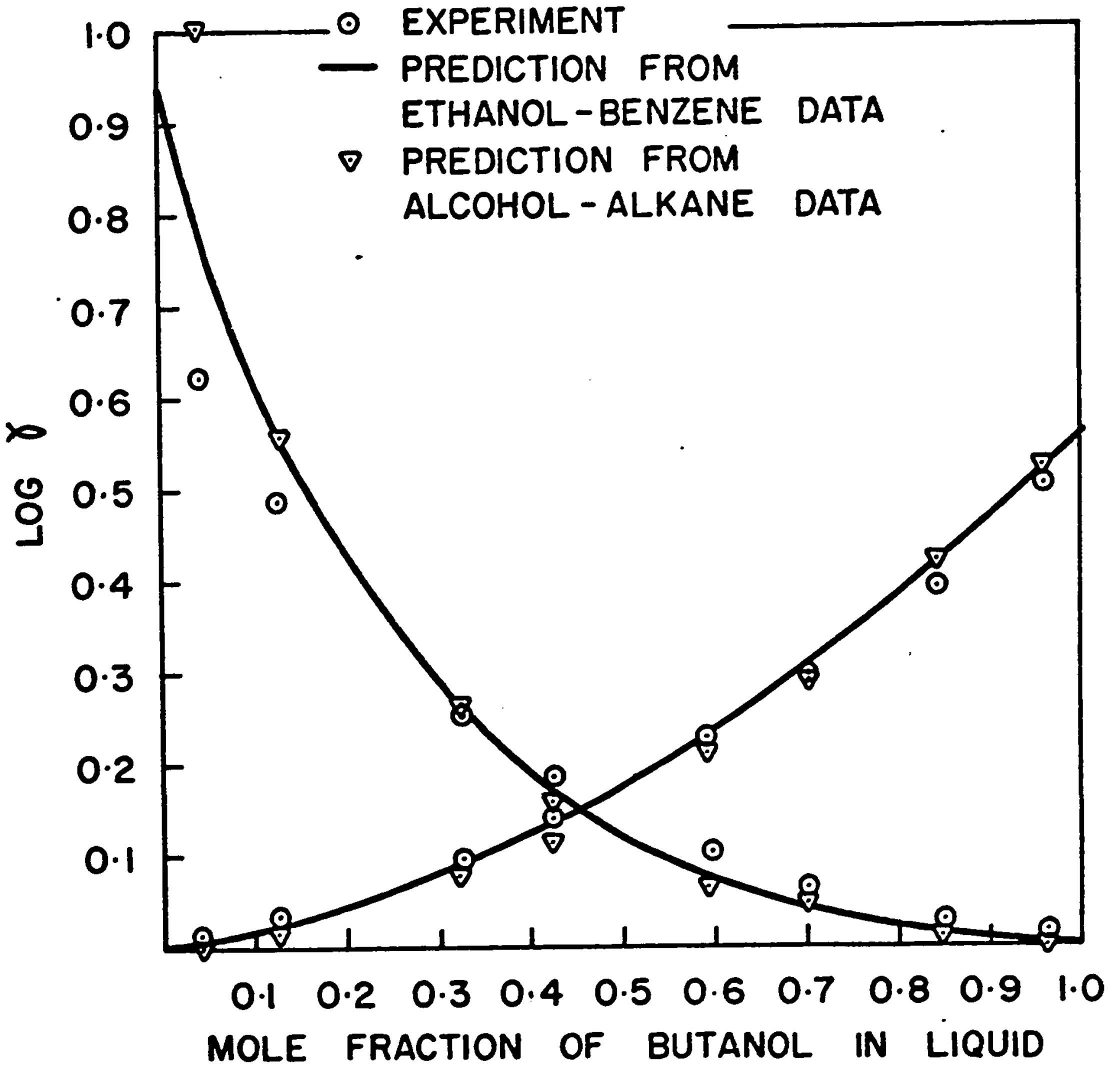


FIGURE 7.34 Activity Coefficients in n-Butanol-Ethyl Benzene Mixtures at 45°C

TABLE 7.1

REDLICH-KISTER CONSTANTS FOR THE SYSTEM ACETONE/N-HEPTANE

$$\log\gamma_1 = x_1x_2\,[B + C(x_1-x_2) + D(x_1-x_2)^2] + x_2\log\left(\frac{\gamma_1}{\gamma_2}\right)$$

$$\log\gamma_2 = x_1x_2\,[B + C(x_1-x_2) + D(x_1-x_2)^2] - x_1\log\left(\frac{\gamma_1}{\gamma_2}\right)$$

$$\log\left(\frac{\gamma_1}{\gamma_2}\right) = B(x_2-x_1) + C(6x_1x_2-1) + D(x_2-x_1)(1-8x_1x_2)$$

$$B = 0.58364$$

$$C = -0.02646$$

$$D = 0.03250$$

$$\log\gamma_2^o = B + C + D = 0.5897$$

$$\log\gamma_1^o = B - C + D = 0.6426$$

TABLE 7.2

FITTED PARAMETERS FOR GROUP CONTRIBUTION FUNCTIONS

$$\log \Gamma_{CH_2} = \sum a_n \, X_{CO}^n$$

$$\log(\Gamma_{CO}/\Gamma_{CO}^*) = \sum a_n \, X_{CO}^n$$

	a_0	a_1	a_2	a_3	a_4	a_5
$\log \Gamma_{CH_2}$	-0.00012	0.04864	3.1215	-19.008	53.177	-56.187
$\log(\Gamma_{CO}/\Gamma_{CO}^*)$	0.79929	-10.2867	76.667	-349.58	838.42	-800.44

TABLE-7.3

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ACETONE - N-HEPTANE

TEMPERATURE = 65 °C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.118	0.599	0.595	0.004
0.238	0.705	0.691	0.014
0.413	0.766	0.768	0.002
0.490	0.785	0.788	0.003
0.578	0.806	0.798	0.008
0.710	0.842	0.838	0.004
0.753	0.856	0.856	0.000
0.867	0.903	0.894	0.009

R.M.S DEVIATION IN Y_I IS 0.0070

TABLE-7.4

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ACETONE - N-HEPTANE

TEMPERATURE = 65 °C

COMPONENT ONE IS KETONE

x_I	x_{CO}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.118	0.0181	0.595	0.599	0.4683	0.4729	0.0153	0.0117
0.238	0.0393	0.691	0.705	0.3155	0.3382	0.0454	0.0391
0.413	0.0772	0.768	0.766	0.2034	0.1923	0.1122	0.1066
0.490	0.0972	0.788	0.785	0.1565	0.1455	0.1496	0.1464
0.578	0.1233	0.798	0.806	0.1137	0.1021	0.2332	0.1987
0.710	0.1707	0.838	0.842	0.0647	0.0507	0.3184	0.2911
0.753	0.1888	0.856	0.856	0.0590	0.0367	0.3470	0.3255
0.867	0.2455	0.894	0.903	0.0191	0.0105	0.4851	0.4323

TABLE-7.5

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ACETONE - N-HEXANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.268	0.477	0.528	0.051
0.375	0.526	0.570	0.044
0.495	0.576	0.613	0.037
0.648	0.645	0.675	0.030
0.690	0.667	0.690	0.023
0.768	0.715	0.740	0.025
0.905	0.844	0.840	0.004
0.975	0.950	0.940	0.010

R.M.S DEVIATION IN Y_I IS 0.0319

TABLE- 7.6

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ACETONE - N-DECANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.345	0.981	0.980	0.001
0.415	0.983	0.984	0.001
0.474	0.984	0.985	0.001
0.564	0.985	0.988	0.003
0.730	0.988	0.989	0.001
0.841	0.990	0.991	0.001
0.888	0.992	0.992	0.000
0.926	0.993	0.994	0.001

R.M.S DEVIATION IN Y_I IS 0.0014

TABLE-7.7

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: METHYL ETHYL KETONE - N-HEXANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.215	0.247	0.260	0.013
0.286	0.283	0.301	0.018
0.392	0.332	0.354	0.022
0.585	0.430	0.439	0.009
0.630	0.458	0.475	0.017
0.684	0.496	0.502	0.006
0.818	0.625	0.595	0.030
0.880	0.713	0.685	0.028
0.945	0.841	0.825	0.016

R.M.S DEVIATION IN Y_I IS 0.0192

TABLE-7.8

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: METHYL ETHYL KETONE - N-OCTANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.058	0.464	0.472	0.008
0.148	0.651	0.655	0.004
0.265	0.738	0.765	0.027
0.376	0.780	0.814	0.034
0.382	0.782	0.816	0.034
0.562	0.830	0.847	0.017
0.576	0.834	0.845	0.011
0.636	0.850	0.855	0.005
0.730	0.877	0.870	0.007
0.810	0.904	0.880	0.024
0.970	0.980	0.968	0.012

R.M.S DEVIATION IN Y_I IS 0.0199

TABLE-7.9

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: METHYL ETHYL KETONE - N-DECANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.264	0.950	0.937	0.013
0.520	0.968	0.972	0.004
0.538	0.969	0.969	0.000
0.550	0.969	0.974	0.005
0.555	0.970	0.975	0.005
0.570	0.970	0.974	0.004
0.648	0.973	0.977	0.004

R.M.S DEVIATION IN Y_I IS 0.0063

TABLE-7.10 .

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: DIETHYL KETONE - N-HEXANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.063	0.053	0.049	0.004
0.248	0.138	0.131	0.007
0.372	0.181	0.182	0.001
0.443	0.207	0.215	0.008
0.508	0.234	0.248	0.014
0.561	0.259	0.268	0.009
0.640	0.305	0.316	0.011
0.702	0.350	0.368	0.018
0.763	0.407	0.412	0.005
0.834	0.498	0.490	0.008
0.874	0.568	0.570	0.002

R.M.S DEVIATION IN Y_I IS 0.0093

TABLE-7.II

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: DIPROPYL KETONE - N-HEXANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.072	0.012	0.012	0.000
0.210	0.027	0.025	0.002
0.420	0.050	0.048	0.002
0.470	0.057	0.058	0.001
0.618	0.086	0.094	0.008
0.745	0.133	0.136	0.003

R.M.S DEVIATION IN Y_I IS 0.0036

TABLE- 7.I2

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ACETONE - N-HEXANE

TEMPERATURE = 65° C

COMPONENT ONE IS KETONE

x_I	x_{CO}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.268	0.0516	0.528	0.477	0.3439	0.2803	0.0242	0.0506
0.375	0.0769	0.570	0.526	0.2506	0.1932	0.0711	0.0909
0.495	0.1096	0.613	0.576	0.1740	0.1229	0.1299	0.1468
0.648	0.1598	0.675	0.645	0.1066	0.0604	0.2183	0.2316
0.690	0.1756	0.690	0.667	0.0873	0.0467	0.2514	0.2575
0.768	0.2078	0.740	0.715	0.0715	0.0250	0.3012	0.3096
0.905	0.2755	0.840	0.844	0.0249	0.0070	0.4488	0.4194
0.975	0.3171	0.940	0.950	0.0191	0.0052	0.5810	0.4837

TABLE- 7.I3

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ACETONE - N-DECANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

x_I	x_{CO}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.345	0.0455	0.980	0.981	0.2589	0.3076	0.0699	0.0698
0.415	0.0585	0.984	0.983	0.2151	0.2527	0.0393	0.1018
0.474	0.0709	0.985	0.984	0.1917	0.2105	0.1102	0.1350
0.564	0.0932	0.988	0.985	0.1475	0.1538	0.1269	0.1975
0.730	0.1493	0.989	0.988	0.0694	0.0708	0.2990	0.3571
0.841	0.2045	0.991	0.990	0.0280	0.0268	0.4615	0.5071
0.888	0.2347	0.992	0.992	0.0191	0.0135	0.5679	0.5883
0.926	0.2632	0.994	0.993	0.0095	0.0078	0.6605	0.6658

TABLE-7.14

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: METHYL ETHYL KETONE - N-HEXANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

x_1	x_{CO}	Y_1		LOG γ_1		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.215	0.0386	0.260	0.247	0.2984	0.2749	0.0252	0.0326
0.286	0.0527	0.301	0.283	0.2413	0.2118	0.0448	0.0523
0.392	0.0751	0.354	0.332	0.1752	0.1402	0.0808	0.0879
0.585	0.1211	0.439	0.430	0.0793	0.0603	0.1700	0.1666
0.630	0.1329	0.475	0.458	0.0703	0.0480	0.1801	0.1867
0.684	0.1477	0.502	0.496	0.0457	0.0352	0.2129	0.2116
0.818	0.1874	0.595	0.625	0.0041	0.0112	0.3253	0.2768
0.880	0.2075	0.685	0.713	0.0023	0.0040	0.3660	0.3092
0.945	0.2299	0.825	0.841	-0.0016	-0.0000	0.3961	0.3453

TABLE- 7.15

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: METHYL ETHYL KETONE - N-OCTANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

x_I	x_{CO}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.058	0.0075	0.472	0.464	0.4864	0.4883	-0.0130	0.0033
0.148	0.0200	0.655	0.651	0.3818	0.3881	0.0036	0.0156
0.265	0.0382	0.765	0.738	0.3074	0.2771	0.0102	0.0427
0.376	0.0579	0.814	0.780	0.2368	0.1924	0.0329	0.0802
0.382	0.0590	0.816	0.782	0.2281	0.1884	0.0296	0.0826
0.562	0.0977	0.847	0.830	0.1261	0.0930	0.1472	0.1684
0.576	0.1011	0.845	0.834	0.0977	0.0874	0.1507	0.1762
0.636	0.1166	0.855	0.850	0.1044	0.0657	0.2315	0.2117
0.730	0.1437	0.870	0.877	0.0618	0.0384	0.3232	0.2732
0.810	0.1702	0.880	0.904	0.0304	0.0200	0.4496	0.3317
0.970	0.2354	0.968	0.980	-0.0010	-0.0003	0.6825	0.4723

TABLE- 7.I6

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: METHYL ETHYL KETONE - N-DECANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

x_I	x_{CO}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.264	0.0314	0.937	0.950	0.2073	0.3144	0.0589	0.0394
0.520	0.0756	0.972	0.968	0.1274	0.1391	0.0840	0.1478
0.538	0.0794	0.969	0.969	0.0667	0.1296	0.1021	0.1585
0.550	0.0821	0.974	0.969	0.1276	0.1235	0.1025	0.1660
0.555	0.0832	0.975	0.970	0.0938	0.1210	0.0614	0.1691
0.570	0.0866	0.974	0.970	0.1188	0.1137	0.1286	0.1788
0.648	0.1060	0.977	0.973	0.0838	0.0799	0.1807	0.2344

TABLE- 7.I7

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: DIETHYL KETONE - N-HEXANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

x_I	x_{CO}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.063	0.0106	0.049	0.053	0.3752	0.4059	0.0138	0.0043
0.248	0.0431	0.131	0.138	0.1899	0.2034	0.0528	0.0386
0.372	0.0661	0.182	0.181	0.1258	0.1217	0.0738	0.0731
0.443	0.0797	0.215	0.207	0.1079	0.0890	0.0936	0.0956
0.508	0.0925	0.248	0.234	0.0995	0.0659	0.1178	0.1173
0.561	0.1031	0.268	0.259	0.0711	0.0510	0.1366	0.1357
0.640	0.1194	0.316	0.305	0.0440	0.0337	0.1517	0.1637
0.702	0.1325	0.368	0.350	0.0475	0.0235	0.1768	0.1860
0.763	0.1457	0.412	0.407	0.0239	0.0156	0.2082	0.2083
0.834	0.1614	0.490	0.498	0.0016	0.0085	0.2419	0.2344
0.874	0.1705	0.570	0.568	0.0077	0.0055	0.2482	0.2493

TABLE- 7.18

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: DIPROPYL KETONE - N-HEXANE

TEMPERATURE = 65°C

COMPONENT ONE IS KETONE

X_I	X_{CO}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.072	0.0119	0.012	0.012	0.3396	0.3124	0.0174	0.0052
0.210	0.0338	0.025	0.027	0.1328	0.1729	0.0187	0.0266
0.420	0.0650	0.048	0.050	0.0387	0.0627	0.0640	0.0720
0.470	0.0726	0.058	0.057	0.0114	0.0478	0.0364	0.0838
0.618	0.0934	0.094	0.086	0.0310	0.0192	0.0891	0.1188
0.745	0.1104	0.136	0.133	-0.0071	0.0069	0.1247	0.1483

TABLE 7.19

COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED VAPOR COMPOSITIONS

System	R.M.S. deviation between experiment and prediction (mole fraction of ketone)
(Acetone/n-Heptane	0.007)
Acetone/n-Hexane	0.032
Acetone/n-Decane	0.001
Methyl Ethyl Ketone/n-Hexane	0.019
Methyl Ethyl Ketone/n-Octane	0.020
Methyl Ethyl Ketone/n-Decane	0.006
Diethyl Ketone/n-Hexane	0.009
Dipropyl Ketone/n-Hexane	0.004
Average R.M.S. deviation for predicted systems	0.013

TABLE 7.20

GROUP CONTRIBUTION FUNCTIONS IN ALCOHOL-AROMATIC HYDROCARBON SYSTEMS

REFERENCE SYSTEM: ETHANOL-BENZENE
COMPONENT ONE IS ALCOHOL

x_1	X_{CH_2}	$\log \Gamma_{CH_2}$	$\log(\Gamma/\Gamma^*)_{OH}$
0.097	0.9829	0.0028	0.9168
0.218	0.9591	0.0106	0.6292
0.314	0.9378	0.0179	0.4917
0.415	0.9127	0.0270	0.3778
0.520	0.8829	0.0382	0.279
0.528	0.8803	0.0389	0.2736
0.616	0.8518	0.0496	0.2038
0.709	0.8170	0.0618	0.1422
0.810	0.7730	0.0772	0.0815
0.919	0.7164	0.0949	0.0293

TABLE- 7.2I

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.097	0.288	0.289	0.001
0.218	0.335	0.337	0.002
0.314	0.360	0.362	0.002
0.415	0.382	0.384	0.002
0.520	0.404	0.406	0.003
0.528	0.407	0.410	0.003
0.615	0.431	0.434	0.003
0.709	0.472	0.475	0.003
0.810	0.542	0.546	0.004
0.919	0.704	0.708	0.004

R.M.S DEVIATION IN Y_I IS 0.0028

TABLE- 7.22

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - TOLUENE

TEMPERATURE = 35°C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.047	0.474	0.475	0.001
0.121	0.592	0.566	0.025
0.208	0.628	0.601	0.025
0.362	0.650	0.635	0.016
0.416	0.659	0.638	0.020
0.593	0.683	0.673	0.010
0.726	0.715	0.716	0.002
0.852	0.782	0.785	0.003

R.M.S DEVIATION IN Y_I IS 0.0162

TABLE- 7.23

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-PROPANOL - BENZENE

TEMPERATURE = 45° C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45° C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.098	0.126	0.119	0.006
0.214	0.160	0.156	0.004
0.297	0.172	0.173	0.001
0.406	0.185	0.193	0.008
0.481	0.203	0.208	0.005
0.525	0.216	0.218	0.002
0.605	0.241	0.240	0.001
0.703	0.285	0.279	0.006
0.798	0.356	0.344	0.013
0.914	0.545	0.525	0.020

R.M.S DEVIATION IN Y_I IS 0.0087

TABLE- 7.24

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ISOPROPANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.093	0.206	0.207	0.000
0.205	0.261	0.266	0.006
0.296	0.286	0.295	0.009
0.386	0.308	0.321	0.014
0.475	0.330	0.346	0.016
0.550	0.356	0.369	0.013
0.620	0.390	0.395	0.005
0.710	0.442	0.438	0.004
0.807	0.530	0.511	0.019
0.912	0.696	0.666	0.030
0.965	0.849	0.825	0.024

R.M.S DEVIATION IN Y_I IS 0.0153

TABLE- 7.25

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.199	0.055	0.058	0.003
0.301	0.066	0.068	0.002
0.400	0.074	0.078	0.004
0.491	0.085	0.088	0.003
0.600	0.106	0.105	0.001
0.707	0.139	0.131	0.008
0.821	0.204	0.189	0.015

R.M.S DEVIATION IN Y_I IS 0.0068

TABLE- 7.26

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - ETHYL BENZENE

TOTAL PRESSURE = 100 MM.

PREDICTED FROM ETHANOL - BENZENE DATA AT 45° C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.960	0.899	0.900	0.001
0.854	0.724	0.739	0.015
0.701	0.596	0.603	0.008
0.591	0.536	0.545	0.009
0.427	0.476	0.477	0.002
0.326	0.446	0.436	0.010
0.129	0.366	0.321	0.044
0.040	0.232	0.166	0.066

R.M.S DEVIATION IN Y_I IS 0.0291

TABLE- 7.27

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - BENZENE

TEMPERATURE = 45° C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.097	0.9829	0.289	0.288	0.7074	0.7044	0.0169	0.0169
0.218	0.9591	0.337	0.335	0.4354	0.4324	0.0638	0.0636
0.314	0.9378	0.362	0.360	0.3126	0.3096	0.1076	0.1076
0.415	0.9127	0.384	0.382	0.2169	0.2139	0.1622	0.1622
0.520	0.8829	0.406	0.404	0.1404	0.1374	0.2292	0.2292
0.528	0.8803	0.410	0.407	0.1365	0.1335	0.2337	0.2337
0.615	0.8518	0.434	0.431	0.0880	0.0849	0.2974	0.2974
0.709	0.8170	0.475	0.472	0.0508	0.0479	0.3710	0.3710
0.810	0.7730	0.546	0.542	0.0209	0.0179	0.4635	0.4632
0.919	0.7164	0.708	0.704	0.0042	0.0012	0.6597	0.5697

TABLE- 7.28

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - TOLUENE

TEMPERATURE = 35°C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.047	0.9931	0.475	0.474	0.9292	0.9230	0.0068	0.0035
0.121	0.9313	0.566	0.592	0.6642	0.6980	0.0294	0.0210
0.208	0.9662	0.601	0.628	0.4850	0.5170	0.0689	0.0525
0.362	0.9347	0.635	0.650	0.2882	0.2980	0.1456	0.1260
0.416	0.9220	0.638	0.659	0.2342	0.2470	0.1835	0.1575
0.593	0.8718	0.673	0.683	0.1128	0.1210	0.3054	0.2940
0.726	0.8226	0.716	0.715	0.0547	0.0590	0.4191	0.4270
0.852	0.7628	0.785	0.782	0.0170	0.0190	0.5587	0.5670

TABLE- 7.29

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-PROPANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.098	0.9832	0.119	0.126	0.6203	0.6440	0.0167	0.0120
0.214	0.9615	0.156	0.160	0.3929	0.4050	0.0571	0.0540
0.297	0.9449	0.173	0.172	0.2901	0.2874	0.0920	0.0888
0.406	0.9217	0.193	0.185	0.1936	0.1860	0.1442	0.1560
0.481	0.9046	0.208	0.203	0.1415	0.1280	0.1845	0.1800
0.525	0.8939	0.218	0.215	0.1171	0.1100	0.2112	0.2040
0.605	0.8736	0.240	0.241	0.0778	0.0745	0.2601	0.2490
0.703	0.8468	0.279	0.285	0.0427	0.0410	0.3268	0.3060
0.798	0.8187	0.344	0.356	0.0199	0.0210	0.3957	0.3660
0.914	0.7809	0.525	0.545	0.0024	0.0050	0.4836	0.4440

TABLE- 7.30

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ISOPROPANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.098	0.9831	0.207	0.206	0.6111	0.6105	0.0157	0.0150
0.205	0.9633	0.266	0.261	0.4132	0.4035	0.0493	0.0510
0.296	0.9452	0.295	0.286	0.2996	0.2806	0.0870	0.0852
0.336	0.9261	0.321	0.308	0.2182	0.1910	0.1287	0.1260
0.475	0.9058	0.346	0.330	0.1564	0.1235	0.1762	0.1710
0.550	0.8876	0.369	0.356	0.1129	0.0845	0.2206	0.2130
0.620	0.8698	0.395	0.390	0.0816	0.0655	0.2664	0.2550
0.710	0.8450	0.433	0.442	0.0474	0.0390	0.3321	0.3120
0.807	0.8159	0.511	0.530	0.0208	0.0205	0.4134	0.3750
0.912	0.7816	0.666	0.696	0.0040	0.0065	0.5111	0.4470
0.965	0.7527	0.825	0.849	0.0	0.0060	0.5645	0.4860

TABLE- 7.3I

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - BENZENE

TEMPERATURE = 45° C

PREDICTED FROM ETHANOL - BENZENE DATA AT 45° C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.199	0.9658	0.058	0.055	0.3839	0.3580	0.0492	0.0420
0.301	0.9472	0.068	0.066	0.2613	0.2460	0.0889	0.0840
0.400	0.9284	0.078	0.074	0.1756	0.1490	0.1335	0.1260
0.491	0.9107	0.088	0.085	0.1200	0.0934	0.1784	0.1626
0.600	0.8886	0.105	0.106	0.0699	0.0590	0.2358	0.2160
0.707	0.8664	0.131	0.139	0.0328	0.0342	0.2980	0.2628
0.821	0.8416	0.189	0.204	0.0128	0.0108	0.3661	0.3162

TABLE- 7.32

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - ETHYL BENZENE

TOTAL PRESSURE = 100 MM.

PREDICTED FROM ETHANOL - BENZENE DATA AT 45°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.960	0.8125	0.900	0.899	0.0188	0.0060	0.5042	0.5120
0.854	0.8429	0.739	0.724	0.0309	0.0120	0.3946	0.4240
0.701	0.8811	0.603	0.596	0.0658	0.0400	0.2989	0.3000
0.591	0.9050	0.545	0.536	0.1070	0.0740	0.2324	0.2280
0.427	0.9364	0.477	0.476	0.1880	0.1700	0.1448	0.1400
0.326	0.9536	0.436	0.446	0.2541	0.2630	0.0954	0.0960
0.129	0.9830	0.321	0.366	0.4899	0.5500	0.0332	0.0200
0.040	0.9949	0.166	0.232	0.6265	0.7920	0.0147	0.0040

TABLE 7.33

COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED VAPOR COMPOSITIONS

System	R.M.S. deviation between experiment & prediction (mole fraction of alcohol)	
	Predicted from ethanol-benzene data	Predicted from alcohol-alkane data
Ethanol-Benzene	0.0028	0.0189
n-Propanol-Benzene	0.0087	0.0073
Isopropanol-Benzene	0.0153	0.013
Ethanol-Toluene	0.0162	0.032
n-Butanol-Benzene	0.0068	0.0048
n-Butanol-Ethyl Benzene	0.0291	0.0605
Average R.M.S. Deviation	0.0131	0.0227

TABLE- 7.34

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.097	0.312	0.289	0.022
0.218	0.359	0.337	0.022
0.314	0.386	0.362	0.024
0.415	0.397	0.384	0.013
0.520	0.425	0.406	0.018
0.528	0.426	0.410	0.016
0.615	0.446	0.434	0.012
0.709	0.479	0.475	0.004
0.810	0.543	0.545	0.003
0.919	0.675	0.708	0.033

R.M.S DEVIATION IN Y_I IS 0.0189

TABLE- 7.35

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - TOLUENE

TEMPERATURE = 35°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.047	0.516	0.475	0.041
0.121	0.595	0.566	0.029
0.208	0.631	0.601	0.030
0.362	0.675	0.635	0.041
0.416	0.687	0.638	0.049
0.593	0.698	0.673	0.025
0.726	0.721	0.716	0.005
0.852	0.776	0.785	0.009

R.M.S DEVIATION IN Y_I IS 0.0320

TABLE- 7.36

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-PROPANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.098	0.126	0.119	0.007
0.214	0.156	0.156	0.000
0.297	0.173	0.173	0.001
0.406	0.196	0.193	0.002
0.481	0.210	0.208	0.002
0.525	0.225	0.218	0.006
0.605	0.246	0.240	0.006
0.703	0.290	0.279	0.011
0.798	0.354	0.344	0.011
0.914	0.538	0.525	0.013

R.M.S DEVIATION IN Y_I IS 0.0073

TABLE- 7.37

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ISOPROPANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.098	0.229	0.207	0.023
0.205	0.268	0.266	0.002
0.296	0.292	0.295	0.004
0.386	0.318	0.321	0.003
0.475	0.339	0.346	0.007
0.550	0.369	0.369	0.000
0.620	0.392	0.395	0.003
0.710	0.451	0.438	0.013
0.807	0.524	0.511	0.013
0.912	0.690	0.666	0.025
0.965	0.843	0.825	0.017

R.M.S DEVIATION IN Y_I IS 0.0130

TABLE- 7.38

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - BENZENE

TEMPERATURE = 45° C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.199	0.050	0.058	0.008
0.301	0.063	0.069	0.006
0.400	0.074	0.078	0.004
0.491	0.085	0.088	0.003
0.600	0.106	0.105	0.001
0.707	0.134	0.131	0.003
0.821	0.196	0.189	0.006

R.M.S DEVIATION IN Y_I IS 0.0048

TABLE- 7.39

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - ETHYL BENZENE

TOTAL PRESSURE = 100 MM.

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

X_I	Y_I-PRED	Y_I-EXP	Y_I-DIFF(ABS)
0.960	0.895	0.900	0.005
0.854	0.722	0.739	0.017
0.701	0.600	0.603	0.003
0.591	0.541	0.545	0.004
0.427	0.487	0.477	0.010
0.326	0.455	0.436	0.019
0.129	0.372	0.321	0.051
0.040	0.328	0.166	0.162

R.M.S DEVIATION IN Y_I IS 0.0608

TABLE- 7.40

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.097	0.9829	0.289	0.312	0.7074	0.7510	0.0168	0.0150
0.218	0.9591	0.337	0.359	0.4354	0.4620	0.0638	0.0480
0.314	0.9378	0.362	0.386	0.3126	0.3340	0.1076	0.0840
0.415	0.9127	0.384	0.397	0.2169	0.2240	0.1622	0.1440
0.520	0.8829	0.406	0.425	0.1404	0.1710	0.2292	0.2250
0.528	0.8803	0.410	0.426	0.1365	0.1620	0.2337	0.2280
0.615	0.8518	0.434	0.446	0.0880	0.1170	0.2974	0.3030
0.709	0.8170	0.475	0.479	0.0508	0.0740	0.3710	0.3840
0.810	0.7730	0.546	0.543	0.0209	0.0360	0.4635	0.4800
0.919	0.7164	0.708	0.675	0.0042	0.0080	0.6597	0.6360

TABLE- 7.4I

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ETHANOL - TOLUENE

TEMPERATURE = 35°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.047	0.9931	0.475	0.516	0.9292	0.9970	0.0068	0.0035
0.121	0.9813	0.566	0.595	0.6642	0.7010	0.0294	0.0175
0.208	0.9662	0.601	0.631	0.4850	0.5060	0.0689	0.0350
0.362	0.9347	0.635	0.675	0.2882	0.3260	0.1456	0.1050
0.416	0.9220	0.638	0.687	0.2342	0.2860	0.1835	0.1400
0.593	0.8718	0.673	0.698	0.1128	0.1500	0.3054	0.2940
0.726	0.8226	0.716	0.721	0.0547	0.0800	0.4191	0.4340
0.852	0.7628	0.785	0.776	0.0170	0.0240	0.5587	0.5880

TABLE- 7.42

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-PROPANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.098	0.9832	0.119	0.126	0.6203	0.6460	0.0167	0.0120
0.214	0.0961	0.156	0.156	0.3929	0.3816	0.0571	0.0432
0.297	0.9449	0.173	0.173	0.2901	0.2760	0.0920	0.0720
0.406	0.9217	0.193	0.196	0.1936	0.1800	0.1442	0.1200
0.481	0.9046	0.208	0.210	0.1415	0.1340	0.1845	0.1680
0.525	0.8939	0.218	0.225	0.1171	0.1130	0.2112	0.1860
0.605	0.8736	0.240	0.246	0.0778	0.0830	0.2601	0.2460
0.703	0.8468	0.279	0.290	0.0427	0.0560	0.3268	0.3120
0.798	0.8187	0.344	0.354	0.0199	0.0290	0.3957	0.3780
0.914	0.7809	0.525	0.538	0.0024	0.0110	0.4836	0.4620

TABLE- 7.43

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: ISOPROPANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.098	0.9831	0.207	0.229	0.6111	0.6660	0.0157	0.0120
0.205	0.9633	0.256	0.268	0.4132	0.4110	0.0493	0.0420
0.296	0.9452	0.295	0.292	0.2996	0.2730	0.0870	0.0660
0.386	0.9261	0.321	0.318	0.2182	0.1940	0.1287	0.1080
0.475	0.9058	0.346	0.339	0.1564	0.1310	0.1762	0.1620
0.550	0.8876	0.369	0.369	0.1129	0.1050	0.2206	0.2100
0.620	0.8698	0.395	0.392	0.0816	0.0660	0.2664	0.2520
0.710	0.8450	0.438	0.451	0.0474	0.0575	0.3321	0.3150
0.807	0.8159	0.511	0.524	0.0208	0.0250	0.4134	0.3900
0.912	0.7816	0.666	0.690	0.0040	0.0110	0.5111	0.4620
0.965	0.7627	0.825	0.843	0.0	0.0020	0.5645	0.5040

TABLE- 7.44

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - BENZENE

TEMPERATURE = 45°C

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.199	0.9558	0.058	0.050	0.3839	0.3180	0.0492	0.0420
0.301	0.9472	0.058	0.063	0.2613	0.2040	0.0889	0.0660
0.400	0.9284	0.078	0.074	0.1756	0.1280	0.1335	0.1020
0.491	0.9107	0.088	0.085	0.1200	0.0800	0.1784	0.1500
0.600	0.8888	0.105	0.106	0.0699	0.0420	0.2358	0.1980
0.707	0.8664	0.131	0.134	0.0328	0.0160	0.2980	0.2640
0.821	0.8416	0.189	0.196	0.0128	-0.0040	0.3661	0.3240

TABLE- 7.45

PREDICTED DATA USING GROUP SOLUTION MODEL

SYSTEM: N-BUTANOL - ETHYL BENZENE

TOTAL PRESSURE = 100 MM.

PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C

COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	Y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.960	0.8125	0.900	0.895	0.0188	0.0020	0.5042	0.5240
0.854	0.8429	0.739	0.722	0.0309	0.0140	0.3946	0.4280
0.701	0.8811	0.603	0.600	0.0658	0.0500	0.2989	0.3000
0.591	0.9050	0.545	0.541	0.1070	0.0680	0.2324	0.2160
0.427	0.9364	0.477	0.487	0.1880	0.1560	0.1448	0.1120
0.326	0.9536	0.436	0.455	0.2541	0.2600	0.0954	0.0800
0.129	0.9830	0.321	0.372	0.4899	0.5580	0.0332	0.0160
0.040	0.9949	0.166	0.328	0.6265	1.0120	0.0147	0.0040

TABLE- 7.45

PREDICTED DATA USING GROUP SOLUTION MODEL
SYSTEM: N-BUTANOL - ETHYL BENZENE
TOTAL PRESSURE = 100 MM.
PREDICTED FROM ALCOHOL - ALKANE DATA AT 40°C
COMPONENT ONE IS ALCOHOL

x_I	x_{CH_2}	y_I		LOG γ_I		LOG γ_2	
		EXPT	PRED	EXPT	PRED	EXPT	PRED
0.960	0.8125	0.900	0.895	0.0188	0.0020	0.5042	0.5240
0.854	0.8429	0.739	0.722	0.0309	0.0140	0.3946	0.4280
0.701	0.8811	0.603	0.600	0.0658	0.0500	0.2989	0.3000
0.591	0.9050	0.545	0.541	0.1070	0.0680	0.2324	0.2160
0.427	0.9364	0.477	0.487	0.1880	0.1560	0.1448	0.1120
0.326	0.9536	0.436	0.455	0.2541	0.2600	0.0954	0.0800
0.129	0.9830	0.321	0.372	0.4899	0.5580	0.0332	0.0160
0.040	0.9949	0.166	0.328	0.6265	1.0120	0.0147	0.0040

APPENDICES

Introduction

The calibration data for all the systems used in the determination of vapor-liquid equilibria are presented in Appendix A (Figures A.1-A.13 and Tables A.1-A.13). All the relevant pure component data used in the computation of activity coefficients are shown in Appendix B. Appendix C gives the computer programs for the calculation of activity coefficient, Redlich-Kister constants, and data prediction.

APPENDIX A

Calibration Data

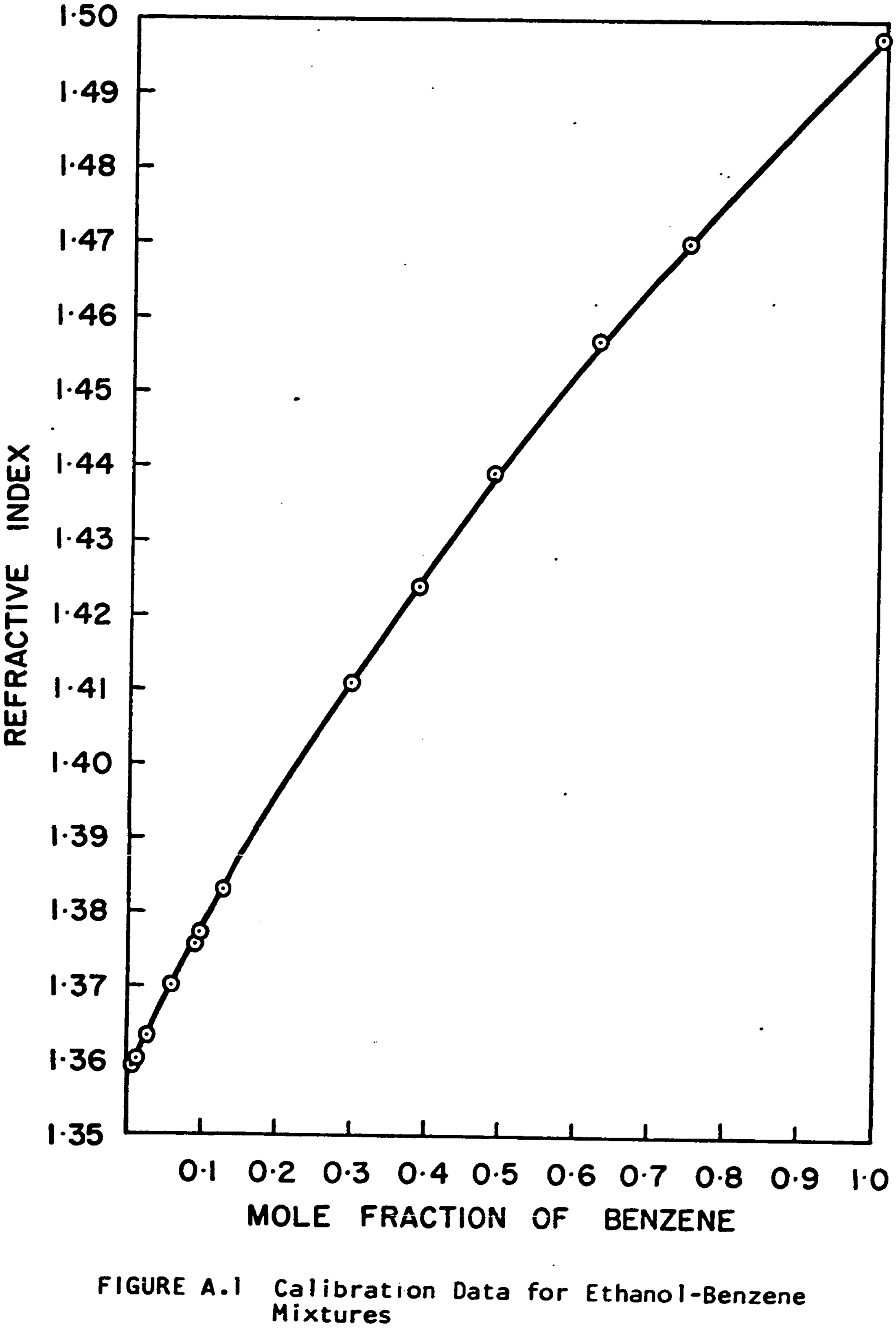


FIGURE A.1 Calibration Data for Ethanol-Benzene Mixtures

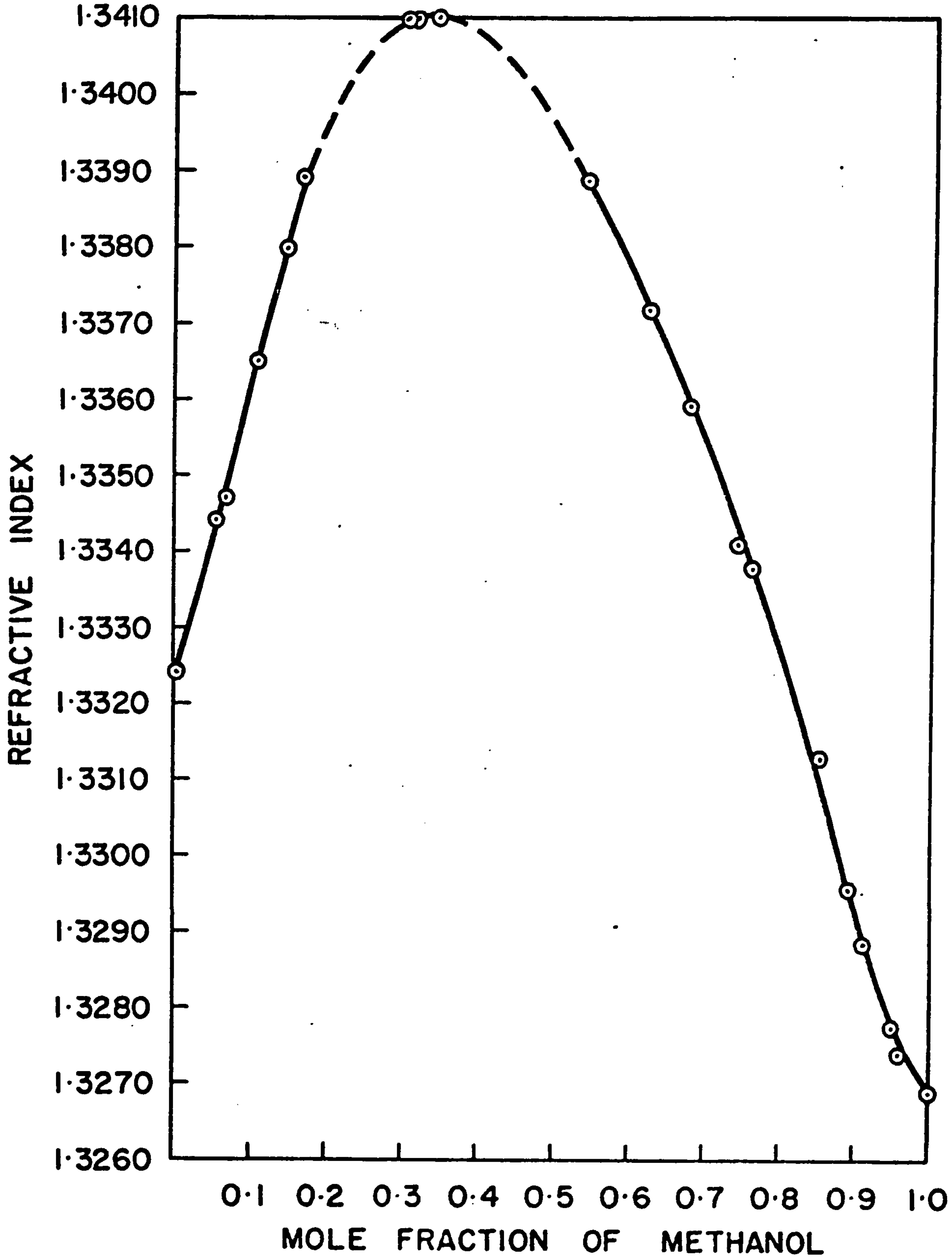


FIGURE A.2 Calibration Data for Methanol-Water Mixtures

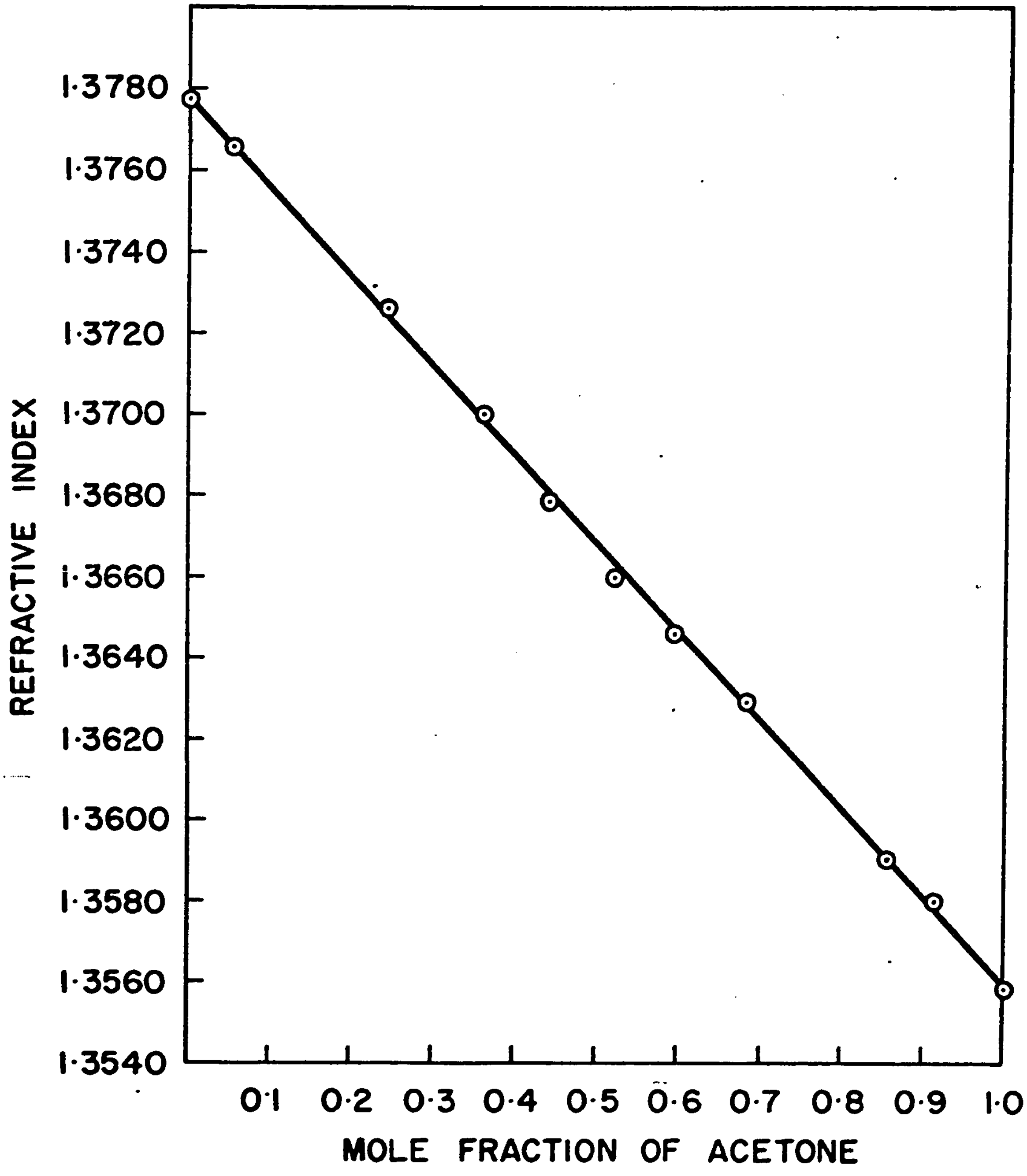


FIGURE A.3 Calibration Data for Acetone/n-Hexane Mixtures

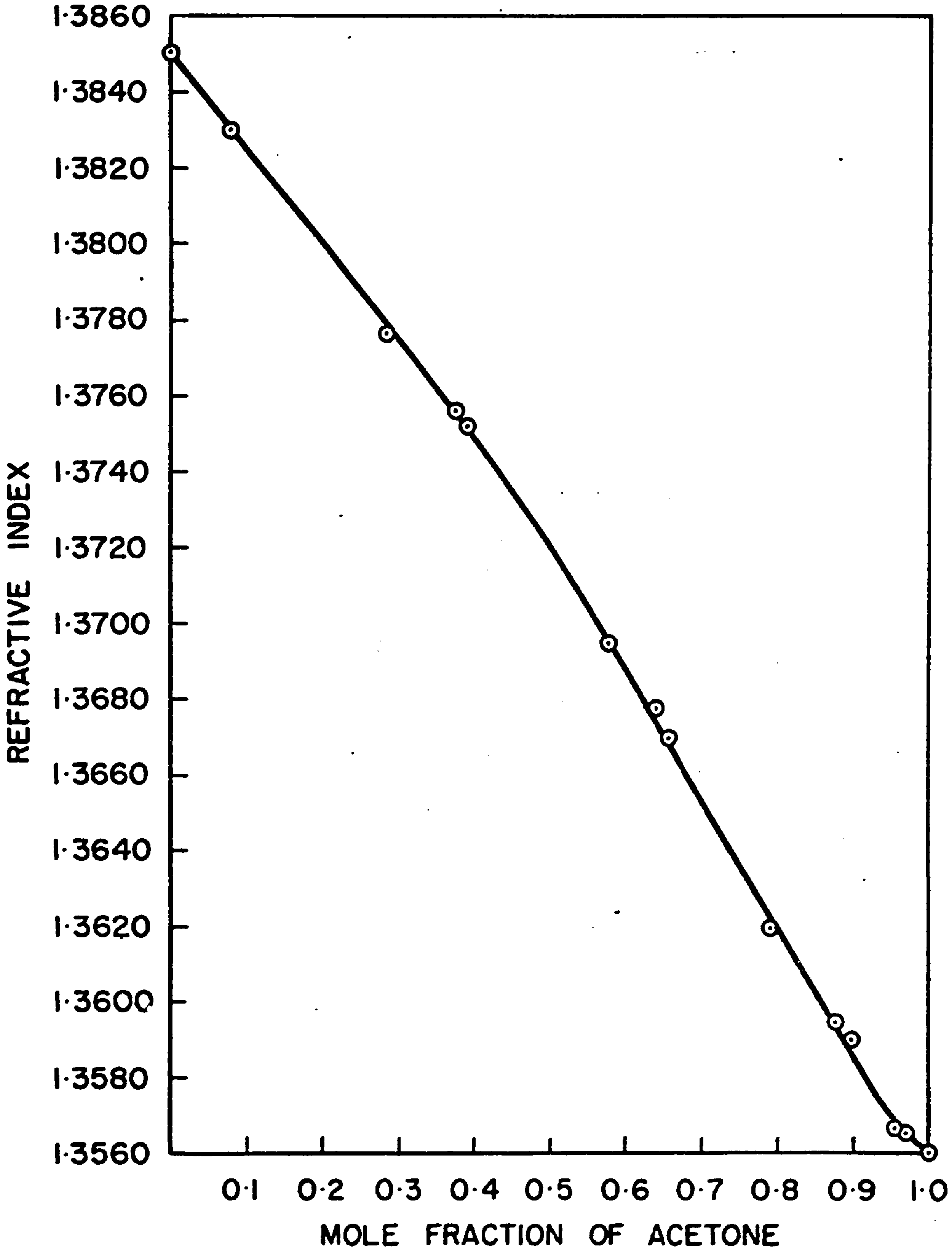


FIGURE A.4 Calibration Data for Acetone/n-Heptane Mixtures

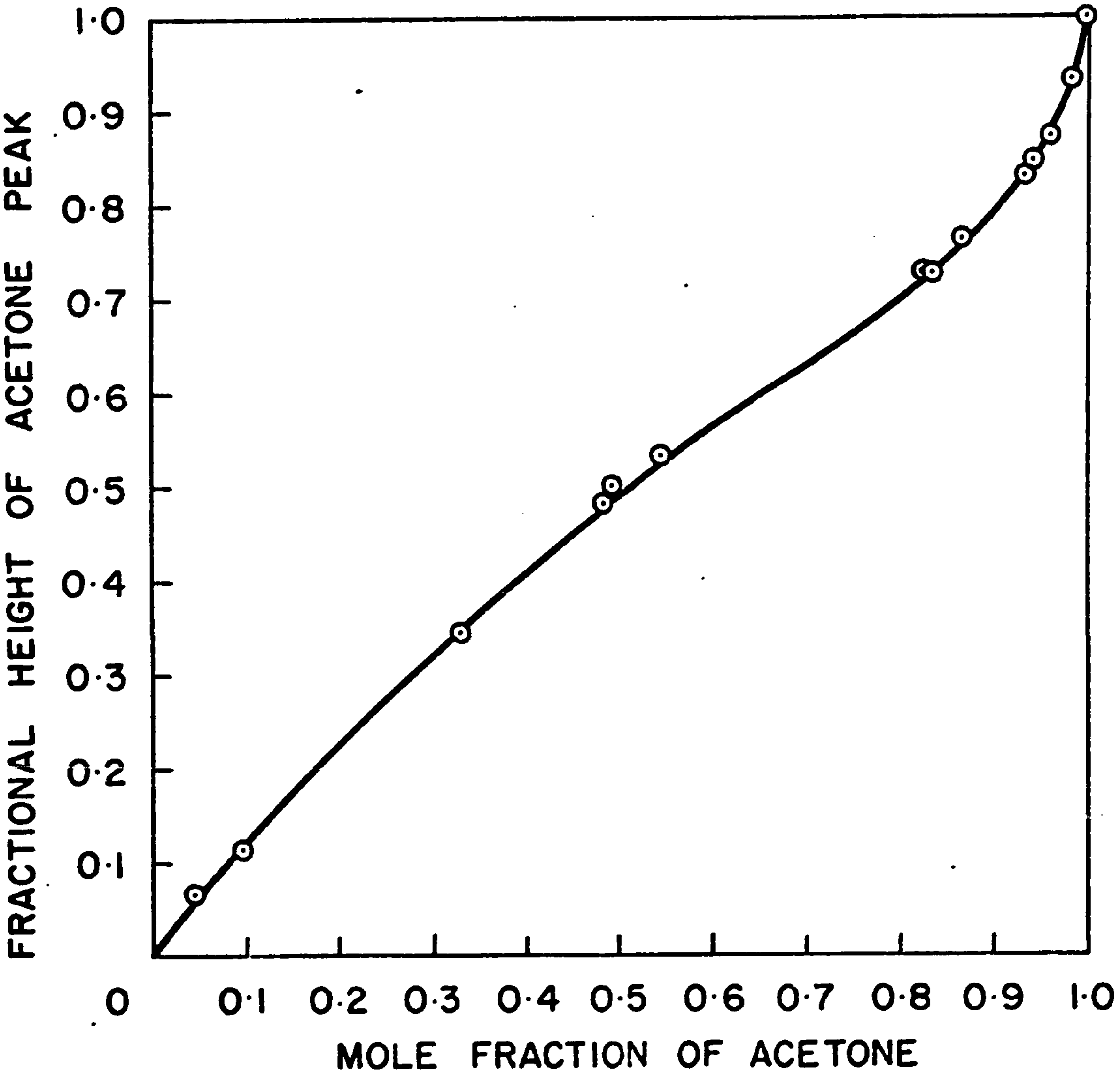


FIGURE A.5 Calibration Data for Acetone/n-Decane Mixtures

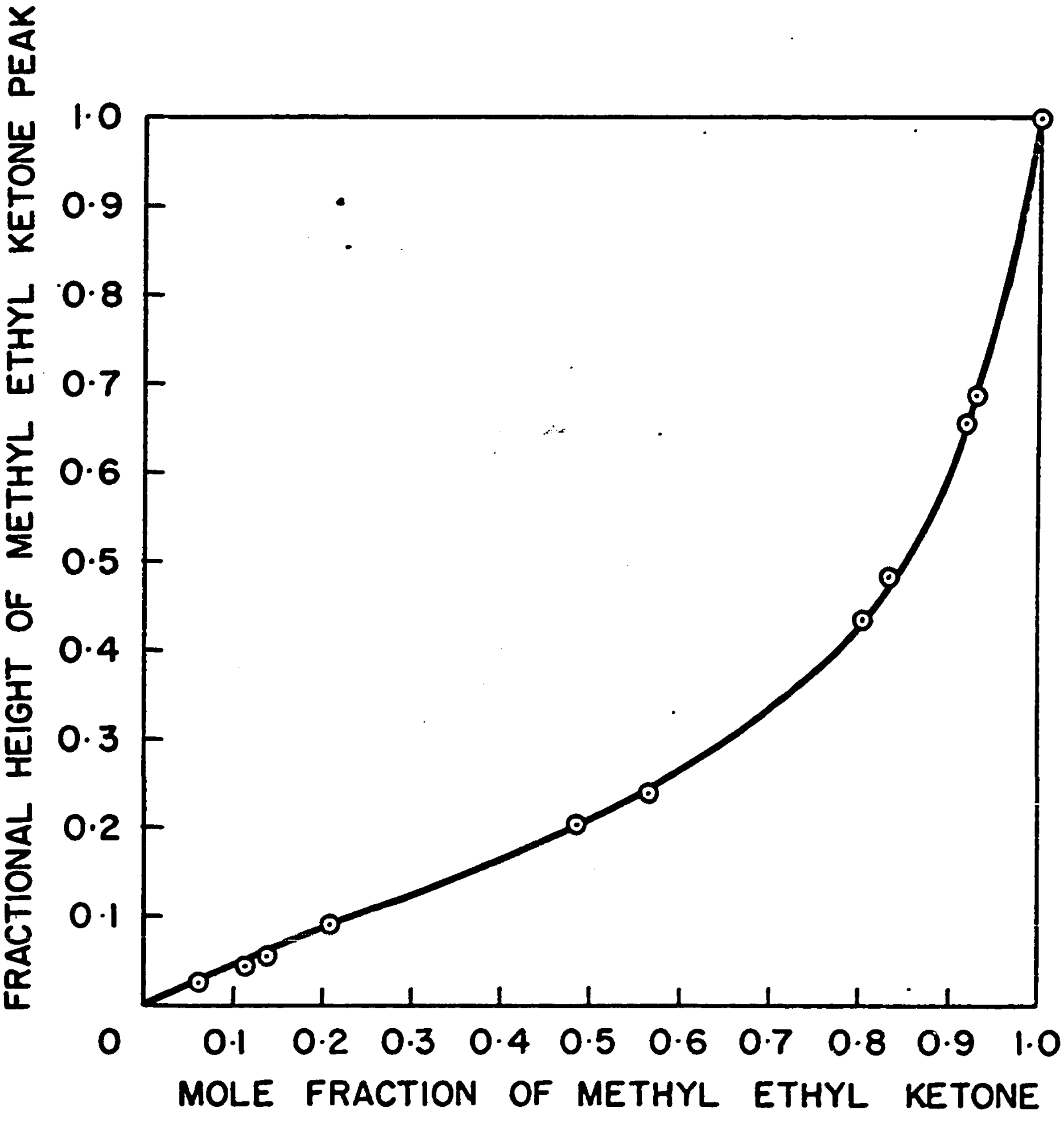


FIGURE A.6 Calibration Data for Methyl Ethyl Ketone/ n-Hexane Mixtures

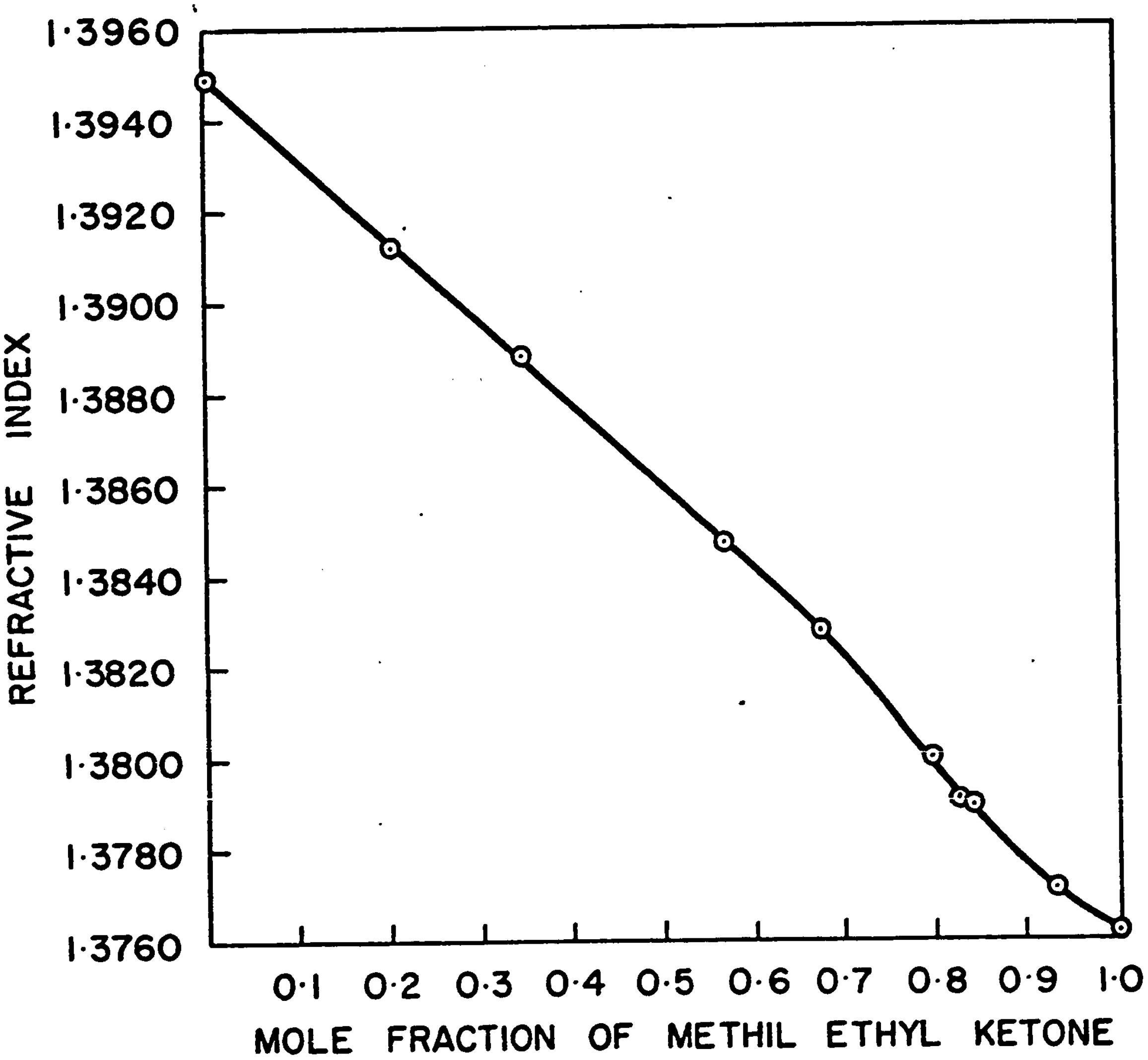


FIGURE A.7 Calibration Data for Methyl Ethyl Ketone/n-Octane Mixtures

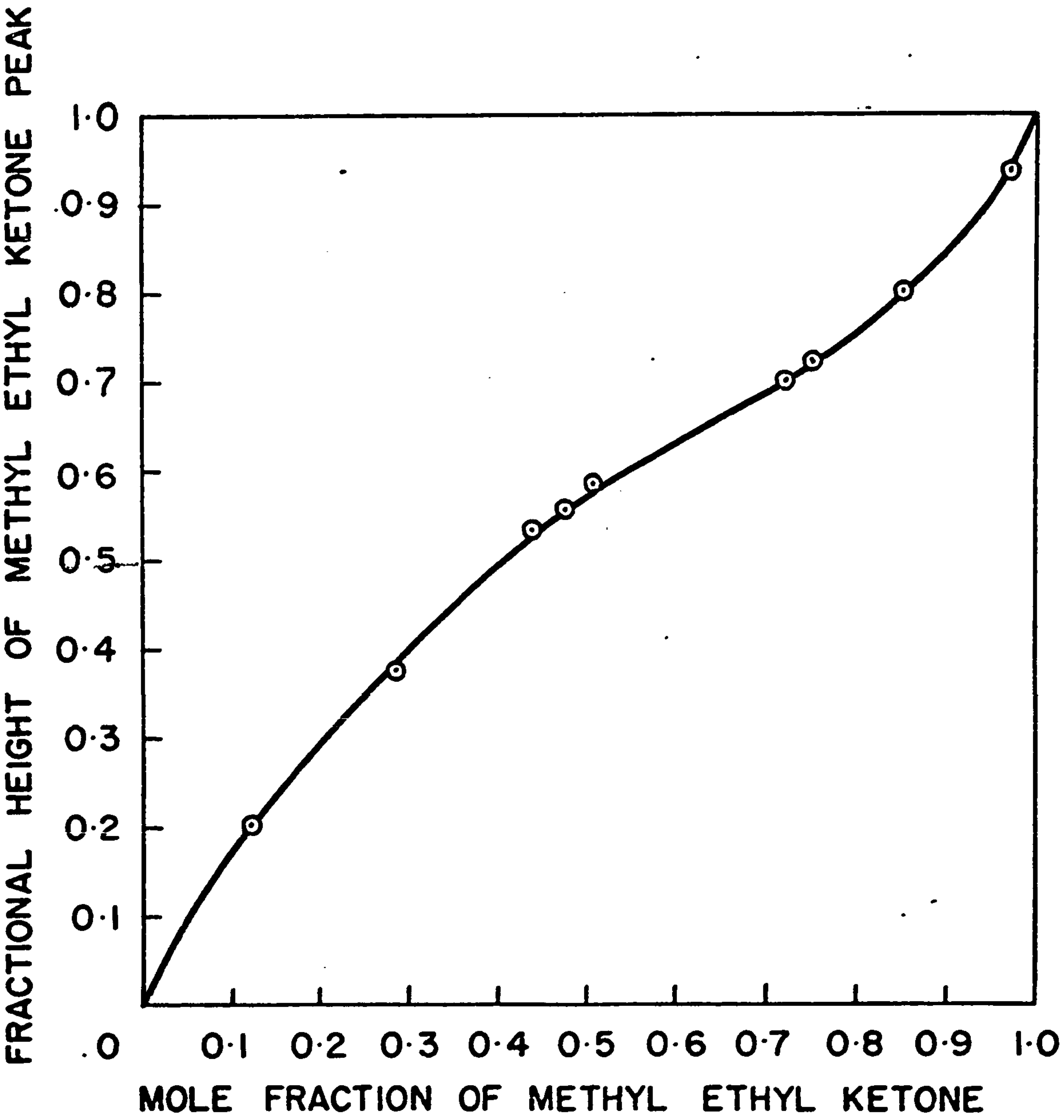


FIGURE A.8 Calibration Data for Methyl Ethyl Ketone/
n-Decane Mixtures

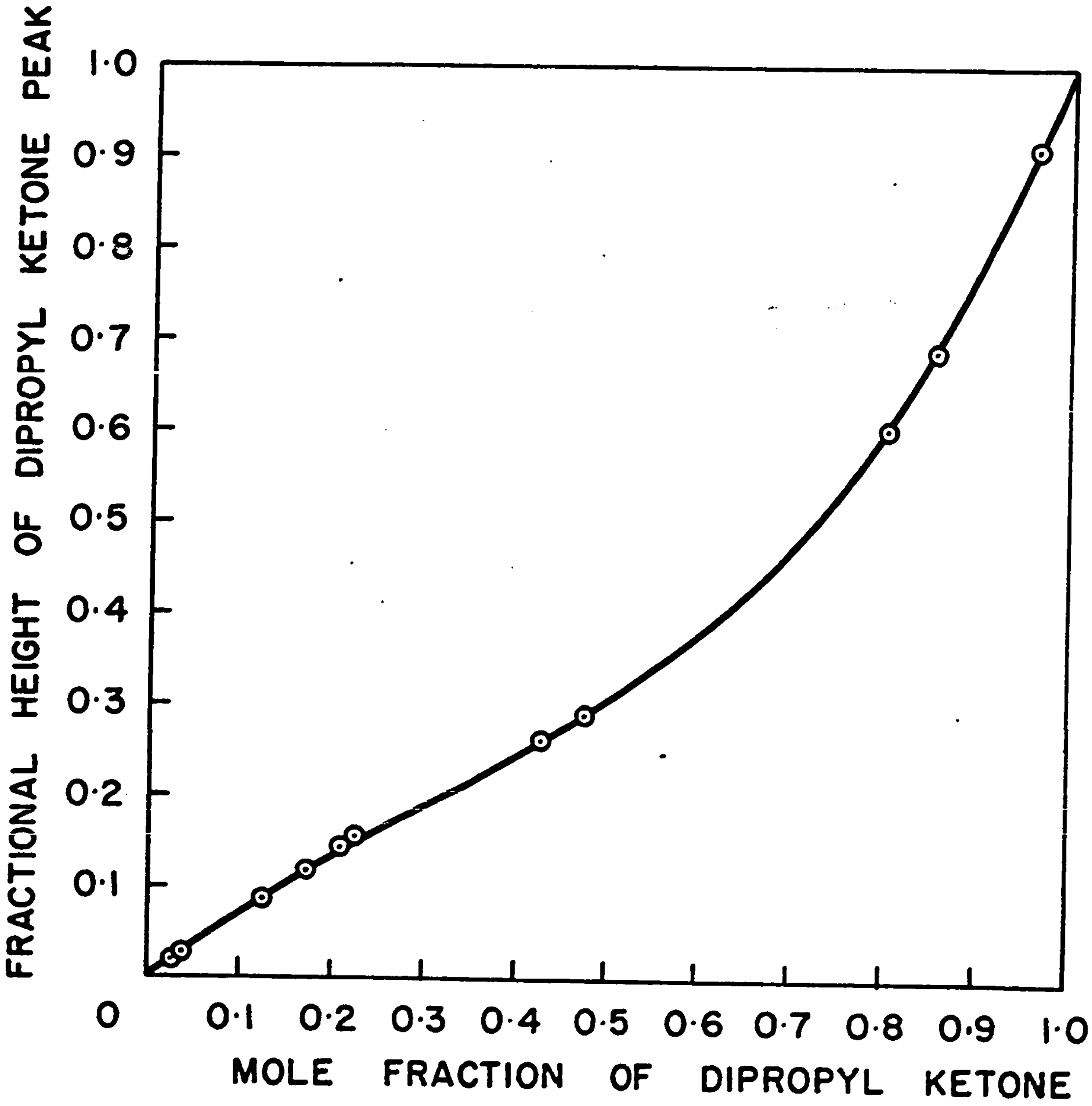


FIGURE A.10 Calibration Data for Dipropyl Ketone/ n-Hexane Mixtures

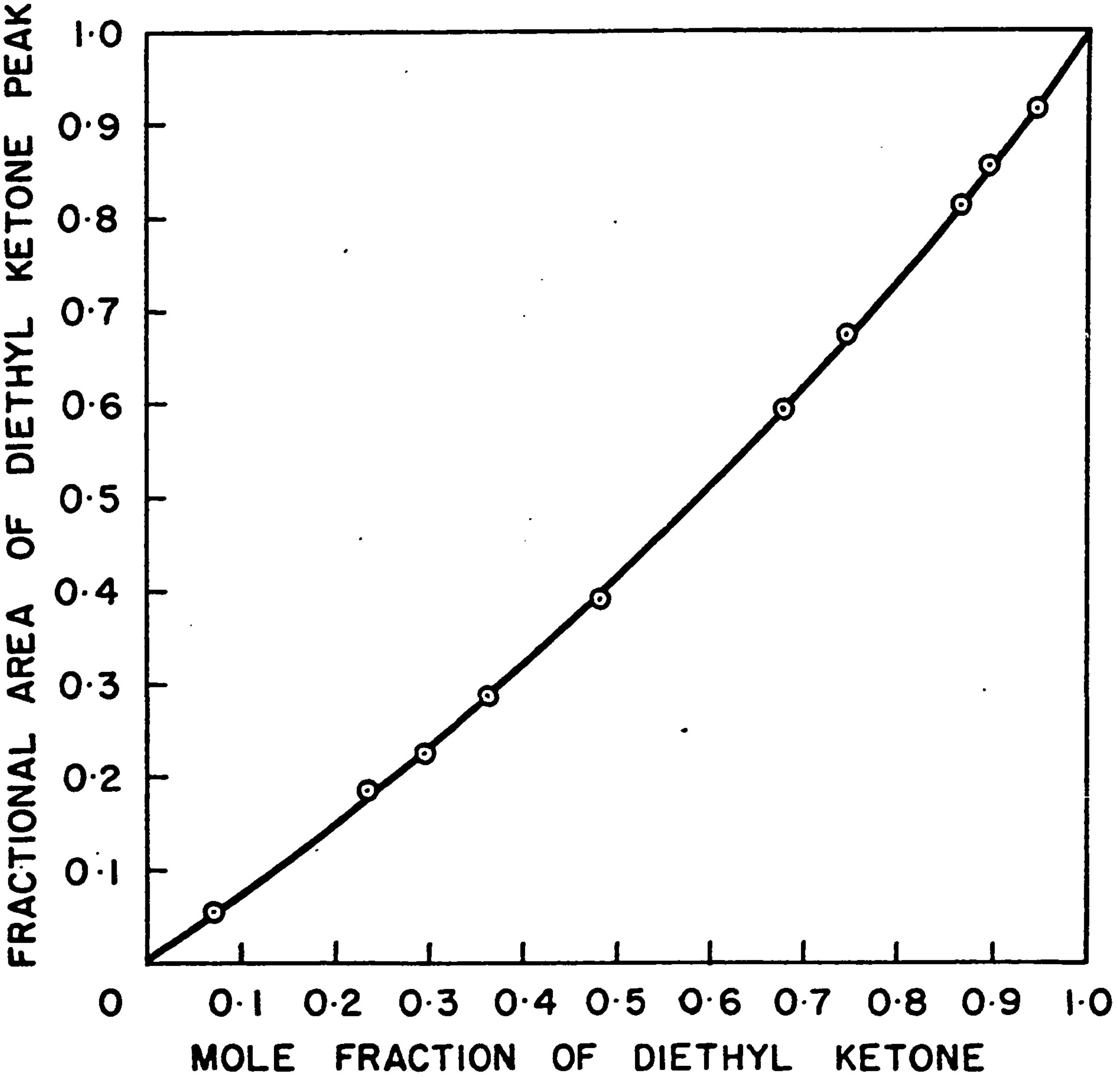


FIGURE A.9 Calibration Data for Diethyl Ketone/ n-Hexane Mixtures

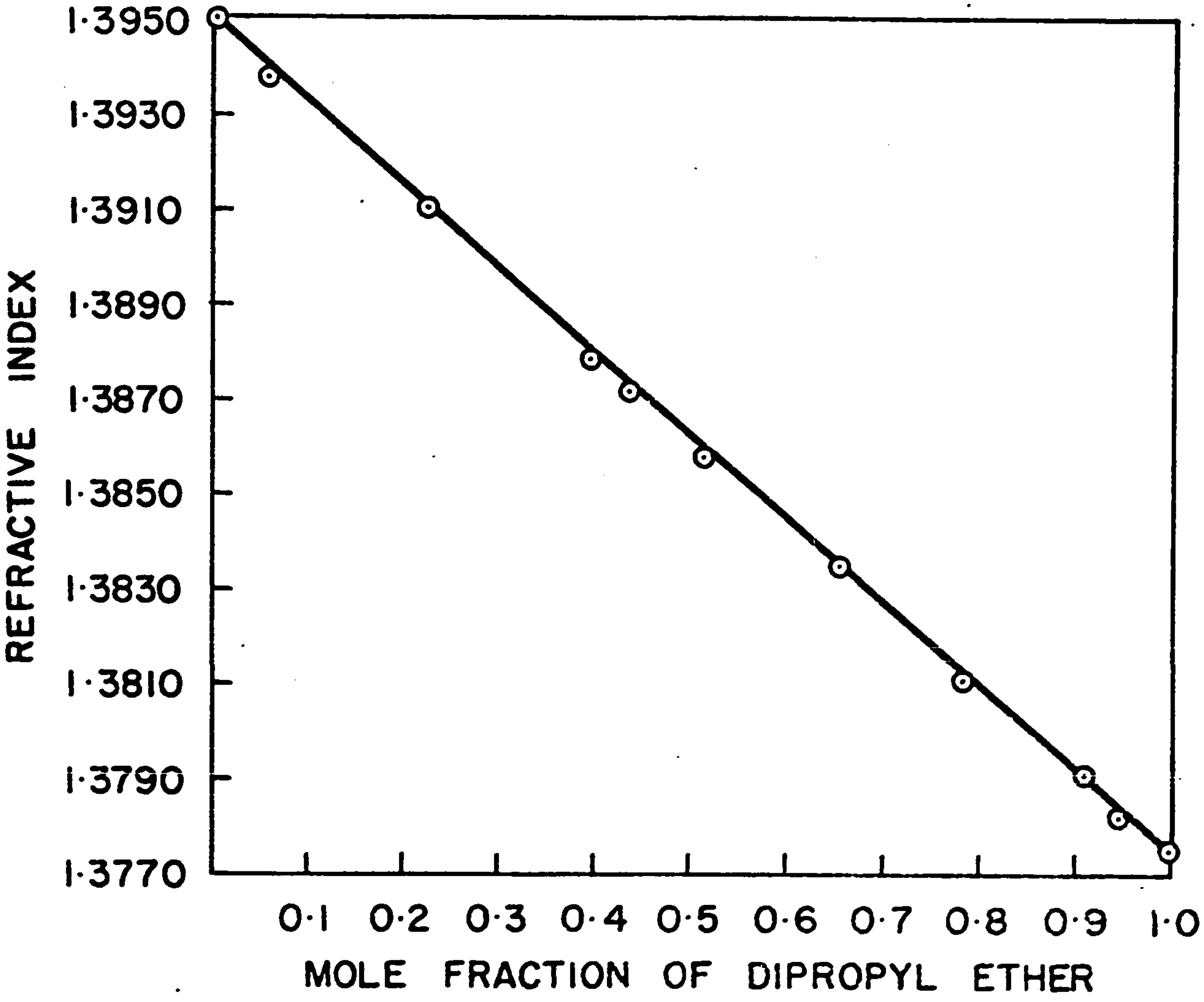


FIGURE A.11 Calibration Data for Dipropyl Ether/ n-Octane Mixtures

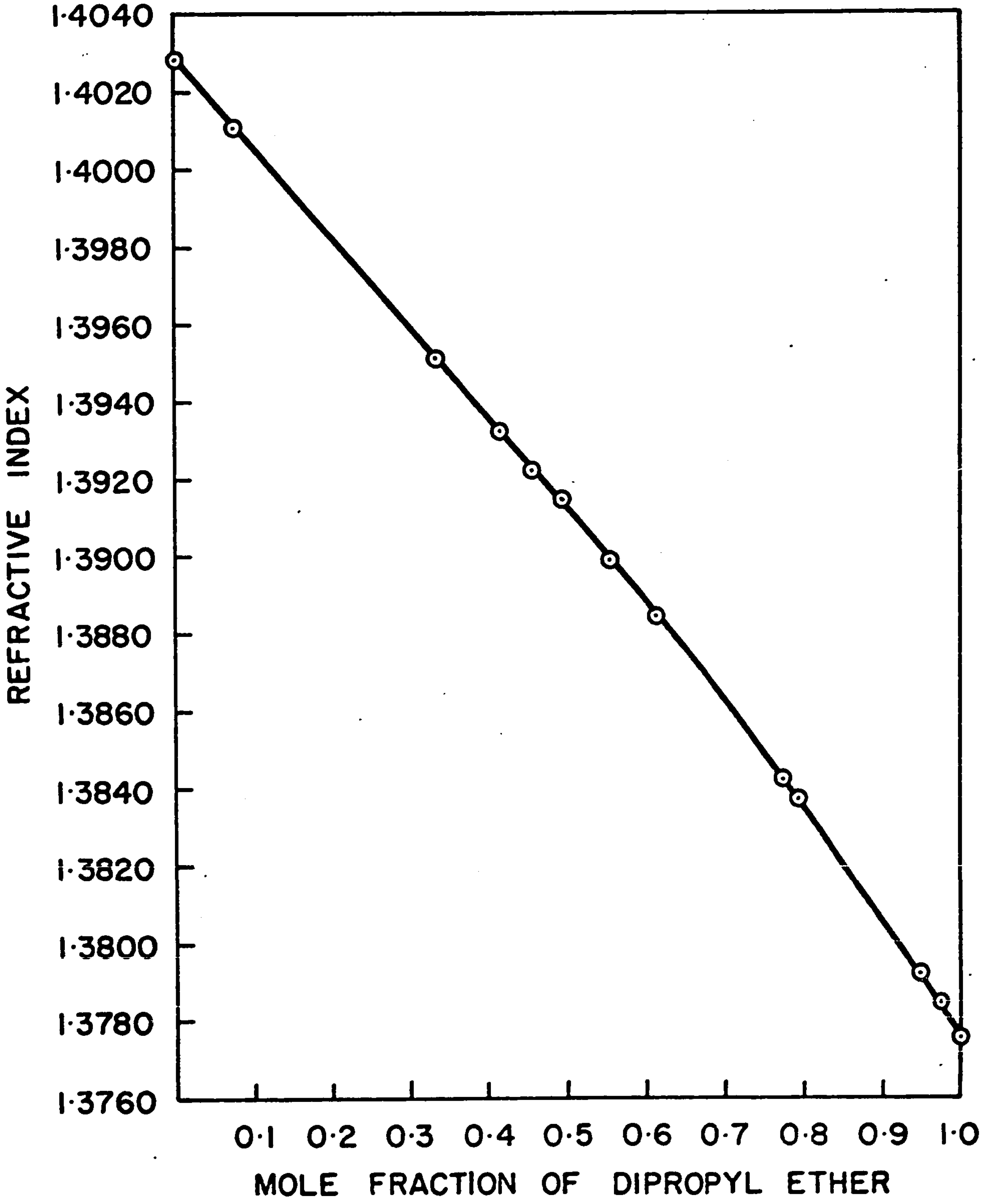


FIGURE A.12 Calibration Data for Dipropyl Ether/ n-Nonane Mixtures

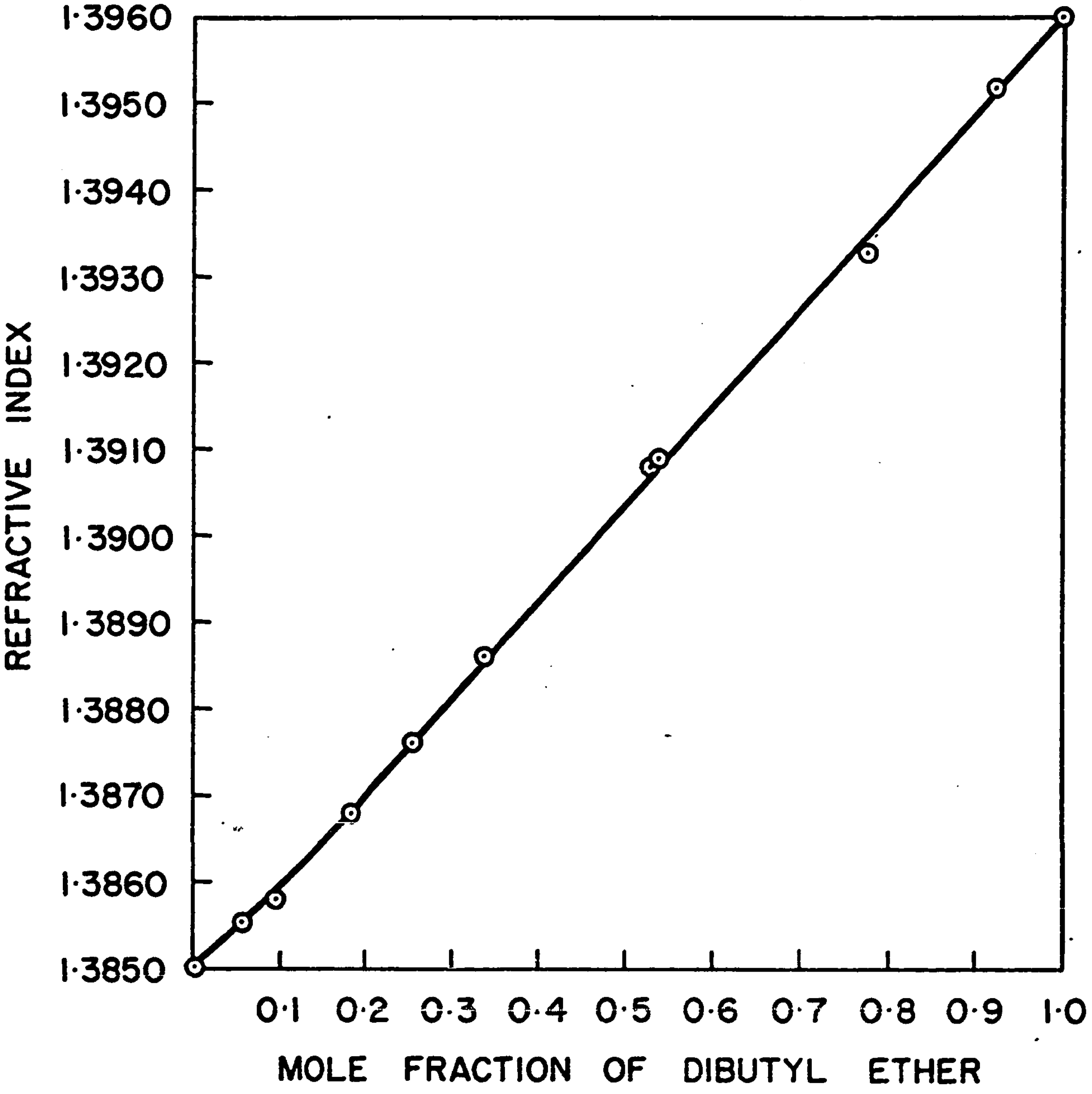


FIGURE A.13 Calibration Data for Dibutyl Ether/ n-Heptane Mixtures

TABLE A.1

CALIBRATION DATA FOR ETHANOL-BENZENE MIXTURES

Mole Fraction of Benzene	Refractive Index at 25°C
0.0	1.3594
0.0077	1.3604
0.0219	1.3632
0.0558	1.3702
0.0849	1.3758
0.0939	1.3773
0.1271	1.3836
0.2933	1.4116
0.3834	1.4244
0.4869	1.4395
0.6277	1.4572
0.7429	1.4707
1.0	1.4978

TABLE A.2

CALIBRATION DATA FOR METHANOL-WATER MIXTURES

Mole Fraction of Methanol	Refractive Index at 25°C
0.0	1.3324
0.0510	1.3344
0.0606	1.3347
0.1078	1.3365
0.1484	1.3380
0.1685	1.3389
0.3087	1.3416
0.3184	1.3410
0.3471	1.3410
0.5445	1.3389
0.6253	1.3372
0.6816	1.3359
0.7473	1.3341
0.7643	1.3338
0.8544	1.3313
0.8966	1.3296
0.9179	1.3289
0.9579	1.3278
0.9673	1.3274
1.0	1.3269

TABLE A.3

CALIBRATION DATA FOR ACETONE/N-HEXANE MIXTURES

Mole Fraction of Acetone	Refractive Index at 25°C
0.0	1.3778
0.0559	1.3766
0.2432	1.3726
0.3609	1.3703
0.4450	1.3679
0.5959	1.3646
0.5209	1.3660
0.6869	1.3629
0.8545	1.3590
0.9115	1.3580
1.0	1.3558

TABLE A.4

CALIBRATION DATA FOR ACETONE/N-HEPTANE MIXTURES

Mole Fraction of Acetone	Refractive Index at 25°C
0.0	1.3850
0.0769	1.3830
0.2827	1.3778
0.3747	1.3756
0.3900	1.3752
0.5791	1.3695
0.6398	1.3678
0.6585	1.3670
0.7906	1.3620
0.8733	1.3595
0.8934	1.3590
0.9619	1.3567
0.9631	1.3565
1.0	1.3560

TABLE A.5

CALIBRATION DATA FOR ACETONE/N-DECANE MIXTURES

Operating Conditions

Injector temperature = 315°C
Oven temperature = 70°C
Carrier gas flow = 30 c.c. per min.
Sample size = 0.5 μl
(Hydrogen and air flows adjusted for optimum response)

Mole Fraction of Acetone	Fractional Height of Acetone Peak
0.0495	0.0642
0.0966	0.1109
0.3298	0.3419
0.4875	0.4866
0.4981	0.5023
0.5443	0.5342
0.8281	0.7304
0.8344	0.7296
0.8697	0.7588
0.9344	0.8321
0.9414	0.8459
0.9601	0.8769
0.9825	0.9344

TABLE A.6

CALIBRATION DATA FOR METHYL ETHYL KETONE/N-HEXANE MIXTURES

Operating Conditions

Injector temperature = 125°C
Oven temperature = 32°C
Carrier gas flow = 30 c.c. per min.
Sample size = 0.5 μl
(Hydrogen and air flows adjusted for optimum response)

Mole Fraction of M.E.K.	Fractional Height of M.E.K. Peak
0.0619	0.0259
0.1126	0.0475
0.1327	0.0572
0.2090	0.0895
0.4835	0.2040
0.5611	0.2403
0.8018	0.4357
0.8362	0.4843
0.9208	0.6582
0.9313	0.6880

TABLE A.7

CALIBRATION DATA FOR METHYL ETHYL KETONE/N-OCTANE MIXTURES

Mole Fraction of M.E.K.	Refractive Index at 25°C
0.0	1.3762
0.2010	1.3912
0.3457	1.3888
0.5692	1.3847
0.6747	1.3828
0.7949	1.3800
0.8262	1.3791
0.8364	1.3790
0.9308	1.3771
1.0	1.3949

TABLE A.8

CALIBRATION DATA FOR METHYL ETHYL KETONE/N-DECANE MIXTURES

Operating Conditions

Injector temperature = 315°C
Oven temperature = 70°C
Carrier gas flow = 30 c.c. per min.
Sample size = 0.5 μl
(Hydrogen and air flows adjusted for optimum response)

Mole Fraction of M.E.K.	Fractional Height of M.E.K. Peak
0.1251	0.2010
0.2882	0.3776
0.4765	0.5606
0.5069	0.5873
0.4406	0.5316
0.7213	0.7029
0.7563	0.7266
0.8518	0.8049
0.9731	0.9390

TABLE A.9

CALIBRATION DATA FOR DIETHYL KETONE/N-HEXANE MIXTURES

Operating Conditions

Injector temperature = 210°C
Oven temperature = 75°C
Carrier gas flow = 30 c.c. per min.
Sample size = 0.5 μl
(Hydrogen and air flows adjusted for optimum response)

Mole Fraction of Diethyl Ketone	Fractional Height of Diethyl Ketone Peak
0.3628	0.2869
0.6781	0.5999
0.7454	0.6733
0.8989	0.8549
0.8687	0.8175
0.9473	0.9195
0.0709	0.0555
0.2356	0.1881
0.2913	0.2276
0.4805	0.3905

TABLE A.10

CALIBRATION DATA FOR DIPROPYL KETONE/N-HEXANE MIXTURES

Operating Conditions

Injector temperature = 210°C
Oven temperature = 75°C
Carrier gas flow = 30 c.c. per min.
Sample size = 0.5 μl
(Hydrogen and air flows adjusted for optimum response)

Mole Fraction of Dipropyl Ketone	Fractional Height of Dipropyl Ketone Peak
0.221	0.1553
0.2048	0.1495
0.0301	0.0200
0.1734	0.1193
0.1252	0.0869
0.0391	0.0264
0.4743	0.2900
0.801	0.6029
0.4279	0.2639
0.8578	0.6902
0.9682	0.9129

TABLE A.11

CALIBRATION DATA FOR DIPROPYL ETHER/N-OCTANE MIXTURES

Mole Fraction of Dipropyl Ether	Refractive Index at 25°C
0.0	1.3950
0.0578	1.3938
0.2256	1.3910
0.3964	1.3878
0.4334	1.3872
0.5172	1.3858
0.6511	1.3835
0.7878	1.3811
0.9076	1.3791
0.9469	1.3783
1.0	1.3775

TABLE A.12

CALIBRATION DATA FOR DIPROPYL ETHER/N-NONANE MIXTURES

Mole Fraction of Dipropyl Ether	Refractive Index at 25°C
0.0	1.4028
0.0793	1.4011
0.3339	1.3951
0.4164	1.3932
0.4553	1.3922
0.4998	1.3915
0.5559	1.3899
0.6197	1.3884
0.7746	1.3842
0.7937	1.3838
0.9449	1.3792
0.9753	1.3785
1.0	1.3775

TABLE A.13

CALIBRATION DATA FOR DIBUTYL ETHER/N-HEPTANE MIXTURES

Mole Fraction of Dibutyl Ether	Refractive Index at 25°C
0.0	1.3850
0.0554	1.3855
0.0966	1.3858
0.1868	1.3868
0.2587	1.3876
0.2468	1.3875
0.3392	1.3886
0.5267	1.3908
0.5313	1.3909
0.7719	1.3933
0.9225	1.3952
1.0	1.3960

APPENDIX B

Auxiliary Data

TABLE B.1

PURE COMPONENT DATA OF ALKANES AND KETONES

Compound	Molecular Weight	Vapor Pressure at 65°C mm. Hg.	Density at 65°C gms./cc.	Critical Pressure P_c Atm.	Critical Temperature T_c °K	Second Virial Coefficient (β) at 65°C cc./gm.mole
n-Hexane	86.18	676.2	0.6158	29.9	507.3	-1337.2
n-Heptane	100.21	249.7	0.6443	27.0	540.3	-1847.3
n-Octane	114.23	96.8	0.6657	24.6	568.6	-2425.0
n-Decane	142.3	14.7	0.6957	20.8	617.6	-3865.2
Acetone	58.08	1016.7	0.7392	46.6	508.7	-866.8
Methyl Ethyl Ketone	72.11	456.8	0.7737	41.0	535.0	-1175.6
Diethyl Ketone	86.13	217.5	0.7742	36.9	561.0	-1544.7
Dipropyl Ketone	114.18	46.7	0.8001	28.77	595.0	-2444.3

TABLE B.2

PURE COMPONENT DATA OF ETHERS AND ALKANES

Compound	Molecular Weight	Vapor Pressure at 90°C mm. Hg.	Density at 65°C gms./cc.	Critical Pressure P_c Atm.	Critical Temperature T_c °K	Second Virial Coefficient (β) at 65°C cc./gm.mole
Dipropyl Ether	102.18	766.2	0.6743	29.4	529.3	-1318.4
Dibutyl Ether	130.2	156.9	0.6938	24.2	580.9	-2218.0
n-Heptane	100.21	585.8	0.6208	27.0	540.3	-1545.1
n-Octane	114.23	251.5	0.6442	24.6	568.6	-2024.6
n-Nonane	128.25	110.1	0.6622	22.5	594.5	-2595.8

APPENDIX C

Computer Programs

1. Experimental Isothermal Activity Coefficients
2. Experimental Isobaric Activity Coefficients
3. Redlich-Kister Constants
4. Prediction of Isothermal Equilibrium Data
5. Prediction of Isobaric Equilibrium Data

PROGRAM - EXPERIMENTAL ISOTHERMAL ACTIVITY COEFFICIENTS

```
 CALCULATION OF ACTIVITY COEFFICIENTS FROM EXPERIMENTAL EQUILIBRIUM
 DATA
 N = NUMBER OF EXPERIMENTAL POINTS
 P = PURE COMPONENT VAPOR PRESSURE
 PC = CRITICAL PRESSURE
 TC = CRITICAL TEMPERATURE
 D = DENSITY GMS/C.C
 W = MOLECULAR WEIGHT
 PHI = TOTAL PRESSURE
 X = MOLE FRACTION IN LIQUID
 Y = MOLE FRACTION IN VAPOR
 V = MOLAR VOLUME
 B = SECOND VIRIAL COEFFICIENT
 GL = LOG GAMA
 RTL = LOG (GAMA1/GAMA2)

 DIMENSION X1(25),X2(25),Y1(25),Y2(25),PHI(25),GL1(25),GL2(25),
1XSG(25),RTL(25),C2(25),C1(25)
 READ 7,K1
7 FORMAT (I2)
 K=0
99 K=K+1
 READ 5,N
5 FORMAT (I2)
 READ 2,P1,P2
2 FORMAT (2F10.5)
 READ 3,PC1,PC2,TC1,TC2,T
3 FORMAT (5F10.5)
 READ 4,D1,W1,D2,W2
4 FORMAT (4F10.5)
 TR1=T/TC1
 TR2=T/TC2
 R=82.06
 Q1=0.0120*TR1
 Q2=0.40/TR1
 Q3=0.1460/ABS(TR1**3.270)
 B1=(R*TC1/PC1)*(0.1970-Q1-Q2-Q3)
 R1=0.0120*TR2
 R2=0.40/TR2
 R3=0.1460/ABS(TR2**3.27)
 B2=(R*TC2/PC2)*(0.1970-R1-R2-R3)
 V1=W1/D1
 V2=W2/D2
 READ 6,(X1(I),Y1(I),PHI(I),I=1,N)
6 FORMAT (3F10.5)
 DO 20 I=1,N
 Y2(I)=1.0-Y1(I)
```

```
      X2(I)=1.0-X1(I)
      GL1(I)=ALOG10(PHI(I)*Y1(I)/(P1*X1(I)))
      GL2(I)=ALOG10(PHI(I)*Y2(I)/(P2*X2(I)))
      C1(I)=((P1-PHI(I))*(V1-B1))/(760.0*2.3026*R*T)
      C2(I)=((P2-PHI(I))*(V2-B2))/(760.0*2.3026*R*T)
      GL1(I)=GL1(I)+C1(I)
      GL2(I)=GL2(I)+C2(I)
      RTL(I)=GL1(I)-GL2(I)
   20 CONTINUE
      PRINT 31
   31 FORMAT (1H1,////////48X,7HTABLE -//)
      PRINT 32
      PRINT 98
   98 FORMAT (40X,33HSYSTEM: DIBUTYL ETHER - N-HEPTANE/)
   32 FORMAT (40X,29HEXPERIMENTAL EQUILIBRIUM DATA/)
      PRINT 33
   33 FORMAT (40X,35HVAPOR PHASE IMPERFECTIONS ACCOUNTED/)
      PRINT 50
   50 FORMAT (40X,18HTEMPERATURE = 90 C/)
      PRINT 51
   51 FORMAT (40X,22HCOMPONENT ONE IS ETHER/)
      PRINT 41
   41 FORMAT (1H0,33X,2HX ,8X,2HY ,5X,5H (MM),6X,3HLOG,7X,3HLOG,
     17X,3HLOG)
      PRINT 34,(X1(I),Y1(I),PHI(I),GL1(I),GL2(I),RTL(I),I=1,N)
   34 FORMAT (1H0,26X,2F10.3,F9.1,3F10.4)
      PRINT 35,P1,P2,PC1,PC2,TC1,TC2,B1,B2
   35 FORMAT (1H1,//////8X,8F14.4)
      PRINT 36,T,D1,W1,D2,W2
   36 FORMAT (//22X,5F12.4/////)
      PRINT 46
   46 FORMAT (1H1,////////48X,7HTABLE -//)
      PRINT 47
   47 FORMAT (40X,33HSYSTEM: DIBUTYL ETHER - N-HEPTANE/)
      PRINT 48
   48 FORMAT (40X,39HACTIVITY COEFFICIENT CORRECTION FACTORS/)
      PRINT 52
   52 FORMAT (40X,18HTEMPERATURE = 90 C/)
      PRINT 53
   53 FORMAT (40X,22HCOMPONENT ONE IS ETHER/)
   45 FORMAT (1H0,30X,2HX ,11X,3HLOG,12X,2HC ,11X,3HLOG,12X,2HC )
      PRINT 45
      PRINT 37,(X1(I),GL1(I),C1(I),GL2(I),C2(I),I=1,N)
   37 FORMAT (1H0,20X,5F14.4)
      IF (K1-K) 100,100,99
  100 STOP
      END
```

PROGRAM - EXPERIMENTAL ISOBARIC ACTIVITY COEFFICIENTS

```
      A,B,C ARE ANTOINES CONSTANTS
      WM = MOLECULAR WEIGHT
      OTHER NOMENCLATURE IS THE SAME AS IN ISOTHERMAL PROGRAM

      READ 8,R
    8 FORMAT (F10.5)
      DIMENSION T(25),X1(25),Y1(25),P1(25),X2(25),Y2(25),P2(25),
     1TR1(25),TR2(25),B1(25),B2(25),V1(25),V2(25),D1(25),D2(25),
     1AFA1(25),AFA2(25),BTA1(25),BTA2(25),GLN1(25),GLN2(25),
     1TA(25),RATL(25)
      READ 9,N
    9 FORMAT (I2)
      READ 2,A11,B11,C11
    2 FORMAT (3F10.5)
      READ 3,A22,B22,C22
    3 FORMAT (3F10.5)
      READ 4,PC1,PC2,TC1,TC2
    4 FORMAT (4F10.5)
      READ 5,WM1,WM2,PHI
    5 FORMAT (3F10.5)
      READ 6,(T(I),X1(I),Y1(I),D1(I),D2(I),I=1,N)
    6 FORMAT (5F10.5)
      DO 100 I=1,N
      P1(I)=EXP(2.303*(A11-(B11/(C11+T(I)))))
      P2(I)=EXP(2.303*(A22-(B22/(C22+T(I)))))
      TA(I)=273.16+T(I)
      TCA1=273.16+TC1
      TCA2=273.16+TC2
      TR1(I)=TA(I)/TCA1
      TR2(I)=TA(I)/TCA2
      V1(I)=WM1/D1(I)
      V2(I)=WM2/D2(I)
      Y2(I)=1.0-Y1(I)
      X2(I)=1.0-X1(I)
      B1(I)=R*TCA1*(0.197-(0.012*TR1(I))-(0.40*(1.0/TR1(I)))
     1-(0.146*(1.0/(TR1(I)**3.27))))/PC1
      B2(I)=R*TCA2*(0.197-(0.012*TR2(I))-(0.40*(1.0/TR2(I)))
     1-(0.146*(1.0/(TR2(I)**3.27))))/PC2
      AFA1(I)=ALOG((PHI*Y1(I))/(P1(I)*X1(I)))
      AFA2(I)=ALOG((PHI*Y2(I))/(P2(I)*X2(I)))
      BTA1(I)=(B1(I)-V1(I))*(PHI-P1(I))/(760.0*R*TA(I))
      BTA2(I)=(B2(I)-V2(I))*(PHI-P2(I))/(760.0*R*TA(I))
      GLN1(I)=(AFA1(I)+BTA1(I))/2.3026
      GLN2(I)=(AFA2(I)+BTA2(I))/2.3026
      RATL(I)=GLN1(I)-GLN2(I)
```

```
100 CONTINUE
    PRINT 12
 12 FORMAT (1H1,//////22X,25H SYSTEM  BENZENE  ETHANOL)
    PRINT 13
 13 FORMAT (1H0,22X,33H SUBSCRIPT  ONE  IS  FOR  ETHANOL)
    PRINT 15
 15 FORMAT (1H0,22X,33H TOTAL  PRESSURE  PHI  IS  760 MM/////)
    PRINT 16
 16 FORMAT (1H0,8X,2HX1,8X,2HY1,10X,2HTA,11X,2HP1,9X,2HP2,
   110X,6HLOGAM1,5X,6HLOGAM2,5X,8HLOGRATIO)
    PRINT 17,(X1(I),Y1(I),TA(I),P1(I),P2(I),GLN1(I),
   1GLN2(I),RATL(I),I=1,N)
 17 FORMAT (1H0,F11.3,F11.3,F13.2,2F12.2,F13.4,F11.4,F13.4)
    PRINT 18
 18 FORMAT (1H1,7X,5HALFA1,7X,5HBETA1,7X,6HLNGAM1,7X,
   12HTA,7X,6HLNGAM2,7X,5HALFA2,7X,5HBETA2,/)
    PRINT 19,(AFA1(I),BTA1(I),GLN1(I),TA(I),GLN2(I),
   1AFA2(I),BTA2(I),I=1,N)
 19 FORMAT (1H0,7F12.6)
    PRINT 31,A11,B11,C11
 31 FORMAT (1H1,3F12.5//)
    PRINT 32,A22,B22,C22
 32 FORMAT (1H0,3F12.5)
    PRINT 33,PC1,PC2,TC1,TC2
 33 FORMAT (1H0,4F15.5)
    PRINT 34,WM1,WM2,PHI
 34 FORMAT (1H0,3F15.5////)
    PRINT 35,(T(I),X1(I),Y1(I),D1(I),D2(I),I=1,N)
 35 FORMAT (1H0,5F15.6)
    STOP
    END
```

PROGRAM - REDLICH KISTER CONSTANTS

THIS PROGRAM CALCULATES R.K CONSTANTS USING THE WEIGHTED LEAST SQUARES FIT ON LOG (GAMA1/GAMA2) FUNCTION.

X= MOLE FRACTION IN LIQUID
Y= MOLE FRACTION IN VAPOR
Z= LOG (GAMA1/GAMA2)
XC= VALUES OF X FOR INTERPOLATION
N= NUMBER OF DATA POINTS
M= NUMBER OF INTERPOLATION POINTS
K1= NUMBER OF SETS OF DATA
B,C,D ARE THE R. K CONSTANTS

```
    READ 128,K1
128 FORMAT (I2)
    K=0
130 K=K+1
    READ 2,N
  2 FORMAT (I2)
    READ 16,M
 16 FORMAT (I2)
    DIMENSION XC(25),PC(25),QC(25),RC(25),AP(25),ASP(25),
   1ASQ(25),AQ(25),AR(25),ASR(25),ZC(25),X(25),Y(25),Z(25),XX(25),
   1YY(25),P(25),Q(25),R(25),A12(25),A21(25),W(25),SK1(25),SK2(25),
   1SK3(25),SK4(25),SK5(25),SK6(25),SK7(25),SK8(25),SK9(25),C1(25),
   1C2(25),C3(25)
    READ 3,(X(I),Y(I),Z(I),I=1,N)
  3 FORMAT (3F10.5)
    READ 15,(XC(J),J=1,M)
 15 FORMAT (8F10.5)
    DO 50 I=1,N
    YY(I)=1.-Y(I)
    XX(I)=1.-X(I)
    P(I)=1.-(2.*X(I))
    Q(I)=-(1.-(6.*X(I))+(6.*ABS(X(I)**2.)))
    R(I)=1.-(10.*X(I))+(24.*ABS(X(I)**2.))-(16.*ABS(X(I)**3.))
    A12(I)=(Y(I)*XX(I))/(X(I)*YY(I))
    A21(I)=1./A12(I)
    W(I)=64.*ABS(((X(I)*XX(I))/(1,+(A21(I)*ABS((XX(I)+(A12(I)
   1*X(I)))**2.)))))**2.)
    AP(I)=ABS(P(I))
    ASP(I)=ABS(AP(I)**2.0)
    AQ(I)=ABS(Q(I))
    ASQ(I)=ABS(AQ(I)**2.0)
    AR(I)=ABS(R(I))
    ASR(I)=ABS(AR(I)**2.0)
    SK1(I)=W(I)*ASP(I)
    SK2(I)=W(I)*P(I)*Q(I)
```

```
      SK3(I)=W(I)*P(I)*R(I)
      SK4(I)=W(I)*P(I)*Q(I)
      SK5(I)=W(I)*ASQ(I)
      SK6(I)=W(I)*Q(I)*R(I)
      SK7(I)=W(I)*P(I)*R(I)
      SK8(I)=W(I)*Q(I)*R(I)
      SK9(I)=W(I)*ASR(I)
      C1(I)=W(I)*P(I)*Z(I)
      C2(I)=W(I)*Q(I)*Z(I)
      C3(I)=W(I)*R(I)*Z(I)
   50 CONTINUE
      SSK1=0.
      SSK2=0.0
      SSK3=0.0
      SSK4=0.0
      SSK5=0.0
      SSK6=0.0
      SSK7=0.0
      SSK8=0.0
      SSK9=0.0
      SSC1=0.0
      SSC2=0.0
      SSC3=0.0
      DO 100 I=1,N
      SSK1=SSK1+SK1(I)
      SSK2=SSK2+SK2(I)
      SSK3=SSK3+SK3(I)
      SSK4=SSK4+SK4(I)
      SSK5=SSK5+SK5(I)
      SSK6=SSK6+SK6(I)
      SSK7=SSK7+SK7(I)
      SSK8=SSK8+SK8(I)
      SSK9=SSK9+SK9(I)
      SSC1=SSC1+C1(I)
      SSC2=SSC2+C2(I)
      SSC3=SSC3+C3(I)
  100 CONTINUE
      DETA=(SSK1*((SSK5*SSK9)-(SSK8*SSK6)))
     1+(SSK2*((SSK6*SSK7)-(SSK9*SSK4)))
     1+(SSK3*((SSK4*SSK8)-(SSK7*SSK5)))
      DETA1=(SSC1*((SSK5*SSK9)-(SSK8*SSK6)))
     1+(SSK2*((SSK6*SSC3)-(SSK9*SSC2)))
     1+(SSK3*((SSC2*SSK8)-(SSC3*SSK5)))
      DETA2=(SSK1*((SSC2*SSK9)-(SSC3*SSK6)))
     1+(SSC1*((SSK6*SSK7)-(SSK9*SSK4)))
     1+(SSK3*((SSK4*SSC3)-(SSK7*SSC2)))
      DETA3=(SSK1*((SSK5*SSC3)-(SSK8*SSC2)))
     1+(SSK2*((SSC2*SSK7)-(SSC3*SSK4)))
     1+(SSC1*((SSK4*SSK8)-(SSK7*SSK5)))
      A=DETA1/DETA
      B=DETA2/DETA
      C=DETA3/DETA
      PRINT 98
   98 FORMAT (1H1,//////20X,7H SYSTEM//)
```

```
      PRINT 97
   97 FORMAT (20X,43H EVALUATION  OF  REDLICH  KISTER  CONSTANTS,//)
      PRINT 5,A
    5 FORMAT (20X,5H B IS,F10.5//)
      PRINT 6,B
    6 FORMAT (20X,5H C IS,F10.5//)
      PRINT 7,C
    7 FORMAT (20X,5H D IS,F10.5/////)
      PRINT 9,(X(I),Y(I),Z(I),I=1,N)
    9 FORMAT (1H0,14X,3F14.4)
      DO 60 J=1,M
      PC(J)=1.-(2.*XC(J))
      QC(J)=-(1.-(6.*XC(J))+(6.*ABS(XC(J)**2.)))
      RC(J)=1.-(10.*XC(J))+(24.*ABS(XC(J)**2.))-(16.*ABS(XC(J)**3.))
      ZC(J)=(A*PC(J))+(B*QC(J))+(C*RC(J))
   60 CONTINUE
      PRINT 95,A,B,C
   95 FORMAT (1H1,/////18X,3F14.4/////)
      PRINT 99,(XC(J),ZC(J),J=1,M)
   99 FORMAT (1H0,14X,2F20.5)
      PRINT 12
   12 FORMAT (1H1,8X,2HPI,8X,2HQI,8X,2HRI,8X,3HA12,8X,3HA21,
     18X,2HXI,8X,2HWI,//)
      PRINT 13,(P(I),Q(I),R(I),A12(I),A21(I),X(I),W(I),I=1,N)
   13 FORMAT (1HK,7F10.5)
      IF (K1-K) 131,131,130
  131 STOP
      END
```

PROGRAM - PREDICTED ISOTHERMAL EQUILIBRIUM DATA

THIS PROGRAMME CALCULATES Y USING TRIAL PROCEDURE FROM PREDICTED ACTIVITY COEFFICIENTS.
INPUT DATA FOR THIS PROGRAMME ARE VIRIAL COEFFICIENTS, DENSITIES, TEMPERATURE, VAPOR PRESSURES AND MOLECULAR WEIGHTS OF THE COMPONENTS. OTHER INPUT DATA INCLUDE X1,Y-EEPERIMENTAL, PREDICTED LOG ACTIVITY COEFFICIENT VALUES, EXPERIMENTAL LOG ACTIVITY COEFFICIENT VALUES, AND GROUP FRACTIONS CORRESPONDING TO VALUES OF X1.
PRINTED OUTPUT GIVES COMPARISON OF PREDICTED AND EXPERIMENTAL VALUES OF Y AND THE R.M.S DEVIATION.
SUBSCRIPTS 1 AND 2 REFER TO THE COMPONENTS.
B = SECOND VIRIAL COEFFICIENT.
D = DENSITY.
R = 82.06
T = ABSOLUTE TEMPERATURE.
P = PURE COMPONENT VAPOR PRESSURE.
W = MOLECULAR WEIGHT.
X1= MOLE FRACTION IN LIQUID.
X = GROUP FRACTION.
YX= EXPERIMENTAL MOLE FRACTION IN VAPOR.
C11 AND C22 ARE VAPOR PHASE CORRECTION FACTORS.
GL1X AND GL2X ARE EXPERIMENTAL LOG GAMAS.
S IS THE R.M.S VALUE IN Y.
Y VALUES ARE CALCULATED GIVING TOTAL PRESSURE PY, AN INCREAMENT OF 0.5 MM. STARTING FROM A VALUE 100MM. LESS THAN THAT CALCULATED USING SIMPLE EQUATION.
N AND G ARE THE NUMBER OF DATA POINTS.

```
      READ 2,N,G
    2 FORMAT (I2,F10.5)
      DIMENSION X1(20),Y1(20),Y2(20),SY(20),PY(20),GL1(20),GL2(20),
     1G1(20),G2(20),C1(20),C2(20),X2(20)
      DIMENSION C11(20),C22(20)
      DIMENSION YD(20),YDD(20),YX(20)
      DIMENSION GL1X(20),GL2X(20),X(20)
      READ 3,B1,B2,D1,D2,R,T,P1,P2,W1,W2
    3 FORMAT (8F10.5)
      READ 4,(X1(I),YX(I),GL1(I),GL2(I),GL1X(I),GL2X(I),X(I),I=1,N)
    4 FORMAT (7F10.5)
      V1=W1/D1
      V2=W2/D2
      PRINT 88
   88 FORMAT (1H1,/////////60X,6HTABLE-/)
      PRINT 81
   81 FORMAT (1H0,44X,41HPREDICTED DATA USING GROUP SOLUTION MODEL/)
```

```
      PRINT 80
   80 FORMAT (45X,33HSYSTEM: DIETHYL KETONE - N-HEXANE/)
      PRINT 50
   50 FORMAT (45X,18HTEMPERATURE = 65 C/)
      PRINT 51
   51 FORMAT (45X,23HCOMPONENT ONE IS KETONE//)
      PRINT 83
   83 FORMAT (46X,2HX ,10X,6HY-PRED,5X,5HY-EXP,8X,11HY-DIFF(ABS)//)
      DO 100 I=1,N
      X2(I)=1.0-X1(I)
      G1(I)=EXP(2.303*GL1(I))
      G2(I)=EXP(2.303*GL2(I))
      PY(I)=(P1*X1(I)*G1(I))+(P2*X2(I)*G2(I))
      PY(I)=PY(I)-100.0
   20 PY(I)=PY(I)+0.50
      C1(I)=(B1-V1)*(PY(I)-P1)/(760.0*R*T)
      C2(I)=(B2-V2)*(PY(I)-P2)/(760.0*R*T)
      C11(I)=C1(I)/2.303
      C22(I)=C2(I)/2.303
      C1(I)=EXP(C1(I))
      C2(I)=EXP(C2(I))
      Y1(I)=(G1(I)*P1*X1(I))/(PY(I)*C1(I))
      Y2(I)=(G2(I)*P2*X2(I))/(PY(I)*C2(I))
      SY(I)=Y1(I)+Y2(I)
      IF (1.0-SY(I)) 20,21,21
   21 YD(I)=ABS(YX(I)-Y1(I))
      YDD(I)=YD(I)*YD(I)
  100 CONTINUE
      SDD=0.0
      DO 40 I=1,N
      SDD=SDD+YDD(I)
   40 CONTINUE
      SS=SDD/G
      S=SQRT(SS)
      PRINT 30,(X1(I),Y1(I),YX(I),YD(I),I=1,N)
   30 FORMAT (1H0,34X,2F14.3,F11.3,F15.3)
      PRINT 32,S
   32 FORMAT (1H0,//44X,27HR.M.S  DEVIATION  IN  Y  IS,F10.4)
      PRINT 60
   60 FORMAT (1H1,/////////60X,6HTABLE-//)
      PRINT 61
   61 FORMAT (45X,41HPREDICTED DATA USING GROUP SOLUTION MODEL/)
      PRINT 63
   63 FORMAT (45X,33HSYSTEM: DIETHYL KETONE - N-HEXANE/)
      PRINT 52
   52 FORMAT (45X,18HTEMPERATURE = 65 C/)
      PRINT 53
   53 FORMAT (45X,23HCOMPONENT ONE IS KETONE//)
      PRINT 64
   64 FORMAT (32X,2HX ,7X,2HX ,14X,2HY ,17X,3HLOG,16X,3HLOG/)
      PRINT 65
   65 FORMAT (51X,4HEXPT,6X,4HPRED,5X,4HEXPT,6X,4HPRED,6X,4HEXPT,6X,
     14HPRED/)
      PRINT 66,(X1(I),X(I),YX(I),Y1(I),GL1X(I),GL1(I),
```

```
  1GL2X(I),GL2(I),I=1,N)
66 FORMAT(1H0,24X,F10.3,F10.4,2F10.3,4F10.4)
   PRINT 39
39 FORMAT (1H1,////////32X,2HX1,10X,2HY1,10X,2HSY,10X,2HPY,10X,
  12HC1,10X,2HC2//)
   PRINT 44,(X1(I),Y1(I),SY(I),PY(I),C11(I),C22(I),I=1,N)
44 FORMAT (1H0,27X,2F10.3,3X,F10.3,F12.1,F11.4,F12.4)
   STOP
   END
```

PROGRAM - PREDICTION OF ISOBARIC EQUILIBRIUM DATA

```
      THIS PROGRAM CALCULATES ISOBARIC EQUILIBRIUM DATA FROM PREDICTED
      ACTIVITY COEFFICIENTS FOR BUTANOL-ETHYL BENZENE SYSTEM.
      YX=EXPERIMENTAL Y
      GL1X=LOG GAMA1 EXPERIMENTAL
      GL2X=LOG GAMA2 EXPERIMENTAL
      XX=MOLE FRACTION IN LIQUID
      X=GROUP FRACTION
      GL1=PREDICTED LOG GAMA1
      GL2=PREDICTED LOG GAMA2
      N,G=NUMBER OF DATA POINTS


      READ 1,N,G
    1 FORMAT (I2,F10.5)
      DIMENSION XX(15),X(15),P1(15),P2(15),YX(15),GL1X(15),
     1GL2X(15),GL1(15),GL2(15),YY(15),YY2(15),YD(15),YDD(15),T(15),
     1TP(15),G1(15),G2(15),SY(15)
      READ 6,(XX(I),X(I),GL1(I),GL2(I),I=1,N)
    6 FORMAT (4F10.5)
      READ 20,(YX(I),GL1X(I),GL2X(I),I=1,N)
   20 FORMAT (3F10.5)
      DO 100 I=1,N
      G1(I)=EXP(2.3026*GL1(I))
      G2(I)=EXP(2.3026*GL2(I))
      T(I)=61.0
   23 T(I)=T(I)+0.02
      TP(I)=(T(I)*1.8)+32.0
      P1(I)=EXP(2.3026*(7.56483-(1416.99/(184.99+T(I)))))
      P2(I)=EXP(2.3026*(5.24358-(2563.659/(351.771+TP(I)))))
      P2(I)=51.71473*P2(I)
      YY(I)=(G1(I)*P1(I)*XX(I))/100.0
      YY2(I)=(G2(I)*P2(I)*(1.0-XX(I)))/100.0
      SY(I)=YY(I)+YY2(I)
      IF (1.0-SY(I)) 24,24,23
   24 YD(I)=ABS(YX(I)-YY(I))
      YDD(I)=YD(I)*YD(I)
  100 CONTINUE
      SDD=0.0
      DO 40 I=1,N
      SDD=SDD+YDD(I)
   40 CONTINUE
      SS=SDD/G
      S=SQRT(SS)
      PRINT 88
   88 FORMAT (1H1,/////////60X,6HTABLE-/)
      PRINT 81
   81 FORMAT (1H0,44X,41HPREDICTED DATA USING GROUP SOLUTION MODEL/)
```

```
      PRINT 80
   80 FORMAT (45X,33HSYSTEM: N-BUTANOL - ETHYL BENZENE/)
      PRINT 55
   55 FORMAT (45X,24HTOTAL PRESSURE = 100 MM./)
      PRINT 98
   98 FORMAT (45X,44HPREDICTED FROM ALCOHOL - ALKANE DATA AT 40 C/)
      PRINT 57
   57 FORMAT (45X,24HCOMPONENT ONE IS ALCOHOL/)
      PRINT 83
   83 FORMAT (1H0,46X,2HX ,10X,6HY-PRED,5X,5HY-EXP,8X,11HY-DIFF(ABS)/)
      PRINT 30,(XX(I),YY(I),YX(I),YD(I),I=1,N)
   30 FORMAT (1H0,34X,2F14.3,F11.3,F15.3)
      PRINT 32,S
   32 FORMAT (1H0,//44X,27HR.M.S  DEVIATION  IN  Y  IS,F10.4)
      PRINT 60
   60 FORMAT (1H1,////////60X,6HTABLE-//)
      PRINT 61
   61 FORMAT (45X,41HPREDICTED DATA USING GROUP SOLUTION MODEL/)
      PRINT 63
   63 FORMAT (45X,33HSYSTEM: N-BUTANOL - ETHYL BENZENE/)
      PRINT 56
   56 FORMAT (45X,24HTOTAL PRESSURE = 100 MM./)
      PRINT 94
   94 FORMAT (45X,44HPREDICTED FROM ALCOHOL - ALKANE DATA AT 40 C/)
      PRINT 58
   58 FORMAT (45X,24HCOMPONENT ONE IS ALCOHOL/)
      PRINT 64
   64 FORMAT (1H0,32X,2HX ,7X,2HX ,14X,2HY ,17X,3HLOG,16X,3HLOG/)
      PRINT 65
   65 FORMAT (51X,4HEXPT,6X,4HPRED,5X,4HEXPT,6X,4HPRED,6X,4HEXPT,6X,
     14HPRED/)
      PRINT 66,(XX(I),X(I),YX(I),YY(I),GL1X(I),GL1(I),
     1GL2X(I),GL2(I),I=1,N)
   66 FORMAT(1H0,24X,F10.3,F10.4,2F10.3,4F10.4)
      PRINT 22
   22 FORMAT (1H1,//////15X,6HSYSTEM////)
      PRINT 12,(XX(I),YY(I),X(I),GL1(I),GL2(I),SY(I),P1(I),P2(I),I=1,N)
   12 FORMAT (1H0,8X,8F10.4)
      STOP
      END
```

SUGGESTIONS FOR FURTHER WORK

1. In view of the relative success of the model in predicting the equilibria of mixtures studied in the present investigation, it is logical to extend the model to mixtures containing other functional groups, particularly multicomponent, multigroup mixtures. Among the groups for immediate further study should be aldehydes, aromatic hydroxyl, and methylene for a logical extension of the model.

2. There is considerable published information on the heats of mixing of aromatic hydrocarbons and alcohols, and these systems should be examined for a treatment using the group solution concept.

3. Since paraffin-ether systems are nearly ideal, examination must be made of the behaviour of ether-alcohol systems and the possibility of predicting their data from those of paraffin-alcohol mixtures.

4. Experimental determination of vapor-liquid equilibria of mixtures with high relative volatility must be confined to static methods.

SUMMARY OF CONCLUSIONS AND CONTRIBUTION TO KNOWLEDGE

1. A modified Gillespie still was constructed to measure vapor-liquid equilibrium data and testing indicated good experimental data can be obtained using the still.

2. Isothermal vapor-liquid equilibrium data on eight alkane-ketone systems at 65°C, and three alkane-ether systems at 90°C, were determined. These data should be useful in engineering designs and testing of models to predict equilibrium data.

3. Data on alkane-ether systems indicate that these mixtures may be regarded as nearly ideal.

4. The group solution model of Ratcliff and Chao was successfully tested on the eight alkane-ketone systems. The model predicts the equilibrium data reasonably well with an average R.M.S. deviation of 0.013 in the mole fraction of y (ketone).

5. The model was also applied to predict equilibrium data on six aromatic hydrocarbon-alcohol systems. The predictions for these systems also are in good agreement with experiment with an average R.M.S. deviation in y (alcohol) of 0.013 mole fraction.

6. Further testing of the model indicates that reasonable estimates of equilibrium data on aromatic hydrocarbon-alcohol systems could be made using alkane-ketone data.

7. The recirculation still is not suitable for measuring equilibrium data on mixtures of high relative volatility. Static methods should prove to be better alternatives.