

PHASE EQUILIBRIA IN THE ACETIC ACID-  
DIETHYLKETONE-WATER SYSTEM

By

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## PREFACE

Isothermal vapor-liquid determinations for the binary mixtures, and liquid-liquid determinations for the ternary system comprised of acetic acid, diethylketone, and water were made at 50, 60, and 70° C. Activity coefficients derived from the binaries were used to predict activity coefficients in the ternary. Experimental results are discussed and evaluated; and comparisons of applicable equations are presented.

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## NOMENCLATURE

$A_{1-2}$	= parameter in the van Laar equation.
$A_{12}$	= parameter in the van Laar equation.
$a_1$	= activity of components.
$a_1$	= van der Waals parameters for pure components.
$a_{12}$	= van der Waals parameters for interaction between unlike molecules.
$a_{1,1}^2$	= Cline Black parameter.
$a_m$	= van der Waals parameter for a mixture.
$b$	= van Laar parameters for pure components.
$b_m$	= van Laar parameters for a mixture.
$c_{11}$	= cohesive energy density of pure components, Scatchard-Hildebrand parameter.
$c_{12}$	= Scatchard-Hildebrand parameter for a mixture.
	= Cline Black parameter.
$E$	= internal energy.
$-E$	= Scatchard-Hildebrand parameter.
$-E_m$	= Scatchard-Hildebrand parameter for a mixture.
$F$	= Gibbs free energy, $H - TS$ .
$f$	= fugacity, force/area.
$H$	= enthalpy, energy.
$h_{1,1}$	= Cline Black parameter.
$K_2$	= acetic acid dimer constants.
$K_4$	= acetic acid tetramer constants.

M	= molecular weights.
n	= number of moles.
P	= total pressure.
$P_1$	= partial pressure of acetic acid monomer in the vapor phase.
$P_2$	= partial pressure of acetic acid dimer in the vapor phase.
$P_4$	= partial pressure of acetic acid tetramer in the vapor phase.
$P_w$	= partial pressure of water in the vapor phase.
$p^0$	= vapor pressure of pure component at the system temperature.
Q	= $F^E/2.3 RT$ .
q	= unspecified molecular property.
R	= gas law constant.
R	= molar refraction for pure component.
$R_m$	= molar refraction for a mixture.
$R_s$	= specific refraction.
$R_{1j}$	= Cline Black parameter $q_1/q_j$ .
S	= entropy, energy/degree.
V	= volume.
$V_1$	= molar volume of component 1.
Y	= mole fraction in the vapor phase.
y	= mole fraction in the vapor phase.

#### Greek Symbols

$\alpha$	= residual volume $(RT/P) - V$ .
$\gamma$	= activity coefficient.
$\Delta$	= change in a property.
$\delta$	= solubility parameter, Scatchard-Hildebrand.
$\varphi$	= fugacity coefficient.

$\phi$  = volume fraction.

$\Sigma$  = summation over.

#### Subscripts

1 = component 1 (lighter component).

i,j,k = components i, j, or k, respectively.

I = ideal state.

m = mixture.

M,R,S = class variables, Cline Black equation.

#### Superscripts

E = excess property.

M = mixing.

o = reference state.

Super  
Bar = partial molar property.

V,L = vapor and liquid phases.

\* = reference to state which would exist in the binary system.

#### Abbreviations

DEK = diethylketone.

HAC = acetic acid.

$\ln$  = logarithm to base e.

## CHAPTER I

### INTRODUCTION

The study of solutions has long been a subject of interest to chemical engineers and physical chemists alike. Many expressions have been developed to describe and predict the behavior of a component in the presence of other components. Some of these expressions have a theoretical basis, while others are empirical. Most of these expressions are quite useful but have a limited range of application. This often results in complicated expressions and the necessity to obtain more actual data on the systems being studied in order to generate enough information for design purposes. Studies of highly non-ideal systems provide further insight and understanding of the nature of the forces existing among groups and molecules and hopefully will hasten the day when solution behavior can be consistently predicted from pure component properties, or from structural considerations alone. This was the objective of the work reported here.

In systems where there are pronounced association or interassociation effects, usually a large number of parameters (at least three and often more) are required to describe the binary systems adequately. Extension of these data to multicomponent systems is frequently difficult.

Black (2) has developed an equation of the van Laar type for which three parameters express each binary system in which there are



association or interassociation effects. For systems where such effects are not present, his equation reduces to the van Laar equation. In addition, Black has provided for a systematic combination of parameters for multicomponent mixtures.

One of the purposes of this investigation was to study mixtures which were sufficiently non-ideal as to form two liquid phases, and determine how well the Black equation expressed this relationship.

The system chosen for this investigation was acetic acid-diethylketone-water. Acetic acid is known to form vapor-phase polymers and it was of particular interest to study the effect of this on activity coefficients. The two acetic acid binaries of this system (i.e., acetic acid-water and acetic acid-diethylketone) are miscible in all proportions and do not form azeotropes. The water-diethylketone binary is relatively immiscible, highly non-ideal and forms a hetroazeotrope (i.e., one vapor phase and two coexisting equilibrium liquid phases). The ternary of this system contains a region of two coexisting equilibrium liquid phases.

Vapor-liquid equilibrium measurements on the two acetic-acid binaries, determination of the hetroazeotrope, and measuring the compositions of the coexisting liquid phases of the ternary were the plan for the experimental part of this investigation. The theoretical part of the work was to calculate the activity coefficients of the binaries and develop a method to predict the ternary behavior.

## CHAPTER II

### LIQUID SOLUTION

#### Ideal Solutions

The concept of an ideal solution is useful in approximating the behavior of many liquid mixtures and in providing a frame of reference for comparing all liquid mixtures. The thermodynamic definition of an ideal solution is "one in which the activity equals the mole fraction over the entire composition range and over a non-zero range of temperature and pressure" (11).

$$a_1^i = f_1^i / f_1^o = x_1 \quad (2-1)$$

where:

$a_1^i$  = the activity of component 1 in an ideal mixture.

$f_1^i$  = the fugacity of component 1 in an ideal mixture.

$f_1^o$  = the fugacity of component 1 in the pure state at  
some "standard" condition.

$x_1$  = the mole fraction of component 1 in the liquid  
mixture.

The fugacity of a substance in the standard state and in a mixture is related to its molal free energy by the equation:

$$\bar{F}_1 - F_1^o = RT \ln (\bar{f}_1 / f_1^o) \quad (2-2)$$

where:

$F_1^\circ$  = the free energy of component 1 at the reference conditions.

$\bar{F}_1$  = the partial molal free energy of component 1 in the mixture.

$f_1^\circ$  = the fugacity of component 1 in the pure state at standard conditions.

$\bar{f}_1$  = the fugacity of component 1 in the mixture at system conditions.

For an ideal solution:

$$\bar{F}_1 - F_1^\circ = RT \ln (\bar{f}_1 / f_1^\circ) = RT \ln x_1 \quad (2-3a)$$

$$\bar{F}_2 - F_2^\circ = RT \ln (\bar{f}_2 / f_2^\circ) = RT \ln x_2 \quad (2-3b)$$

$$\begin{aligned} \Delta F^M &= n_1 (\bar{F}_1 - F_1^\circ) + n_2 (\bar{F}_2 - F_2^\circ) \\ &= n_1 (RT \ln x_1) + n_2 (RT \ln x_2) \end{aligned}$$

$$\Delta F^M = RT(n_1 \ln x_1 + n_2 \ln x_2). \quad (2-4)$$

Differentiating Equation (2-4) at constant composition

$$(\partial \Delta F^M / \partial T)_{p, x} = -\Delta S^M = R(n_1 \ln x_1 + n_2 \ln x_2) \quad (2-5)$$

$$\Delta F^M = -T \Delta S^M \quad (2-6)$$

$$\text{and since } F = H - TS \quad (2-7)$$

$$\Delta F = \Delta H - T \Delta S - S \Delta T. \quad (2-8)$$

At constant temperature

$$\Delta F^M = \Delta H^M - T \Delta S^M. \quad (2-9)$$

Combining Equations (2-6) and (2-9)

$$\Delta H^M = 0. \quad (2-10)$$

In a similar manner, it can be shown that

$$\Delta V^M = (\partial \Delta F^M / \partial P)_{T,x} = 0 \quad (2-11)$$

Therefore, it can be seen that "when an ideal solution is formed from the pure liquid components at constant temperature and pressure, there is no volume change and no heat of mixing."

#### Non-Ideal Solutions

For non-ideal solutions, the activity of a component is not equal to its mole fraction.

$$a_1 = \bar{f}_1 / f_1^0 = \gamma_1 x_1 \quad (2-12)$$

$\gamma_1$  = the activity coefficient, defined by (2-12).

$$\Delta F^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2). \quad (2-13)$$

The first term on the right-hand of the equation represents the ideal free energy of mixing, while the second term represents the departure from ideal behavior and is termed the "excess" free energy of mixing.

#### Immiscible Solutions

Immiscible solutions are formed when the excess free energy is sufficiently high such that a minimum free energy of mixing is achieved by separation into two liquid phases. These systems always display positive deviations from Raoult's Law.

## Equations for Predicting Activity Coefficients

Methods for predicting heats of mixing from pure component properties have been devised by van Laar, Scatchard, and others. Both the above methods are inadequate where strong "chemical association" effects are present. Black has endeavored to improve the van Laar equation by adding a heat function to account for these associative effects. These three equations will be discussed.

### Van Laar Equation

In 1906, van Laar derived an expression for the vapor pressures of binary liquid mixtures based upon the van der Waals equation for the mixture and the pure components. The van der Waals "a" for the mixture had been expressed as  $a_m = n_1^2 a_1 + 2n_1 n_2 a_{12} + n_2^2 a_2$  where  $a_{12}$  is the interaction between unlike molecules. The van der Waals b for the mixture was assumed to be a weighted average of the b's for the pure components:

$$b_m = n_1 b_1 + n_2 b_2. \quad (2-14)$$

The heat of mixing for unexpanded liquids ( $v = b$ ) was given

$$\Delta H^M = \frac{n_1 a_1}{b_1} + \frac{n_2 a_2}{b_2} - \frac{a_m}{b_m}. \quad (2-15)$$

By further assuming the Berthelot relation

$$a_{12} = \sqrt{a_1 a_2}, \quad (2-16)$$

the following equation resulted:

$$\Delta H^M = \frac{n_1 n_2 b_1 b_2}{n_1 b_1 + n_2 b_2} \left[ \frac{a_1^{1/2}}{b_1} - \frac{a_2^{1/2}}{b_2} \right]^2. \quad (2-17)$$

The assumption of the Berthelot relation, while simplifying the equation, is one of the chief reasons for its failure to express adequately the relationships in polar solutions, or where specific interactions such as solvation or association take place.

Pursuing this further, van Laar and Lorentz improved the equation by substituting molal volumes for the van der Waals volumes  $b_1$  and  $b_2$  yielding

$$\Delta H^M = \frac{n_1 n_2 v_1 v_2}{n_1 v_1 + n_2 v_2} \left[ \frac{a_1^{1/2}}{v_1} - \frac{a_2^{1/2}}{v_2} \right]^2. \quad (2-18)$$

#### Scatchard-Hildebrand Equation

In 1931, Scatchard published a paper which gave a "method of freeing the van Laar treatment from the inadequacies of the van der Waals equation." His assumptions were (1) the mutual energy of two molecules depends only upon the distance between them and their relative orientation, and not at all on the nature of the other molecules between or around them, or on the temperature; (2) the distribution of the molecules in position and orientation is random, independent of the temperature, and of the nature of the other molecules present; (3) the change of volume on mixing at constant pressure is zero. These assumptions permit writing the cohesive energy of a mole of liquid mixture as

$$-E_m = \frac{c_{11} v_1^2 x_1^2 + 2c_{12} v_1 v_2 x_1 x_2 + c_{22} v_2^2 x_2^2}{v_1 x_1 + v_2 x_2}. \quad (2-19)$$

For pure components

$$-E_1 = c_{11} v_1 \text{ and, therefore, } c_{11} = \frac{-E_1}{v_1} \quad (2-20)$$

which has been termed "cohesive energy density." Making the assumption that the Berthelot relationship is satisfied

$$c_{12} = \sqrt{c_{11} c_{22}}. \quad (2-21)$$

$$\text{Then, } \Delta E^M = (x_1 v_1 + x_2 v_2) \varphi_1 \varphi_2 (c_{11}^{1/2} - c_{22}^{1/2})^2. \quad (2-22)$$

$E_1, E_2$  = Energy of vaporization of components 1, 2.

$v_1, v_2$  = Molal volumes of components 1, 2.

$x_1, x_2$  = Mole fraction of components 1, 2.

$\varphi_1, \varphi_2$  = Volume fraction of components 1, 2.

Assuming the vapor to be ideal for liquids at ordinary temperatures, Scatchard identified  $-E$  with  $\Delta E^V$ , the energy of vaporization.

Scatchard's equation is

$$\Delta E^M = (x_1 v_1 + x_2 v_2) \left[ \left( \frac{\Delta E_1^V}{v_1} \right)^{1/2} - \left( \frac{\Delta E_2^V}{v_2} \right)^{1/2} \right] \varphi_1 \varphi_2 \quad (2-23)$$

which is identical to the van Laar-Lorenz equation. This term  $\left( \frac{\Delta E^V}{v_1} \right)^{1/2}$  has been given the name solubility parameter and is designated by  $\delta$ .

The Scatchard-Hildebrand relationship presents the only practical means for estimating solution behavior solely from pure component properties. It is quite useful for mixtures where small non-directed interactions are involved, but is erratic where the  $a_{12}$  interaction cannot be expressed by  $a_{12} = \sqrt{a_1 a_2}$ , due to "chemical effects". It cannot predict negative deviations from ideality.

### Black Equation

In order to circumvent some of the shortcomings of the van Laar equation, Black added an empirical correction term. This term was to provide a means of accommodating the combined deviations due to association and interassociation.

The partial excess free energy is related to activity coefficient as follows:

$$\ln \gamma_1 = \bar{F}_1^E / RT. \quad (2-24)$$

If Q is defined as

$$Q = F^E / 2.3 RT \quad (2-25)$$

$$Q = Q_v + Q_e. \quad (2-26)$$

$Q_v$  is the van Laar function, and  $Q_e$  is the additive function which accounts for the combined association and interassociation effects.

The activity coefficient in a binary system is expressed

$$\ln \gamma_1 = \frac{A}{\left[ \frac{A_{x1}}{B_{x2}} + 1 \right]^2} + E_1 \quad (2-27)$$

where:

$$A = a_{12}^2 \quad (2-28)$$

$$B = a_{21}^2 \quad (2-29)$$

and

$$E_1 = c_{12} x_2 (x_1 - x_2) (3x_1 - x_2 - 3x_1^2 + 3x_1 x_2). \quad (2-30)$$

The constants A and B are determined by plotting  $(\ln \gamma_1)^{1/2}$  versus  $(\ln \gamma_2)^{1/2}$ . A line is drawn tangent to the curve, such that the logarithm



of the activity coefficient at infinite dilution  $A_{12}$  minus the correction  $c_{12}$  gives the square of the intercept  $a_{12}^2$  of the tangent line.

$$a_{12}^2 = A_{12} - c_{12} \quad (2-31)$$

and since the correction term  $c_{12} = c_{21}$  the tangent line is adjusted until  $a_{12}^2 = A_{12} - c_{12}$  and  $a_{21}^2 = A_{21} - c_{21}$ . (2-32)

These equations can be extended to ternary and multicomponent systems as shown in Appendix A.

## CHAPTER III

### DETERMINATION OF ACTIVITY COEFFICIENTS

Activity coefficients of the components of a solution may be determined in a number of ways. One principal method is through the determination of vapor-liquid equilibria.

Activity is defined as the ratio of the fugacity of the component in the mixture compared to the fugacity of the component in its pure form at some arbitrary reference state. Activity coefficient is a measure of the departure from ideality.

$$a_i = \frac{\bar{f}_i}{f_i^o} \quad (2-1)$$

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i^o} \quad (2-2)$$

where:

$a_i$  = the activity of component  $i$ .

$\gamma_i$  = the activity coefficient of component  $i$  in a mixture.

$\bar{f}_i$  = the fugacity of component  $i$  in the mixture.

$f_i^o$  = the fugacity of pure component  $i$  at the system temperature and at some reference pressure.

Fugacity is a term with units of pressure developed as a convenient function for use in making equilibrium calculations. Starting with the

relation

$$dF = -SdT + VdP \quad (3-3)$$

$$\left(\frac{\partial F}{\partial P}\right)_T = V \text{ which on integration at } T = \text{constant} \quad (3-4)$$

yields

$$F_2 - F_1 = \int_{P_1}^{P_2} V dP \quad (3-5)$$

$$\text{for a perfect gas } V = \frac{RT}{P} \quad (3-6)$$

$$\text{and } F_2 - F_1 = RT [\ln P_2 - \ln P_1] \quad (3-7)$$

$$= RT \ln \frac{P_2}{P_1}. \quad (3-8)$$

For a real gas

$$F_2 - F_1 = RT \ln \frac{f_2}{f_1} = \int_{P_1}^{P_2} V dP. \quad (3-9)$$

The difference between the ideal gas volume and the actual gas volume is defined as  $\alpha$ .

$$\alpha = \frac{RT}{P} - V \quad (3-10)$$

$$RT \ln \frac{f_2}{f_1} = RT \ln \frac{P_2}{P_1} - \int_{P_1}^{P_2} \alpha dP. \quad (3-11)$$

As  $P_1$  approaches zero

$$RT \ln \frac{f}{P} = - \int_0^P \alpha dP. \quad (3-12)$$

For mixture components

$$RT \ln \frac{\bar{f}_i}{f_i^o} = \int_{p^o}^P V_i dP \quad (3-13)$$

$$RT \ln \frac{\bar{f}_1}{y_1^P} = \int_0^P (\bar{V}_1 - \frac{RT}{P}) dP. \quad (3-14)$$

Therefore, to determine the fugacity coefficient of a component in the vapor, the volume of the mixture must be known for a sufficient composition range, and for pressures from zero to the system pressure. Alternatively, it may be evaluated from appropriate equations of state or from generalized charts.

#### Activity Coefficients in Acetic Acid Systems

The molecular state of acetic acid vapor has been studied by Ritter and Simons (15) and by MacDougall (13). The results of these investigators are quite comparable. The data of Ritter and Simons indicate the relationship of the molecular weight of acetic acid vapor with temperature and pressure. A portion of their data was used to produce Figure 1, which shows the relationship between molecular weight and temperature at saturation. This curve shows the molecular weight of acetic acid at saturation to be above 100 at 120° C and to increase with decreasing temperature.

This behavior of acetic acid vapor has been attributed to the tendency to form higher polymers, in particular to dimers and to a lesser extent tetramers.

Ritter and Simons postulated that if monomer and dimer are in equilibrium according to the reaction



the equilibrium constant  $K_2$  may be defined as

$$p_{2a} = K_2 p_{1a}^2 \quad (3-16)$$

and similarly for the tetramer

$$p_{4a} = K_4^4 p_{1a}^4 \quad (3-17)$$

The total pressure of acetic acid can be expressed as the sum of the partial pressures of monomer, dimer, and tetramer.

$$P_a = p_{1a} + p_{2a} + p_{4a} \quad (3-18)$$

The dimer and tetramer constants are related to temperature in the following manner:

$$\ln K_2 = (3645/T) - 11.997 \quad (3-19)$$

$$\ln K_4 = (3390/T) - 13.52 \quad (3-20)$$

Pressure is expressed in millimeters of mercury and T is in degrees Kelvin. It should be restated that the above relationships hold for pure acetic acid vapor.

For binary systems containing acetic acid as one of the components, the rigorous expression for calculating the activity coefficients from vapor-liquid data follows from the definitions of fugacity and activity coefficients, i.e.,

$$\gamma_1 = \frac{f_1}{x_1 f_1^0} = \frac{p_{y1} \phi_1}{x_1 f_1^0} \quad (3-21)$$

where  $\phi_1 = \frac{f_1}{p_{y1}}$ , the fugacity coefficient.

The application of Equation (3-21) involves computing  $\phi_1$  values via an equation of state and establishing the values of  $f_1^0$ , the reference state fugacity. As is brought out later, these steps are simplified in the present work.

In their study of the acetic acid-water system at 25° C, Hansen, Miller, and Christian (10) assumed that when acetic acid vapor is mixed with water vapor, the acetic acid further dissociates to give these relationships:

$$P = p_a + p_w \quad (3-22)$$

and

$$p_a = p_{1a} + p_{2a} + p_{4a} \quad (3-23)$$

$$= p_{1a} + K_2^2 p_{1a}^2 + K_4^4 p_{1a}^4 \quad (3-24)$$

where  $p_a$  and  $p_w$  are the partial pressures of acetic acid and water vapor, respectively. In other words, when acetic acid vapor is mixed with any other vapor the total volume is greater than the sum of the volumes of the pure components. Hansen et al., further assumed that in the liquid phase the acetic acid was present only as the monomer.

To calculate activity coefficients for the acetic acid-diethylketone system, and for the acetic acid-water system, the method used was similar to that used by Hansen, Miller, and Christian.

Let  $p_1$ ,  $p_2$ , and  $p_4$  represent the partial pressures of acetic acid monomer, dimer, and tetramer, respectively, in the vapor phase;  $n_1$ ,  $n_2$ , and  $n_4$  the corresponding moles of condensate;  $p_w$  and  $n_w$  the partial pressure and moles of water in the condensate;  $P_T$  the total pressure, and  $Y_A$  the experimental mole fraction of acid in the condensate considering all the acid as monomer.

$$Y_A = \frac{n_1 + 2n_2 + 4n_4}{n_1 + 2n_2 + 4n_4 + n_w} = \frac{p_{1a} + 2p_{2a} + 4p_{4a}}{p_{1a} + 2p_{2a} + 4p_{4a} + p_w} \quad (3-25)$$

$$= \frac{p_{1a} + 2p_{2a} + 4p_{4a}}{P_T + p_{2a} + 4p_{4a}} \quad (3-26)$$

$$Y_A (P_T + p_{2A} + 3p_{4A}) = p_{1A} + 2p_{2A} + 4p_{4A}. \quad (3-27)$$

Since  $p_{2A} = K_2^2 p_{1A}^2$  and  $p_{4A} = K_4^4 p_{1A}^4$

$$Y_A (P_T + K_2^2 p_{1A}^2 + 3K_4^4 p_{1A}^4) = p_{1A} + 2(K_2^2 p_{1A}^2) + 4(K_4^4 p_{1A}^4) \quad (3-28)$$

and

$$P_T - Y_A P_T + (2 - Y_A)(K_2^2 p_{1A}^2) + (4 - 3Y_A)(K_4^4 p_{1A}^4) = 0 \quad (3-29)$$

which may be solved for  $p_{1A}$ .

If  $f_A$  = the acetic acid fugacity and  $P_A = p_{1A} + p_{2A} + p_{4A}$ , the total acetic acid partial pressure, then

$$\ln \frac{f_A}{P_A} = \frac{1}{RT} \int_0^{P_A} (V_A - \frac{RT}{P_A}) dP_A. \quad (3-30)$$

It is here assumed that deviations from ideality are due entirely to the associations indicated so that

$$\ln \frac{f_A}{P_A} = \int_0^{P_A} \left( \frac{1}{p_{1A} + 2p_{2A} + 4p_{4A}} - \frac{1}{P_A} \right) dP_A \quad (3-31)$$

$$= \int_0^{P_A} \left( \frac{1}{p_{1A} + 2K_2^2 p_{1A}^2 + 4K_4^4 p_{1A}^4} - \frac{1}{P_A} \right) dP_A \quad (3-32)$$

and since  $P_A = p_{1A} + K_2^2 p_{1A}^2 + K_4^4 p_{1A}^4$

$$\frac{dP_A}{dp_{1A}} = 1 + 2K_2^2 p_{1A} + 4K_4^4 p_{1A}^3. \quad (3-33)$$

So, Equation (3-30) is equivalent to

$$\ln \frac{f_A}{P_A} = \int_0^{P_A} \left( \frac{1}{p_{1A} (dP_A/dp_{1A})} - \frac{1}{P_A} \right) dP_A \quad (3-34)$$

$$= \int_0^{P_A} \frac{dP_{1A}}{P_{1A}} - \int_0^{P_A} \frac{dP_A}{P_A} \quad (3-35)$$

$$= \ln P_{1A} - \ln P_A \quad (3-36)$$

$$= \ln \frac{P_{1A}}{P_A} \quad (3-37)$$

Therefore,  $f_A = P_{1A}$ .

The activity of the acetic acid is expressed

$$a_A = \frac{f_A}{f_A^0} = \frac{P_{1A}}{P_{1A}^0} \quad (3-38)$$

$$\gamma_A = \frac{P_{1A}}{x_A P_{1A}^0} \quad (3-39)$$

$P_{1A}^0$  is the partial pressure of the monomer in equilibrium with pure acetic acid at the temperature of reference. For the activity coefficient of water,

$$\gamma_w = \frac{P_w}{x_w P_w^0} = \frac{P_T - P_{1A} - K_2^2 P_{1A}^2 - K_4^4 P_{1A}^4}{x_w P_w^0} \quad (3-40)$$

Activity coefficients are calculated similarly for the acetic acid-diethylketone system.



## CHAPTER IV

### EXPERIMENTAL APPARATUS

There are many systems of industrial importance whose equilibrium relations cannot be calculated from Raoult's and Dalton's laws, or from other theoretical considerations, but must be obtained from experimental measurement.

Meaningful vapor-liquid equilibria data require the separation and analysis of vapor and liquid samples which are in true equilibrium, and necessitate accurate measurement and control of the conditions under which they were obtained.

In their book, Hala, Pick, Fried, and Vilim (8) discuss in detail some of the important methods and precautions of temperature and pressure measurement. They also describe the construction and operation of twenty-five different stills, comparing some of the advantages and disadvantages of each.

Very consistent data have been obtained for the chloroform-methanol system in a still designed by Scatchard, Raymond, and Gilman (17). This type of still was used in this investigation for the runs involving only one liquid phase. A still described by Hands and Norman (9) was used where two liquid phases were present. Both are vapor-recirculating stills.

### The Scatchard Still

This apparatus has two boilers, the bottom one heated by means of an external electric heater. Vapors leave this boiler and enter the second boiler through a Cottrel pump which recirculates the liquid. Equilibrium between the liquid in this chamber and the vapor leaving this chamber is, thus, achieved, and superheating of the vapor is avoided. The mixture of vapor and liquid is discharged onto the thermowell. A spiral winding on the external surface of the thermowell helps provide good liquid contact and aids in disengaging liquid and vapor.

The original design was modified to prevent liquid build-up in the second chamber through addition of an overflow line back to the first boiler as shown in Figure 3. Design of this type of apparatus requires that proper consideration be given to the relative hydrostatic head in the boilers as emphasized in the publication by Scatchard.

### The Hands and Norman Still

The Hands and Norman still, Figure 4, was designed specifically for systems whose condensate forms two liquid phases. Due to phase separation, no condensate receiver is used, since sampling would not provide for a representative distribution of the separate phases.

The still is equilibrated with all condensate being returned directly to the boiler. When a distillate sample is to be taken, a stopcock is turned so that the distillate is diverted to a receiver. While removing the sample, the composition of the liquid in the still will change slightly (if there is only one liquid phase present). The still pot is made quite large to minimize this change, and the quantity of distillate sample is kept as small as is feasible.

When two liquid phases are present in the residue, the still pressure and the composition of each phase remains constant, although the relative amounts of each phase will change slightly. This latter condition provides an accurate means of determining the vapor pressure of the two-phase region, and of removing a sufficient sample of heteroazeotrope to determine the relative volumes of both phases.

#### Cloud Point Titrator

When two liquids are mutually soluble, a beam of light passing through the solution remains intact. However, even a small quantity of one liquid dispersed in another liquid scatters the light, producing a cloudy mixture. By accurately measuring the liquid additions required to reach this condition of light scattering, the solubility limits may be determined for binary or multicomponent systems. This was the method used for determining the solubility envelopes for the ternary system water-diethylketone-acetic acid.

In order to determine the solubility envelope for the system water-diethylketone-acetic acid, an apparatus was constructed similar to that described by Smith and Bonner (18) and shown in Figure 5. This apparatus consisted of a pyrex tube 8 inches by 45 mm. diameter sealed at one end and closed at the top with a neoprene stopper. The tube was jacketed, and the temperature was maintained constant by circulation of water from a constant temperature bath. The constant temperature bath was a Colora Ultra thermostat which controlled the temperature to  $\pm 0.01^{\circ}\text{C}$ .

## Chemicals

The reagents used in this work were:

Acetic Acid - Baker reagent grade assaying 99.9 percent by weight, used without further purification.

Diethylketone - Matheison-Coleman and Bell practical grade, distilled in a forty plate Oldershaw column at 10-1 reflux ratio. The first light boiling portion of about 10 percent of the starting volume was discarded, and a cut comprising 70 percent of the volume was removed as product. This was then dried over five angstrom molecular sieves which had previously been fired at 600 °F for 24 hours.

Two samples of the diethylketone were analyzed with the hydrogen ionization chromatograph by Dr. Berlin of the Chemistry Department. The results showed no visible organic impurity, which represents a probable impurity of less than 0.001 percent.

Water - The water used was deionized and distilled. Where refractive index measurements were made, the water was degassed by boiling away one-third of its volume.

## Physical Properties

	<u>Acetic Acid</u>	<u>Diethylketone</u>	<u>Water</u>
B.P. °C	117.72 (5)	101.70 (5) 101.9 (12) 101.91 *	100.00
$n_D^{25}$	1.36995 (5)	1.39003 (5) 1.38996 (12) 1.38982 *	1.33258*
Density 25/4 °C	1.04365 (5)	0.80953 (5)	0.99707

## Vapor Pressure - mm. Hg\*

<u>Temp.</u>	<u>Acetic Acid</u>	<u>Diethylketone</u>	<u>Water</u>	<u>2-Phase H<sub>2</sub>O-DEK</u>
50°	57.6	117.0	92.5	195.0
60°	91.4	176.6	149.4	304.8
70°	138.2	260.3	233.7	462.5

\*Determined in this investigation.

## CHAPTER V

### EXPERIMENTAL PROCEDURE

#### Binary Vapor-Liquid Equilibria

##### Operation of the Scatchard Still

The still was charged with the desired mixture, and the pressure reduced to a value close to that at which the mixture was expected to boil. As boiling proceeded, the pressure was adjusted to maintain the desired temperature. When equilibrium was reached, no further adjustment in pressure was required. After the pressure was constant for thirty minutes, equilibrium was assumed to have been reached. Nitrogen was bled rapidly into the still, and samples of liquid were removed from the condensate receiver.

The length of time required to reach equilibrium depended on the closeness of the composition of the initial charges to that of the final composition. With a distillate rate of 50 drops per minute, two hours generally was sufficient. In order to save time and conserve materials, the three isotherms were run consecutively for each composition. Since the compositions did not change appreciably with temperature, less time was required to reach equilibrium. The still was insulated with layers of glass wool.

### Operation of the Hands and Norman Still

The still was charged with 500 - 600 cc. of liquid, and the pressure was reduced to a figure corresponding to that of the expected boiling point. When boiling began, the pressure was adjusted so as to maintain the desired temperature. The distillate receiver was attached with a pressure-tight connection to the discharge leg of the still. After equilibrium was reached, the pressure and temperature were recorded. The distillate receiver was then evacuated to system pressure by slowly opening the valve leading to a line preceding the manostat. The stopcock was turned, and the condensate diverted into the receiver. During this time, the pressure was adjusted to maintain as near isothermal operation as possible. After the sample was collected, the stopcock was turned back to its original position, and the sample was removed. Some time was allowed for the system to again come to equilibrium at the required temperature, and the final pressure was recorded.

### Temperature Measurement

The temperature was measured with a total immersion thermometer inserted in the temperature well. Mercury was used in the well to provide rapid heat transfer to the thermometer. The thermometer was graduated to 0.1 °C, and was calibrated to 0.01 °C. An emergent stem correction was made to compensate for that portion of the thermometer extending out of the temperature well.

### Pressure Control

The desired pressure was maintained by means of a cartesian manostat. This was a #8 Manostat from Manostat Corporation, New York, and was capable of control to  $\pm 0.1$  mm. Hg. A slight amount of nitrogen was bled to the system through a drying tube to permit proper operation of the pressure controller. The nitrogen and any vapors from the still were scrubbed in a slightly alkaline water solution to prevent corrosion of the manostat and vacuum pump.

### Pressure Measurement

The pressure was measured by means of a mercury manometer open at one end to the atmosphere with the other end attached to the system. The nitrogen gas used for pressure control also served to keep vapors swept away from the mercury manometer. The mercury meniscus was viewed with a cathetometer which could be read to 0.05 mm. Atmospheric pressure was read from a mercury barometer, and all mercury heights were corrected to a 0 °C basis. Over-all precision of pressure measurement was generally  $\pm 0.1$  mm., except as noted later.

### Sample Analyses

Miscible Systems. The use of acetic acid as one of the binary components presented a simple method of analysis. Samples of distillate and residue were pipetted into ground-glass covered weighing bottles, and were weighed on a Mettler B6 100 gm. balance. The cover and the bottle were rinsed into a beaker, and the solution was titrated with 0.1 normal sodium hydroxide to the phenolphthalein end point.



The analyses were reproducible with a difference of less than 0.1 percent by weight.

Immiscible System. Diethylketone-water distillate samples consisting of two phases were analyzed in the following manner: The sample was placed in a constant temperature bath at 30° C, and was agitated periodically. The two phases were allowed to separate, and the volumes of the phases were measured. The volumes for large samples (30 - 50 cc.) were read in a graduated cylinder. When a phase was present in small quantity, it was removed with a graduated hypodermic syringe.

The over-all composition was easily determined, since the density and composition of each phase was known from literature values (7) and through determinations made during this investigation.

### Ternary Liquid-Liquid Equilibria:

#### Phase Diagrams

#### Determination of the Solubility Envelope

Fifty ml. of water was placed in the tube and allowed to reach the desired temperature. Diethylketone was added one drop at a time from a burette and the solution was vigorously agitated with a magnetic stirrer. As cloudiness was observed, the titration was stopped and the reading was noted. One drop of acetic acid was added. If the cloudiness disappeared, the previous diethylketone volume was recorded and more acetic acid was added. This volume of acid was then recorded. Diethylketone was again added dropwise until cloudiness appeared. Continuing in this manner, over one-half the solubility envelope was determined. The tube was emptied and dried, and fifty ml. of diethylketone

was added. Water from a burette was added a drop at a time until cloudiness appeared. Acid was added as before, and the other one-half of the solubility envelope was determined. When acetic acid was not being added, the acetic acid burette was removed to prevent condensation on the tip. The temperature of all the reagents used was recorded, and volumes converted to weights and weight percent. These data are listed in Tables XVI - XVIII (Appendix C).

#### Determination of Tie Lines

Synthetic two-phase mixtures were placed in the constant temperature bath. Following a twenty-four hour period, a sample of each of the two phases was withdrawn, weighed and titrated for acetic acid content. The composition of each phase was then derived from the solubility envelope.

Solubility envelopes and equilibrium solubilities were determined at 50, 60, and 70° C. Tables XIX - XXI list the equilibrium solubility data. The solubility envelope and the tie-lines are shown as ternary diagrams in Figures 44-46.

## CHAPTER VI

### EXPERIMENTAL RESULTS

In conducting this investigation, vapor-liquid equilibria data were determined for the binary systems at 50, 60, and 70° C. From these data, activity coefficients were calculated which were checked for thermodynamic consistency by means of the relation

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx = \frac{1}{RT} \int_{p_0}^P V dp.$$

To determine constants for the Cline Black modification,  $(\ln \gamma_1)^{1/2}$  was plotted against  $(\ln \gamma_2)^{1/2}$ . A curve drawn through the points was extended until it intersected both coordinates. The values at the coordinates are termed  $(A_{12})^{1/2}$  and  $(A_{21})^{1/2}$ . A straight line intersecting both coordinates, at points designated  $a_{12}$  and  $a_{21}$ , was drawn tangent to the curved line and adjusted so that

$$A_{12} - a_{12}^2 = A_{21} - a_{21}^2 = c_{12} = c_{21}.$$

The constants  $a_{12}^2$ ,  $a_{21}^2$ , and  $c_{12}$  are the Cline Black constants (expressed in terms of the natural logarithm), and were used to predict activity coefficients in the ternary system. Their relationship to the van Laar equation has been shown in Equations (2-17) to (2-30).

Compositions of equilibrium phases of the ternary system were determined. Predicted activities of each component of both phases were calculated using the Black equation, the ternary van Laar equation as derived by Wohl, and an equation evolved during the course of this investigation, which to the knowledge of the author, has not been previously presented. The activities of each component are compared with the measured value.

#### Diethylketone: Vapor Pressure

##### Versus Temperature

Vapor pressure for pure diethylketone was determined in the Scatchard still, covering a temperature range from 50° to 100°. The vapor pressures at 50, 60, and 70° C were derived from a plot of these data (Table I, Appendix C).

#### Diethylketone-Water

##### Vapor Pressure Versus Temperature

In a similar manner, the vapor pressure of the mixture of water and diethylketone was determined in the Hands and Norman still, and these data are shown in Table II.

##### Refractive Index Versus Composition

Refractive index determinations were made of known water and diethylketone solutions in the single-phase region, and of the saturated phases. The water-rich region gave very good results which permit an accurate determination of the solubility of diethylketone in water. These data are given in Table III and are shown graphically in Figure 6.

Refractive indices on the ketone-rich solution were not satisfactory due to very slight change of refractive index with composition. These measurements indicate that the excess volume is negative.

### Activity Coefficients

Activity coefficients were calculated over the two liquid-phase region, which included the region from 0.01 to 0.85 mole fraction diethylketone, using the determined vapor pressure and vapor composition. These were constant over this composition range for each isotherm.

Extension of the runs beyond these concentration ranges was unsatisfactory. Formation of two liquid phases in the condensate gave rise to a fluctuating pot composition as the condensate was recirculated. True equilibrium could not be established in this region. The data are shown graphically in Figures 7, 8, 9, (Appendix D), and are listed in, Tables V, VI, and VII (Appendix C).

### Thermodynamic Consistency Check

The natural logarithm of  $\gamma_d/\gamma_w$  was plotted versus  $x_d$ , and extrapolated to  $x_d = 0$  and  $x_d = 1$ . The area included by the curve, and the line  $\ln(\gamma_d/\gamma_w) = 0$  was measured. The consistency was good for all three isotherms in this system and the areas were equal.

### Black Constants

Black constants were derived by plotting  $(\ln \gamma_w)^{1/2}$  versus  $(\ln \gamma_d)^{1/2}$  as shown in Figures 13, 14, and 15. This system gave the smoothest curves and most readily defined constants of the three binary systems.

### Summary of Diethylketone-Water System

<u>Temp. °C</u>	<u><math>a_{dw}^s</math></u>	<u><math>a_{wd}^s</math></u>	<u><math>c_{dw}</math></u>	<u><math>A_{dw}</math></u>	<u><math>A_{wd}</math></u>
50	3.37	1.59	1.24	4.65	2.82
60	3.53	1.69	1.04	4.56	2.74
70	3.37	1.69	1.06	4.34	2.74

### Acetic Acid Binaries

The systems water-acetic acid and diethylketone-acetic acid are quite similar in behavior and are completely miscible systems. Both systems exhibit positive deviations from ideality, despite a negative excess volume of mixing. The departure is of the same order of magnitude for both systems (Table XV).

### Activity Function and x - y Data

Vapor-liquid equilibria compositions were determined by acetic acid titrations and recorded in weight percents for diethylketone-acetic acid (Tables IX and XI) and water-acetic acid (Tables XII through XIV).

Compositions expressed as mole fraction, activity coefficients, the natural logarithm of the activity coefficient ratios, and the square root of the natural logarithm of the activity coefficients were also derived for water-acetic acid (Tables XXVI - XXVII).

The x - y data for these systems are presented in Figures 16 through 21,  $\gamma_x$  data in Figures 22 through 27 and the graphical integration of  $\ln \gamma_1/\gamma_2$  versus x (used to check thermodynamic consistency of the data) are shown in Figures 28 through 33 for water-acetic acid and diethylketone-acetic acid, respectively. Inconsistency was expressed

as a percentage of the area summation value divided by the sum of the absolute values of the areas above and below the zero line.

### Black Constants

Black constants were determined from plots of  $(\ln \gamma_1)^{1/2}$  versus  $(\ln \gamma_2)^{1/2}$  made for the two systems (Figures 34-39) and as there was some question regarding the line best representing the data, two sets of constants were calculated. One was the van Laar constants without a correction factor; the other constants were derived by drawing the best curved line through the points and adjusting somewhat for the fact that the straight line should be tangent in the region of  $x_1 = x_2 = 0.5$ .

The activity coefficients at infinite dilution differed from those determined from the plot of  $\ln(\gamma_1/\gamma_2)$  versus  $x$ . Nevertheless, calculations on the ternary system were made using both sets of constants.

### Summary of Acetic Acid Binaries

#### Limiting Activity Coefficient

#### Black Constants (Natural Logarithm Basis)

##### Water-Acetic Acid

Temp. °C	$\ln \gamma_{aw}$	$\ln \gamma_{wa}$	$a_{aw}^2$	$a_{wa}^2$	$c_{aw}$
50	1.092	.632	.872	.676	.423
60	1.075	.422	.963	.598	.304
70	.944	.350	1.050	.568	.250

##### Diethylketone-Acetic Acid

Temp. °C	$\ln \gamma_{kd}$	$\ln \gamma_{dk}$	$a_{kd}^2$	$a_{dk}^2$	$c_{kd}$
50	.619	.386	.739	.433	.107
60	.632	.371	.893	.308	.182
70	.560	.426	.746	.362	.100

## CHAPTER VII

### DISCUSSION OF RESULTS

#### Binary Systems

##### Diethylketone-Water

The diethylketone-water system is one of limited miscibility, having activity coefficients of 1 to 100 over the range of compositions. Activity coefficients calculated from the solubility of diethylketone in water and the total vapor pressure of the heteroazeotrope produce results which compare favorably with those calculated from the composition and vapor pressure of the heteroazeotrope. For example, at 60° C

$$P = x_d \gamma_d p_d^0 + x_w \gamma_w p_w^0 \quad (7-1)$$

$$\gamma_d = (304.8 - 148)/(.00909)(176.6) = 97.5$$

$$\gamma_d = y_d P / x_d p_d^0 \quad (7-2)$$

$$= (.52)(304.8)/(.00909)(176.6) = 98.8.$$

There is little value in attempting to determine x - y data with one liquid phase existing in the still pot and the condensate forming two layers. Not only are the data probably too poor for theoretical calculations, but they also are unlikely to represent the physical situation in a column operating with a different degree of mixing on the trays.



### Water-Acetic Acid

This system has a negative excess volume of mixing, and a positive deviation from ideality. This is unusual, since negative excess volume is usually accompanied by evolution of heat on mixing and negative deviation from ideality. This must be attributed to a negative excess entropy of mixing, indicating clustering of like molecules.

The  $x - y$  data show a limiting activity coefficient which decreases with increasing temperature. There is a tendency for the water activity coefficients to pass through a maximum and decline at high acetic acid concentrations. This is more pronounced at the higher temperatures.

The data show a thermodynamic inconsistency of -4.2, +7.7, and -12.5 percent at 50, 60, and 70° C, respectively. Arich and Tagliavini (1) investigated this system at 70, 80, and 90° C in an Othmer-type still, and their data show a thermodynamic inconsistency of -11 to -12 percent. They attribute this failure to hydration of acetic acid in the vapor.

### Diethylketone-Acetic Acid

This system also shows positive deviation from ideality, coupled with a negative excess volume of mixing. The effect of temperature on activity coefficient is slight. The thermodynamic inconsistency was -5.4, -3.3, and +5.1 percent at the three temperatures. There are several possible points of inflection on the curve of  $\ln(\gamma_1/\gamma_2)$  versus  $x$ . These data resemble those of Drickamer, Brown and White (6) for toluene - 2, 2, 4, trimethylpentane at 760 mm. Data should be taken at much closer intervals in order to define these inflection points.

### Ternary System

Solubility envelope determinations were made with results reproducible to better than 0.1 percent by weight. Equilibrium solubilities were also good, with reproducibility to plus or minus 0.2 percent.

The activity of each component in the equilibrium phases was calculated by the ternary van Laar equation, the Black equation, and one isotherm was calculated with an equation described later.

### van Laar Equation

The results from the ternary van Laar equation were extremely poor. The reason for this being due to the assumption in the derivation that

$$\frac{A_{31}}{A_{13}} = \frac{A_{32}}{A_{23}} \cdot \frac{A_{21}}{A_{12}} \quad (7-3)$$

which, in this instance, was far from true.

### Black Equation

The Black equation in its expanded form (A-16) also has this characteristic. However, by introducing the split interaction, the simplified Equation (A-20) gives much better results.

Even so, activities calculated for each phase differed too much to be useful. The calculated vapor pressures of the phases were in better agreement, but ranged from 75 to 90 percent of the measured vapor pressure.

Part of the inability of the Black equation to express the ternary relationship is associated with the fact that the binary systems are not well represented by the equation.

### Proposed Method

A method which was found to be the most satisfactory for calculating activity coefficients is based on the following assumption: The apparent molecular weight of acetic acid vapor may be calculated from the PVT data of Ritter and Simons, ignoring completely the differentiation between monomer, dimer, etc. For calculation of activity coefficients

$$\gamma_1 = \frac{p y_1(a)}{p_1^0 x_1(a)} \quad (7-4)$$

The assumption is made that the molecular weight for acetic acid in the liquid is the same as for pure acetic acid vapor. This assumption is obviously questionable in the water-rich region of the acetic acid-water system since acetic acid ionizes in this region. Nevertheless, use of this assumption gives calculated activity coefficients which are more satisfactory than the other methods. The experimentally determined values for the acetic acid binary systems are listed in Tables IX-XIV. These data were converted to a mole fraction basis and are presented with the calculated activity coefficients in Tables XXV-XXXI (Appendix C). Figures 22-27 (Appendix D) are xy diagrams for these binaries.

The calculations to obtain the mol fractions on an associated acetic acid basis were made with Equations (2-19), (2-20), and (2-24) of Chapter II. Values of  $p_1$  and  $(M_{\text{a}}(a)/M_{\text{a}}(60))$  are included in Tables XXXVIII and XXXIX. The activity coefficients were also calculated on an associated acetic acid basis, using Equation (7-4). Values of the pure component vapor pressure,  $p_1^0$ , at 70° C for this calculation are the first and the last entries in the third column of Tables XXXVIII and XXXIX.

Activity coefficients for the binary systems of acetic acid are computed on an associated basis in Tables XXXVIII and XXXIX. Values of  $x$  and  $y$  for these two binaries are given on Figures 40 and 41.

Activity coefficients for these binaries are plotted in Figures 42 and 43 on an associated acetic acid basis.

For the diethylketone-water system, mutual solubilities of the components, vapor composition, and total pressure were determined. The composition of the heteroazeotrope was determined for several runs and these compositions were used to determine the activity coefficients for the components in the two liquid-phase region by using the following simple relationship:

$$\gamma_1 = \frac{y_1 p}{x_1 p_1^0} \quad (7-5)$$

for both components of binary.

Temperature-pressure determinations for this binary were made in the Hands and Norman still for pure diethylketone and for the diethylketone, and for the diethylketone-water system with two liquid phases present. Because of slight fluctuations in pressure especially with the two liquid-phase system, these data were plotted and a smooth curve drawn through the points. The vapor pressure corresponding to the desired isotherm was read from the graph. These were the values used in determining activity coefficients by Equation (7-5). From Table I for diethylketone,  $p_1^0$  at 70° C is 260.3 mm. Total pressure for the two liquid-phase system at 70° C was 462.5 mm. Hg. Composition of the heteroazeotrope was determined by averaging of several runs at 70° C, which are listed in Table IV.

The composition of the vapor in equilibrium with the two liquid-phase region for this diethylketone-water system was found to be  $y_w = 0.470$  and  $y_d = 0.530$ . From these and the vapor pressure at 70° C (233.7 mm. Hg. for water and 260.3 mm. Hg. for diethylketone), the activity coefficients can be calculated as

$$\gamma_{wd} = \frac{(0.470)(462.5)}{233.7 x_w} = \frac{0.930}{x_w} \quad (7-6)$$

$$\gamma_{dw} = \frac{(0.530)(462.5)}{260.3 x_d} = \frac{0.940}{x_d} \quad (7-7)$$

For the ternary system values of  $x_w$  and  $x_d$  should be calculated via

$$x_w = \frac{x_w(a)}{x_w(a) + x_d(a)} \quad \text{and} \quad x_d = \frac{x_d(a)}{x_w(a) + x_d(a)} \quad (7-8)$$

#### Ternary Data Analysis

The following empirical relationship was used in calculating ternary system activity coefficients from the binary system activity coefficients given in Tables XXXVIII and XXXIX and on Figures 42 and 43.

$$\ln \gamma_1 = \frac{x_2}{x_2 + x_3} \ln \gamma_{12} + \frac{x_3}{x_2 + x_3} \ln \gamma_{13} + C_1 x_2 x_3 \quad (7-9)$$

where:

$\gamma_{13}$  = activity coefficient of component "1" in a binary

with component "3" evaluated at  $x_1/(x_1 + x_3)$ , and

$C_1$  = empirical interaction coefficient.

Similar expressions for components "2" and "3" are obtained by rotation of the subscripts. The  $x_2/(x_2 + x_3)$  term is suggested as the probability that the "1,2" binary will exist. Likewise, the term  $x_3/(x_2 + x_3)$

is suggested as the probability that the "1,3" binary will exist. For a ternary, such as the one studied in this work, these two mol fraction probability terms may also be written as  $x_j/(1 - x_i)$ .

Colburn and Schoenborn (3) proposed a somewhat similar method to the above. After obtaining the activity coefficients for the binary systems, these authors plotted "in a special manner in three figures as  $\ln \gamma_1$  versus  $x_1$  with curves for the binaries '1,2' and '1,3',  $\ln \gamma_2$  versus  $x_2$  with curves for the binaries '2,1' and '2,3' and  $\ln \gamma_3$  versus  $x_3$  with curves for the binaries '3,1' and '3,2'."

For ternary compositions, Colburn and Schoenborn (3) obtained activity coefficients by interpolating between the binary curves on a liquid volume fraction basis. The activity coefficient evaluated in this manner assumes that the two binary solutions, containing the same mole fraction of the third component, behave ideally when mixed in the ratios necessary to give the desired ternary mixture. Such an assumption is valid if the two solvents are identical or quite similar.

It was found in this work, that neither of the above methods gave good agreement for calculated activities of the components in the coexisting liquid phases unless the correction term was applied. This is not surprising for a system forming two liquid phases with three components. The system in this study is highly non-ideal, but not so non-ideal as to form three liquid phases.

There is some theoretical basis for this type of a correction factor. In deriving ternary equations for the Margules, van Laar, and Scatchard equations, Wohl (19) has shown that this type of correction term appears. For example in a two-suffix symmetrical system

$$\ln \gamma_1 = A_{12}x_2^2 + A_{13}x_3^2 + x_2x_3(A_{12} + A_{13} - A_{23}) \quad (7-10)$$

where:

$$\lim \ln \gamma(x_1 \rightarrow 0, x_2 \rightarrow 1) = \lim \ln \gamma_2(x_2 \rightarrow 0, x_1 \rightarrow 1) = A_{12}$$

The first two terms of this equation represent the logarithms of the activity coefficients of component 1 in each of the binaries (also evaluated at  $x_1$  ternary =  $x_1$  of the binary). This is valid only where  $A_{12} = A_{21}$ ,  $A_{13} = A_{31}$  and where  $A_{12} \approx A_{13}$  and where molecular size of the components is approximately equal. In Equation (7-9), the coefficient,  $c_1$ , for the  $(x_2x_3)$  term is expressed only as an arbitrary constant although its magnitude undoubtedly depends on the relationship of the activity coefficients of the components at infinite dilution.

Calculation of  $[x_j/(1 - x_i)] \ln \gamma_{ij}$  in the solution of Equation (7-9) for  $\ln \gamma_i$  in the ternary liquid-liquid system involves using the activity coefficients of the binaries. The acetic acid binary activity coefficients were derived on an associated acetic acid basis so the ternary mol fractions must be put on a similar basis. This requires knowing the molecular weight of the associated acetic acid relative to the unassociated molecular weight. These calculations were done in the manner illustrated below for the liquid-liquid point  $I_w$ , the first equilibrium tie-line of Table XL.

The ratio of apparent, or associated, molecular weight of acetic acid to 60.05 is given in Column 5 of Table XL. These ratios were found via Equation (3-16) through (3-20) which relate partial pressures of the monomer, dimer, and tetramer to get the total vapor pressure of acetic acid.

Compositions of the ternary liquid phase are given on an acetic acid molecular weight of 60.05 basis in Columns 1-3 of Table XL. The measured pressures at the experimental temperature of 70° are given in Column 4. For the calculations of mol fractions on an associated basis, the values of  $x_a(\epsilon_0)$ ,  $x_d(\epsilon_0)$ , and  $x_w(\epsilon_0)$  are assumed to represent the number of mols of each substance on a 60.05 mol weight basis, i.e.,  $N_a(\epsilon_0) = 0.0964$ ,  $N_d(\epsilon_0) = 0.0406$  and  $N_w(\epsilon_0) = 0.8629$ .

Calculation of associated mol fraction:

		$\frac{N_i(a)}{}$	$\frac{x_i(a)}{}$
Acetic Acid:	$0.0964/1.895$	$= 0.0509$	$0.0534$
Diethylketone:	same as $N_d(\epsilon_0)$	$= 0.0406$	$0.0425$
Water:	same as $N_w(\epsilon_0)$	$= 0.8629$	$0.9041$
	$\Sigma$	$0.9544$	$1.000$

The values of  $\Sigma N_i(a)$  are given in Column 6 and values of  $x_i(a)$  are listed in Column 7, 8, and 9 of Table XL.

The next step is to find the uncorrected values of the activity coefficients of the three components of the ternary, these uncorrected activity coefficients being the sum of the first and second right-hand numbers of Equation (7-9), i.e.,

$$\ln \gamma'_a(a) = \frac{x_d(a)}{x_d(a) + x_w(a)} \ln \gamma_{ad}(a) + \frac{x_w(a)}{x_d(a) + x_w(a)} \ln \gamma_{aw}(a) \quad (7-11)$$

$$\ln \gamma'_d(a) = \frac{x_a(a)}{x_a(a) + x_w(a)} \ln \gamma_{da}(a) + \frac{x_w(a)}{x_a(a) + x_w(a)} \ln \gamma_{dw}(a) \quad (7-12)$$

$$\ln \gamma'_w(a) = \frac{x_a(a)}{x_a(a) + x_d(a)} \ln \gamma_{wa}(a) + \frac{x_d(a)}{x_a(a) + x_d(a)} \ln \gamma_{wd}(a) \quad (7-13)$$



The application of these equations for the uncorrected activity coefficients is illustrated by the following sample calculation for acetic acid in the  $I_w$  liquid phase. The value of the acetic acid in water activity coefficient is found from Figure 43 at

$$x_w = \frac{0.9041}{0.9041 + 0.0534} = 0.943$$

giving

$$\ln \gamma_{aw}(a) = 0.1700.$$

For acetic acid in diethylketone, Figure 42 is used at

$$x_d = \frac{0.0425}{0.0425 + 0.0534} = 0.443$$

giving

$$\ln \gamma_{ad}(a) = -0.005.$$

Substituting into Equation (7-11) gives

$$\begin{aligned} \ln \gamma'_a(a) &= (0.955)(0.1700) + (0.045)(-0.005) \\ &= 0.1622. \end{aligned}$$

Similar calculations were made for the other components, using Equation (7-9).

Interaction corrections are made next by the following

$$\ln \gamma_a(a) = \ln \gamma'_a(a) + C_a(x_d(a)x_w(a)) \quad (7-14)$$

$$\ln \gamma_d(a) = \ln \gamma'_d(a) + C_d(x_a(a)x_w(a)) \quad (7-15)$$

$$\ln \gamma_w(a) = \ln \gamma'_w(a) + C_w(x_a(a)x_d(a)). \quad (7-16)$$

The interaction coefficients were found empirically by using the requirement that  $a = \gamma_{ii}$  must be the same for the coexisting equilibrium liquid phases. The values found are

$$C_a = -3.20$$

$$C_d = 2.4$$

$$C_w = 4.3$$

Equation (7-14) is applied to the above calculation as follows, to get the corrected activity coefficient for acetic acid in the ternary system

$$\begin{aligned}\ln \gamma_a(a) &= 0.1622 - 3.2(0.0425)(0.9041) \\ &= 0.0392 \\ \gamma_a(a) &= 1.040.\end{aligned}$$

Values of activity coefficients, computed in this way for each component of the ternary at the liquid-liquid equilibrium states, are given in Column 10, 11, and 12 of Table XL. Values of the activity coefficients  $\gamma_{dw}$  and  $\gamma_{wd}$  were obtained from Equations (7-6) and (7-7) for the solution of Equations (7-14)-(7-16).

Activity is the product of the activity coefficient and the mol fraction. For the sample calculation

$$a_a(a) = (1.040)(0.0534) = 0.0555.$$

Values of activities are given in Columns 13, 14, and 15 of Table XL.

Partial pressures of each component of the ternary are the product of the vapor pressure of the pure component and the activity. For the sample calculation point

$$p_a(a) = (P_a)(a_a(a)) = (138.2)(0.0555) = 7.65 \text{ mm. Hg.}$$

Columns 16, 17, and 18 of Table XL give the partial pressure values found in this way. The sum of these partial pressures, which is given

in Column 19, may be compared with the experimentally found system pressures in Column 4. Agreement is very good, as can be seen.

Activities for the ternary system were also calculated by application of the interaction "correction factor" to the Colburn interpolation method. Again Equation (7-9) was used:

$$\ln \gamma_1 = \frac{x_2}{x_2 + x_3} \ln \gamma_{12} + \frac{x_3}{x_2 + x_3} \ln \gamma_{13} + C_1 x_2 x_3.$$

In this case, however,  $\ln \gamma_{12}$  and  $\ln \gamma_{13}$  were evaluated at  $x_1$  of the ternary.

The interaction constants for use with the Colburn interpolation method are

$$C_a = -3.0$$

$$C_d = 0.0$$

$$C_w = 2.4.$$

The results listed in page 3 of Table XL, show satisfactory agreement of component activities in the coexisting phases, and were more easily obtained than those on page 2 of the same table.

The Colburn method is more satisfactory from another standpoint. Consider a ternary system wherein  $x_1 = x_2 = x_3 = 0.333$ . In evaluating  $\ln \gamma_1$  the system is evaluated at  $x_1 = .333$ . If  $x_2$  is the same component as  $x_3$ , then the system is really a binary for which  $x_1$  should be evaluated at  $x_1 = .333$ . The curves  $\ln \gamma_1$  versus  $x_1$  are identical for both binary systems 1-2 and 1-3, and no interaction correction term for  $x_2 x_3$  will be required. This is illustrated in Figure 47.

## CHAPTER VIII

### CONCLUSIONS AND RECOMMENDATIONS

This investigation has been concerned with (a) a study of liquid solution theory, (b) the experimental determinations of isothermal vapor-liquid equilibria for the binary systems diethylketone-water, water-acetic acid, and diethylketone-acetic acid at 50, 60, and 70° C, (c) derivation of binary constants for the van Laar and Cline Black equations, (d) ternary liquid-liquid determinations for these isotherms, and (e) a study of the applicability of the Black equation to accurately predict activity coefficients in ternary mixtures containing associating components from the binary constants so derived.

#### Conclusions

The major conclusions from this study may be summarized as follows:

1. Activity coefficients in systems of limited miscibility can be accurately obtained from the vapor pressure and composition of the heteroazeotrope through the range of compositions where immiscibility exists.
2. The van Laar and the Black equations do not adequately express the binary data for these systems.
3. All the binaries studied exhibit a negative excess volume of mixing, and a positive deviation from ideality, indicating a tendency to clustering of like molecules.

4. Application of the correction for dimer and tetramer formation in pure acetic acid vapor appears to be acceptable for the vapor mixture of acetic acid-diethylketone at 50, 60, and 70° C, and for the vapor mixtures of acetic acid and water at 50 and 60° C, but is not acceptable at higher temperatures.
5. The van Laar equation is completely inadequate for expressing the ternary system in terms of binary systems.
6. The Black equation gives a much better representation of activities than the van Laar, but still is not adequate for expressing the ternary relationships.
7. An apparent molecular weight for acetic acid is used without regard to distribution of monomer, dimer, or other polymeric forms. It is assumed that the molecular weight for acetic acid is the same in both gas and liquid phases. This gives results which are qualitatively more consistent with the observed negative excess volume for both of the acetic acid binary systems.
8. A new combining equation is presented which can utilize binary data available either in graphical form or as equations. Activities for the components in the two liquid phases of the ternary system were calculated by means of this equation and compared well.
9. Application of an interaction "correction factor" gives comparable results using Colburn's interpolation method.

## Recommendations

1. In order to eliminate the uncertainties regarding the behavior of acetic acid mixtures in the vapor phase, isothermal pressure-volume determinations should be made on known mixtures of acetic acid and argon or helium and acetic acid and water.
2. The acetic acid-water system should be studied at 25° C to determine if a "group" interaction method may be used to reconcile the endothermic heat of mixing with the negative excess volume of mixing for the liquids.

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## APPENDIX A

### DEVELOPMENT OF THE BLACK MODIFICATION OF THE VAN LAAR EQUATION

# DEVELOPMENT OF THE BLACK MODIFICATION OF THE VAN LAAR EQUATION

## Basis of Black Equations

Non-ideal behavior in solutions may be attributed to association between like molecules and interassociation of unlike molecules. In the derivation of his equations, Black considers the combined effect of these two factors.

The excess free energy  $F^E$  per mole defined by Scatchard (16) as the excess above the ideal value per mole. The partial excess free energy is related to activity coefficient as follows:

$$\ln \gamma_1 = \bar{F}_1^E / RT. \quad (A-1)$$

If  $Q$  is defined as

$$Q = F^E / 2.3 RT \quad (A-2)$$

then

$$\bar{Q}_1 = \log \gamma_1. \quad (A-3)$$

The partial quantity  $\bar{Q}_1$  is related thermodynamically to  $Q$ .

$$\bar{Q}_1 = Q + \partial Q / \partial x_1 - \sum_j x_j \partial Q / \partial x_j \quad (A-4)$$

Black suggests that

$$Q = Q_v + Q_a \quad (A-5)$$

where  $Q_a$  is an additive function to the van Laar function  $Q_v$ , which accounts for the combined association and interassociation effects.

For component  $i$  at infinite dilution in liquid  $j$ , the common logarithm of the activity coefficient is denoted by  $A_{ij}$ , the contribution of the empirical term by  $c_{ij}$ , and the contribution of the van Laar-type term, also at infinite dilution, by

$$a_{ij}^2 = A_{ij} - c_{ij} \quad (A-6)$$

The subscripts of  $c$  are interchangeable, as

$$c_{ij} = c_{ji} \quad (A-7)$$

The above paragraph is the basis by which  $a_{ij}$  and  $c_{ij}$  constants are determined from the activity coefficient-composition relations of the binary systems, as described in Chapter I.

The ratio  $a_{ij}^2/a_{ji}^2$  is defined as  $R_{ij}$ . Defining a molecular interaction coefficient,  $h_{ij}$ , by

$$h_{ij}^2 = a_{ij}^2/q_i \quad (A-8)$$

where  $q_i$  is some unspecified molecular property;

$$h_{ij}^2 = h_{ji}^2 \quad (A-9)$$

Since

$$q = \sum_i x_i q_i \quad (A-10)$$

then

$$a_{ij}^2/a_{ji}^2 = q_i/q_j = R_{ij} \quad (A-11)$$

which leads to the ternary relationship

$$R_{13} = R_{12}R_{23} \quad (A-12)$$

## Multi-Component Systems

A multi-component system can be classified by grouping all members of a homologous series in one class. There may be  $n$  classes of components, and each class may consist of  $1 - m$  components.

Let  $R$  and  $M$  distinguish any two class variables, while  $r$  and  $m$  are variables denoting components within classes  $R$  and  $M$ , respectively.  $Q_e$  of Equation (A-5) is empirically defined

$$Q_e = 0.5 \sum_{\substack{R, M \\ R \neq M}} [(X_R - X_M)^2 \sum_{r, m} c_{r, m} x_r x_m]. \quad (A-13)$$

Since  $Q_v$  and  $Q_e$  are homogeneous functions of  $x$  of the first and fourth order respectively, from Equations (A-4) and (A-5)

$$\log \gamma_i = \partial Q_v / \partial x_i + \partial Q_e / \partial x_i - 3Q_e. \quad (A-14)$$

$Q_v$  is represented by the van Laar-type relation

$$Q_v = 0.5 \sum_{i, j} h_{ij}^2 z_i z_j = 0.5 \sum_{i, j} a_{ij}^2 R_{j2} x_i x_j / \sum_j R_{j2}. \quad (A-15)$$

Performing the operations indicated in Equation (A-14)

$$\log \gamma_i = q_i [\sum_j h_{ij}^2 z_j^2 + 0.5 \sum_j z_j z_j (h_{ij}^2 + h_{ik}^2 - h_{jk}^2)] + E_{s_i} \quad (A-16)$$

where

$$\begin{aligned} E_{s_i} = & \sum_R [(X_s - X_R)^2 (\sum_r c_{ir} x_r)] + \\ & \sum_R [(X_s - X_R) \{2 - 3(X_s - X_R)\} \times \\ & (\sum_{s, r} c_{s, r} x_s x_r)] - 3/2 \sum_{\substack{R, M \\ R \neq M}} [(X_R - X_M)^2 \times \\ & (\sum_{r, m} c_{r, m} x_r x_m)]. \end{aligned} \quad (A-17)$$

The designation  $RM$  indicates the  $R$  and  $M$  assume every value except  $S$ , and  $jk \neq$  indicates that  $j$  and  $k$  assume every value except  $j = k$ .

By designating

$$h_{ij}^2 = (h_i - h_j)^2 \quad (A-18)$$

$$h_{ij} = h_i - h_j.$$

Thus,  $h_{13} = h_{23}$  and Equation (A-16) is simplified to

$$\log \gamma_i = q_i \left[ \sum_j h_{ij} z_j \right] + E_{s_i} \quad (A-19)$$

$$= \left[ \sum_j a_{ij} R_{j2} x_j / \sum_k x_k R_{k2} \right]^2 + E_{s_i}. \quad (A-20)$$

The expansion of the first portion of this equation should provide no difficulty. In order to properly expand the  $E_{s_i}$  term, it must be remembered that  $r$  and  $m$  refer only to components within the classes  $R$  and  $M$ , and that  $R$  and  $M$  assume every value except  $S$ .

Another form of the correction term given by Black (2) is:

$$\begin{aligned} E_{s_i} = & \sum_R [(X_S - X_R)^2 (\sum_r c_{ir} x_r)] + \\ & 2 \sum_R (X_S - X_R) (\sum_{s,r} c_{sr} x_s x_r)] - \\ & 3/2 \sum_{RM} [(X_R - X_M)^2 (\sum_{rm} c_{rm} x_r x_m)] . \end{aligned} \quad (A-21)$$

In this form,  $R$  and  $M$  assume every value including  $S$ .

For a ternary system with each component in a different class,  $X_s$  and  $X_R$  equal  $x_s$  and  $x_r$ . The correction term  $E_1$  is expressed

$$\begin{aligned} E_1 = & [(x_1 - x_2)^2 c_{12} x_2 + (x_1 - x_3)^2 c_{13} x_3] + \\ & 2[(x_1 - x_2) c_{12} x_1 x_2 + (x_1 - x_3) c_{13} x_1 x_3] - \end{aligned}$$

$$3[(x_1 - x_2)^2 c_{12} x_1 x_2 + (x_1 - x_3)^2 c_{13} x_1 x_3 + (x_2 - x_3)^2 c_{23} x_2 x_3]. \quad (\text{A-22})$$

When determining correction terms of the other components, the subscripts are rotated  $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ .

## APPENDIX B

### DETERMINATION OF EXCESS VOLUME FROM REFRACTIVE INDEX MEASUREMENTS

## DETERMINATION OF EXCESS VOLUME FROM REFRACTIVE INDEX MEASUREMENTS

Analysis of components are often made by comparing the refractive index of the solution with previously determined values obtained on mixtures of known composition.

By the application of the well-known principle of molar refraction, refractive index measurements will yield information from which excess volumes may be determined.

### Basis of the Determination

Molar refraction is an additive, and partly constitutive property of a substance. Lorenz and Lorentz have shown on the basis of electromagnetic theory of light that the specific refraction  $R_s$  should be constant, independent of temperature for any given substance. The molar refraction is obtained by multiplying  $R_s$  by the molecular weight of the substance.

$$R_M = R_s M = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} \quad (\text{B-1})$$

where  $M$  is the molecular weight of the substance, and  $d$  is the density measured at the same temperature as the refractive index.



## Derivation of the Equation

The molar volumes of the pure components are expressed as  $M_i/d_i = V_i$  where  $M_i$  is the molecular weight in grams per mole, and  $d_i$  is in grams per cc.  $V_i$  has units of cc. per mole. For an ideal mixture, the molar volume of an intermediate composition would be

$$V_M^I = \frac{\sum_i n_i V_i}{\sum_i n_i} \quad (B-2)$$

For two components

$$V_M^I = \frac{n_1 V_1 + n_2 V_2}{n_1 + n_2} \quad (B-3)$$

$$= x_1 V_1 + x_2 V_2 \quad (B-4)$$

Since this is a linear relation,

$$V_M^I = V_1 + x_2 (V_2 - V_1) \quad (B-5)$$

$$= x_1 [V_1 - V_2] + V_2 \quad (B-6)$$

The molecular weight of the mixture is

$$M_m = x_1 M_1 + x_2 M_2 \quad (B-7)$$

The molar refraction of the mixture is

$$R_m = x_1 R_1 + x_2 R_2 \quad (B-8)$$

Substituting Equation (B-7) into (B-1) for  $M$ ,

$$R_m = \frac{n^2 - 1}{n^2 + 2} \frac{x_1 M_1 + x_2 M_2}{d} \quad (B-9)$$

Combining (B-8) and (B-9) yields

$$x_1 R_1 + x_2 R_2 = \frac{n^2 - 1}{n^2 + 2} \frac{x_1 M_1 + x_2 M_2}{d} \quad (B-10)$$

Since the molar volume of the mixture

$$V_m = \frac{x_1 M_1 + x_2 M_2}{d} \quad (B-11)$$

$$V_m = (x_1 R_1 + x_2 R_2) \frac{n^2 + 2}{n^2 - 1} \quad (B-12)$$

$$= [x_1 (R_1 - R_2) + R_2] \frac{n^2 + 2}{n^2 - 1} \quad (B-13)$$

Excess volume is the actual molar volume minus the ideal molar volume.

$$V_m^E = [x_1 (R_1 - R_2) + R_2] \frac{n^2 + 2}{n^2 - 1}$$

$$[x_1 (V_1 - V_2) + V_2] \quad (B-14)$$

Molar refraction is independent of temperature and volume; however, less error is likely to be incurred in determining excess volume of mixtures if the molar refractions of the pure components are determined at the system temperature.

## APPENDIX C

### TABLES

TABLE I  
VAPOR PRESSURE VERSUS TEMPERATURE  
SYSTEM: DIETHYLKETONE

T° C	Pressure mm. Hg.
101.70*	760.0*
101.17	743.2
95.88	631.2
92.72	570.0
<u>88.91*</u>	<u>507.5*</u>
88.79	502.2
85.85	455.4
81.87	397.6
80.00	372.4
<u>80.02</u>	<u>372.7</u>
80.03	372.7
77.19	337.4
75.04*	315.5*
74.16	303.5
<u>71.44</u>	<u>274.7</u>
68.59	246.2
63.68	203.3
60.88	183.0
60.76	181.4
<u>60.29</u>	<u>178.1</u>
59.16	169.7
57.11	156.7
55.45	145.8
55.37	146.1
<u>54.45</u>	<u>140.1</u>
54.34	139.4
51.73	125.8
51.24*	123.76*
50.05	117.0

\*From Reference (5)

TABLE II  
VAPOR PRESSURE VERSUS TEMPERATURE  
SYSTEM: WATER-DIETHYLKETONE  
(TWO LIQUID-PHASE REGION)

T ° C	Pressure mm. Hg.
76.45	598.5
76.49	596.7
76.09	590.4
74.50	554.0
<u>74.30</u>	<u>548.0</u>
71.30	487.4
71.13	485.1
69.98	465.5
68.21	430.2
<u>67.86</u>	<u>426.2</u>
65.45	386.2
65.45	386.2
62.21	336.2
61.94	332.7
<u>59.95</u>	<u>303.8</u>
58.84	290.7
58.38	284.2
55.97	256.1
54.80	243.1
<u>53.23</u>	<u>224.8</u>
51.24	205.3

TABLE III  
REFRACTIVE INDEX VERSUS COMPOSITION  
SYSTEM: DIETHYLKETONE-WATER

$n_d^{30}$	Wt. % DEK
1.33196	0.00
1.33284	0.81
1.33361	1.60
1.33436	2.38
1.33509	3.14
1.33583	3.90
1.33655	4.64
1.33668*	4.78

\*Saturation value - weight percent determined by extrapolation.

TABLE IV  
DETERMINATION OF HETEROAZEOTROPE COMPOSITIONS  
SYSTEM: WATER-DIETHYLKETONE

Temp.	Sample No.	Volume of Equil Phase, mls.*	
		H <sub>2</sub> O Layer	DEK Layer
50°	1	1.14	9.06
	2	0.81	6.44
	3	1.17	8.89
60°	1	1.26	9.34
	2	1.26	9.31
70°	1	1.37	9.63
	2	1.26	9.04
	3	1.25	8.75
	4	1.34	9.30
	5	1.30	9.20

\*The distillate sample was allowed to reach equilibrium in a constant temperature bath at 30° C. The volumes of the layers were then measured.

The water layer contains 4.78 wt. % diethylketone with a specific gravity of 0.9901. The diethylketone layer contains 98.17 wt. % diethylketone with a specific gravity of 0.8108.

The average of the runs gives the following compositions for the heteroazeotropes:

Temp.	$\frac{Y_W}{Y_D}$	$\frac{Y_D}{Y_W}$	P mm. Hg.
50°	0.445	0.555	195.0
60°	0.459	0.541	304.8
70°	0.470	0.530	462.5

TABLE V

VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
DIETHYLKETONE-WATER AT 50° C

Wt. % Diethylketone			Pressure mm. Hg.	
Liquid		Vapor	Initial	Final
Initial	Final			
0.00				92.5
*	0.10	1.62		93.0
2.70	1.57	81.35	176.0	147.6
4.03	2.70	85.65	198.7	176.0
4.03**		85.65		198.7
96.43**		85.65		198.7
		84.80	197.3	185.7
		87.40	185.7	176.1
		87.58	176.1	162.5
		92.06	162.5	136.5
		96.95	136.5	125.6
100.00		100.00		117.0

\*Run to equilibrium on Scatchard still.

\*\*Solubility limit.



TABLE VI

VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
DIETHYLKETONE-WATER AT 60° C

Wt. % Diethylketone			Pressure mm. Hg.	
Liquid		Vapor	Initial	Final
Initial	Final			
0.0				149.4
		14.79	152.7	150.5
		23.7	186.7	164.1
		28.8	220.4	213.4
1.43	1.02	67.8	237.0	223.0
2.10	1.43	79.10	262.3	232.0
	2.10	81.55	299.5	262.3
4.20**		84.80		304.8
96.32**		84.80		304.8
		84.7	294.7	294.9
		86.14	294.9	265.3
		88.90	265.3	260.0
		94.06	260.0	208.0
		97.44	208.0	191.9
100.00				176.6

\*\*Solubility limit.

TABLE VII

VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
DIETHYLKETONE-WATER AT 70° C

Wt. % Diethylketone			Pressure mm. Hg.	
Liquid		Vapor	Initial	Final
Initial	Final			
0				233.7
*	0.005	0.09		234.5
0.45	0.10	7.3	369.6	241.8
0.82	0.45	19.6	309.8	269.6
1.05	0.82	53.9	313.2	309.8
1.51	1.05	71.4	358.1	313.2
2.45	1.51	81.8	388.7	358.1
4.54**		84.36		462.5
95.80**		84.36		462.5
96.10	96.37	85.08	453.7	441.4
96.37	96.54	87.88	441.4	435.6
96.54	96.73	87.53	435.6	427.9
96.73	96.90	86.92	427.9	418.5
96.90	97.17	87.95	428.1	420.7
97.17	97.73	88.12	420.7	400.5
97.73	97.87	92.45	400.5	396.8
97.87	98.41	90.75	396.8	393.2
98.41	98.60	91.95	381.2	355.6
98.60	98.96	95.89	337.3	320.6
98.96	99.13	95.88	320.6	309.5
99.13	99.25	97.30	309.1	299.5
100.00				260.3

\*Run to equilibrium on Scatchard still.

\*\*Solubility limit.

TABLE VIII  
 SPECIFIC GRAVITY AND REFRACTIVE INDEX VERSUS COMPOSITION  
 SYSTEM: DIETHYLKETONE-ACETIC ACID

Wt. % HAC	$n_d^{30}$	50° C	60° C	70° C
0.000	1.38758	0.7875	0.7779	0.7684
6.144	1.38717	0.7998	0.7901	0.7803
11.308	1.38656	0.8109	0.8022	0.7921
20.425	1.38528	0.8271	0.8172	0.8086
29.980	1.38376	0.8464	0.8368	0.8274
39.111	1.38213	0.8661	0.8557	0.8470
46.100	1.38069	0.8804	0.8700	0.8608
56.233	1.37863	0.9041	0.8938	0.8842
65.782	1.37656	0.9260	0.9188	0.9059
76.301	1.37408	0.9519	0.9414	0.9307
86.423	1.37187	0.9781	0.9672	0.9570
100.00	1.36839	1.0155	1.0050	0.9940

TABLE IX  
VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
DIETHYLKETONE-ACETIC ACID AT 50° C

Liquid		Vapor		Pressure mm. Hg.
DEK	HAC	DEK	HAC	
100.00	0.00	100.00	0.00	117.0
97.46	2.54	99.25	0.75	115.6
92.36	7.64	96.93	3.07	112.3
86.18	13.82	93.73	6.27	106.3
<u>78.57</u>	<u>21.43</u>	<u>88.49</u>	<u>11.51</u>	<u>100.5</u>
66.04	33.96	79.62	20.38	94.1
57.36	42.64	72.69	27.31	89.7
51.85	48.15	66.89	33.11	85.8
43.95	56.05	58.87	41.13	81.6
<u>32.03</u>	<u>67.97</u>	<u>46.11</u>	<u>53.89</u>	<u>74.1</u>
28.76	71.24	40.71	59.29	72.0
22.32	77.68	32.39	67.61	70.8
16.43	83.57	25.38	74.62	66.7
10.10	89.90	15.63	84.37	65.0
3.93	96.09	6.15	93.85	62.4
0.00*	100.00	0.00	100.00	57.6

\*Extrapolated value.

TABLE X

VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
DIETHYLKETONE-ACETIC ACID AT 60° C

Weight %				
Liquid		Vapor		Pressure mm. Hg.
DEK	HAC	DEK	HAC	
100.00	0.00	100.00	0.00	176.6
97.60	2.40	99.21	0.79	176.9
93.37	6.63	97.51	2.49	170.7
87.51	12.39	94.30	5.70	162.9
81.68	18.32	90.86	9.14	151.8
<u>66.55</u>	<u>33.45</u>	<u>79.06</u>	<u>20.94</u>	<u>142.2</u>
62.67	37.33	74.98	25.02	140.1
54.93	45.07	69.55	30.45	134.1
46.68	53.32	61.59	38.41	127.3
33.55	66.45	47.16	52.84	116.7
<u>31.33</u>	<u>68.67</u>	<u>43.20</u>	<u>56.80</u>	<u>115.1</u>
23.64	76.36	34.14	65.86	109.6
18.02	81.98	25.81	74.19	104.4
10.75	89.25	16.16	83.84	99.3
4.22	95.78	7.25	92.75	95.3
0.00*	100.00	0.00	100.00	91.4

\*Extrapolated value.

TABLE XI  
 VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
 DIETHYLKETONE-ACETIC ACID AT 70° C

Liquid		Vapor		Pressure mm. Hg.
DEK	HAC	DEK	HAC	
100.00	0.00	100.00	0.00	260.3
97.45	2.55	99.08	0.92	259.5
93.62	6.38	97.44	2.56	245.7
90.04	9.96	95.44	4.56	245.2
<u>88.23</u>	<u>11.77</u>	<u>94.39</u>	<u>5.61</u>	<u>242.1</u>
81.96	18.04	90.41	9.59	232.2
68.76	31.24	81.25	18.75	216.6
64.69	35.31	78.25	21.75	211.3
56.29	43.71	70.95	29.05	203.5
<u>49.92</u>	<u>50.08</u>	<u>65.49</u>	<u>34.51</u>	<u>194.2</u>
38.24	61.76	51.10	48.90	178.1
32.34	67.66	45.02	54.98	173.8
25.22	74.78	35.35	64.65	166.9
18.95	81.05	27.07	72.93	160.1
<u>12.44</u>	<u>87.56</u>	<u>19.92</u>	<u>80.08</u>	<u>152.9</u>
4.44	95.56	6.87	93.17	144.6
0.00*	100.00	0.00	100.00	138.2

\*Extrapolated value.

TABLE XII  
VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
WATER-ACETIC ACID AT 50° C

Liquid		Vapor		Pressure mm. Hg.
Water	HAC	Water	HAC	
0.00*	100.00	0.00	100.00	57.6
0.31	99.69	0.21	99.79	58.0
1.06	98.94	1.82	98.18	59.8
2.66	97.34	4.52	95.48	65.0
<u>4.03</u>	<u>95.97</u>	<u>7.03</u>	<u>92.97</u>	<u>69.0</u>
7.40	92.60	11.05	88.95	72.6
11.44	88.56	16.31	83.69	75.8
12.94	87.06	19.89	80.11	78.0
15.56	84.44	20.70	79.30	77.3
<u>20.99</u>	<u>79.01</u>	<u>27.34</u>	<u>72.66</u>	<u>79.8</u>
27.48	72.52	33.89	66.11	83.8
37.64	62.36	45.02	54.98	85.9
54.80	45.20	60.71	39.29	87.5
55.42	44.58	64.08	35.82	87.9
75.36	24.64	81.68	18.32	90.7
100.00	0.00	100.00	0.00	92.5

\*Extrapolated value.

TABLE XIII  
VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
WATER-ACETIC ACID AT 60° C

Liquid		Vapor		Pressure mm. Hg.
Water	HAC	Water	HAC	
0.00*	100.00	0.00	100.00	91.4
0.18	99.82	0.04	99.96	91.8
1.50	98.50	1.91	98.09	94.2
3.03	96.97	4.77	95.23	102.9
<u>4.71</u>	<u>95.29</u>	<u>7.76</u>	<u>92.24</u>	<u>109.3</u>
7.85	92.15	12.29	87.71	115.4
11.47	88.53	16.12	83.88	119.5
15.91	84.09	22.05	77.95	125.0
21.71	78.29	28.68	71.32	128.7
<u>28.90</u>	<u>71.10</u>	<u>37.64</u>	<u>62.36</u>	<u>132.8</u>
38.66	61.34	47.74	52.26	137.4
56.76	43.24	63.22	36.78	142.5
75.48	24.52	80.66	19.34	145.6
100.00	0.00	100.00	0.00	149.4

\*Extrapolated value.



TABLE XIV  
VAPOR-LIQUID EQUILIBRIA DATA SYSTEM:  
WATER-ACETIC ACID AT 70° C

Liquid		Vapor		Pressure mm. Hg.
Water	HAC	Water	HAC	
0.00*	100.00	0.00	100.00	138.2
0.73	99.27	0.14	99.86	139.6
1.23	98.77	1.85	98.15	143.1
3.09	96.91	5.15	94.85	158.9
<u>5.14</u>	<u>94.86</u>	<u>8.61</u>	<u>91.39</u>	<u>168.3</u>
8.92	91.08	13.68	86.32	179.1
13.13	86.87	19.29	80.71	187.4
16.93	83.07	23.85	76.15	193.1
22.33	77.67	30.98	69.02	200.3
<u>30.47</u>	<u>69.53</u>	<u>39.32</u>	<u>60.68</u>	<u>208.5</u>
41.70	58.30	51.12	48.88	215.9
56.81	43.19	65.28	34.72	223.6
75.85	24.15	81.41	18.59	228.6
100.00	0.00	100.00	0.00	233.7

\*Extrapolated value.

TABLE XV

EXCESS VOLUME VERSUS COMPOSITION SYSTEM:  
WATER-ACETIC ACID AT 25° C

Mole Fr.	$\bar{V}$ Ideal	d Ideal	d Actual	$\frac{\bar{V}}{\text{Actual}}$ cc.	$V^E$ cc.
0.0	18.052	.9971	.9971	18.052	-0.000
.10	21.994	1.0094	1.0317	21.519	-0.475
.20	25.936	1.0179	1.0502	25.138	-0.798
.30	29.877	1.0241	1.0592	28.887	-0.990
.40	33.819	1.0290	1.0635	32.722	-1.097
.50	37.762	1.0327	1.0646	36.630	-1.132
.60	41.705	1.0358	1.0641	40.596	-1.109
.70	45.646	1.0384	1.0617	44.644	-1.002
.80	49.667	1.0406	1.0577	48.864	-0.803
.90	53.529	1.0424	1.0518	53.051	-0.478
1.00	57.471	1.0440	1.0440	57.471	-0.0

TABLE XVI

TERNARY SOLUBILITY DATA SYSTEM: WATER-ACETIC  
ACID-DIETHYLKETONE AT 50° C

Water	HAC	Water	HAC	DEK
95.97	0	0.9913	0.0000	0.0087
84.87	8.83	0.9553	0.0298	0.0148
76.02	15.82	0.9217	0.0576	0.0207
67.72	21.14	0.8865	0.0830	0.0305
59.75	24.87	0.8483	0.1060	0.0456
52.01	27.06	0.8062	0.1259	0.0679
50.55	27.36	0.7975	0.1295	0.0729
48.96	27.51	0.7879	0.1329	0.0792
47.44	27.65	0.7783	0.1361	0.0855
45.95	27.73	0.7687	0.1392	0.0921
44.51	27.79	0.7590	0.1422	0.0988
43.12	27.82	0.7493	0.1450	0.1056
41.77	27.82	0.7395	0.1478	0.1126
37.50	27.71	0.7063	0.1566	0.1371
35.33	27.62	0.6878	0.1613	0.1509
33.04	27.43	0.6669	0.1661	0.1669
30.58	27.15	0.6428	0.1713	0.1859
28.16	26.69	0.6173	0.1756	0.2071
25.78	26.01	0.5903	0.1787	0.2310
23.35	25.14	0.5603	0.1810	0.2586
21.03	24.00	0.5293	0.1813	0.2895
18.79	22.60	0.4966	0.1793	0.3241
16.66	20.87	0.4629	0.1740	0.3631
14.46	18.85	0.4244	0.1660	0.4095
12.61	16.49	0.3892	0.1528	0.4579
10.78	13.93	0.3510	0.1361	0.5129
10.66	13.63	0.3485	0.1337	0.5178
10.17	12.09	0.3383	0.1207	0.5410
8.77	10.48	0.3044	0.1092	0.5864
7.06	8.86	0.2585	0.0974	0.6441
4.90	4.76	0.1942	0.0566	0.7492
3.57	0.00	0.1503	0.0000	0.8497

TABLE XVII  
 TERNARY SOLUBILITY DATA SYSTEM: WATER-ACETIC  
 ACID-DIETHYLKETONE AT 60° C

Weight %		Mole Fraction		
Water	HAC	Water	HAC	DEK
95.80	0.00	0.9909	0.0000	0.0091
91.52	3.81	0.9774	0.0122	0.0104
87.44	7.28	0.9637	0.0241	0.0122
83.46	10.42	0.9498	0.0359	0.0146
79.76	13.28	0.9361	0.0468	0.0171
76.17	15.85	0.9222	0.0576	0.0202
72.75	18.16	0.9082	0.0680	0.0237
69.46	20.23	0.8941	0.0781	0.0278
66.11	22.01	0.8791	0.0878	0.0331
62.87	23.55	0.8639	0.0971	0.0390
59.62	24.81	0.8478	0.1059	0.0463
56.33	25.78	0.8307	0.1141	0.0552
53.10	26.52	0.8129	0.1218	0.0653
49.85	27.06	0.7938	0.1293	0.0769
46.70	27.21	0.7742	0.1354	0.0905
43.71	27.28	0.7541	0.1412	0.1047
40.93	27.25	0.7340	0.1466	0.1194
38.44	27.19	0.7146	0.1517	0.1337
36.19	27.11	0.6959	0.1564	0.1476
34.12	26.98	0.6776	0.1608	0.1616
44.76	27.26	0.7613	0.1391	0.0996
43.21	27.26	0.7506	0.1421	0.1073
41.57	27.22	0.7388	0.1452	0.1160
39.71	27.17	0.7247	0.1488	0.1265
37.70	27.09	0.7087	0.1528	0.1385
35.38	27.01	0.6889	0.1578	0.1532
33.03	26.79	0.6676	0.1625	0.1699
30.57	26.45	0.6436	0.1671	0.1893
28.06	25.95	0.6171	0.1713	0.2116
25.50	25.26	0.5878	0.1747	0.2375
22.99	24.32	0.5565	0.1767	0.2668
20.66	23.08	0.5249	0.1760	0.2991
18.36	21.57	0.4909	0.1731	0.3360
16.19	19.72	0.4558	0.1666	0.3775
14.08	17.54	0.4184	0.1564	0.4251
12.05	14.97	0.3788	0.1412	0.4800
9.83	12.03	0.3300	0.1212	0.5488
7.64	8.59	0.2754	0.0929	0.6317
5.91	4.59	0.2272	0.0530	0.7200
3.68	0.00	0.1544	0.0000	0.8456

TABLE XVIII

TERNARY SOLUBILITY DATA SYSTEM: WATER-ACETIC  
ACID-DIETHYLKETONE AT 70° C

Weight %		Mole Fraction		
Water	HAC	Water	HAC	DEK
95.46	0.00	0.9901	0.0000	0.0099
91.32	3.80	0.9769	0.0122	0.0109
87.13	7.25	0.9630	0.0240	0.0130
83.24	10.39	0.9492	0.0356	0.0152
79.58	13.24	0.9356	0.0467	0.0177
75.22	15.64	0.9193	0.0574	0.0234
72.58	18.12	0.9077	0.0680	0.0243
69.30	20.18	0.8935	0.0781	0.0284
65.95	21.95	0.8785	0.0877	0.0337
62.69	23.47	0.8632	0.0970	0.0399
59.28	24.64	0.8464	0.1056	0.0480
55.75	25.51	0.8281	0.1137	0.0582
52.21	26.06	0.8085	0.1211	0.0704
48.87	26.43	0.7886	0.1280	0.0834
45.63	26.57	0.7679	0.1342	0.0979
42.59	26.58	0.7470	0.1399	0.1131
39.94	26.58	0.7272	0.1452	0.1275
37.36	26.42	0.7067	0.1500	0.1433
35.08	26.27	0.6872	0.1544	0.1584
39.41	26.44	0.7233	0.1456	0.1311
37.14	26.37	0.7049	0.1502	0.1449
34.84	26.16	0.6852	0.1544	0.1604
32.28	25.90	0.6615	0.1593	0.1793
29.71	25.46	0.6250	0.1663	0.2087
27.18	24.79	0.6085	0.1665	0.2250
24.62	23.91	0.5784	0.1686	0.2530
22.07	22.77	0.5457	0.1689	0.2853
19.69	21.31	0.5124	0.1664	0.3212
17.38	19.54	0.4769	0.1609	0.3622
15.22	17.39	0.4407	0.1511	0.4082
13.13	14.86	0.4021	0.1366	0.4614
10.91	11.94	0.3561	0.1170	0.5269
8.82	8.53	0.3076	0.0893	0.6031
6.61	4.58	0.2488	0.0517	0.6994
4.39	0.00	0.1800	0.0000	0.8200

TABLE XIX  
EQUILIBRIUM SOLUBILITY DATA SYSTEM: WATER-ACETIC  
ACID-DIETHYLKETONE AT 50° C

Water-Rich Layer			DEK-Rich Layer			Tie- line*
Weight %			Weight %			
Water	HAC	DEK	Water	HAC	DEK	
52.50	27.03	20.47	27.83	26.67	45.50	
52.00	27.16	20.84	28.36	26.84	44.80	
66.50	21.87	11.63	16.63	20.97	62.40	I
66.50	21.85	11.65	16.57	21.03	62.40	
76.30	15.81	7.89	11.00	14.56	74.44	II
76.30	15.82	7.88	11.00	14.57	74.43	
80.80	12.65	6.55	8.72	11.28	80.00	III
81.50	12.22	6.28	8.64	11.14	80.20	
90.10	5.00	4.90	4.95	4.05	91.00	IV
90.00	5.10	4.90	4.91	3.99	91.10	

Mole Fraction			Mole Fraction		
Water	HAC	DEK	Water	HAC	DEK
0.8090	0.1250	0.0660	0.6136	0.1765	0.2099
0.8061	0.1263	0.0676	0.6194	0.1759	0.2047
0.8808	0.0870	0.0322	0.4622	0.1749	0.3629
0.8808	0.0868	0.0323	0.4602	0.1759	0.3639
0.9227	0.0574	0.0200	0.3555	0.1412	0.5033
0.9227	0.0574	0.0199	0.3555	0.1413	0.5032
0.9400	0.0442	0.0159	0.3023	0.1174	0.5803
0.9424	0.0424	0.0152	0.3004	0.1162	0.5833
0.9727	0.0162	0.0111	0.1951	0.0483	0.7566

\*Figure 44.

TABLE XX

EQUILIBRIUM SOLUBILITY DATA SYSTEM: WATER-ACETIC  
ACID-DIETHYLKETONE AT 60° C

Water-Rich Layer			DEK-Rich Layer			Tie- line*
Weight %			Weight %			
Water	HAC	DEK	Water	HAC	DEK	
65.30	22.26	12.44	18.21	21.29	60.50	I
64.50	22.68	12.82	15.84	19.36	64.80	
63.50	23.11	13.39	17.01	20.39	62.60	
75.50	16.31	8.19	11.91	15.09	73.00	II
75.40	16.35	8.25	11.52	14.68	73.80	
74.50	17.05	8.45	11.28	14.47	74.30	
80.20	13.04	6.76	9.45	11.55	79.00	III
80.20	12.99	6.81	9.13	11.07	79.80	
79.60	13.44	6.96	9.19	11.01	79.80	
90.20	5.18	4.62	5.62	4.18	90.20	IV
90.07	5.23	4.70	5.63	4.07	90.30	
89.84	5.36	4.80	5.63	4.09	90.28	

Mole Fraction			Mole Fraction		
Water	HAC	DEK	Water	HAC	DEK
0.8755	0.0896	0.0349	0.4888	0.1715	0.3397
0.8717	0.0920	0.0363	0.4499	0.1650	0.3851
0.8671	0.0947	0.0383	0.4696	0.1689	0.3615
0.9195	0.0596	0.0209	0.3756	0.1428	0.4816
0.9191	0.0598	0.0210	0.3673	0.1404	0.4923
0.9154	0.0629	0.0217	0.3619	0.1393	0.4987
0.9377	0.0458	0.0165	0.3209	0.1177	0.5613
0.9378	0.0456	0.0167	0.3132	0.1140	0.5728
0.9355	0.0474	0.0171	0.3148	0.1132	0.5720
0.9728	0.0168	0.0104	0.2183	0.0487	0.7330
0.9724	0.0169	0.0106	0.2187	0.0474	0.7338
0.9717	0.0174	0.0109	0.2187	0.0477	0.7336

\*Figure 45.

TABLE XXI  
EQUILIBRIUM SOLUBILITY DATA SYSTEM: WATER-ACETIC  
ACID-DIETHYLKETONE AT 70° C

Water-Rich Layer			DEK-Rich Layer			Tie- line*
Weight %			Weight %			
Water	HAC	DEK	Water	HAC	DEK	
62.60	23.31	14.09	18.15	20.15	61.8	I
62.04	23.66	14.30	18.67	20.53	60.8	
74.28	16.92	8.80	12.95	14.55	72.5	II
74.05	17.05	8.90	12.93	14.47	72.6	
79.38	13.32	7.30	10.44	11.06	78.5	III
79.16	13.44	7.40	10.39	11.01	78.6	
89.47	5.33	5.20	6.32	4.18	89.5	IV
89.44	5.36	5.20	6.21	4.09	89.7	

Mole Fraction			Mole Fraction		
Water	HAC	DEK	Water	HAC	DEK
0.8629	0.0964	0.0406	0.4889	0.1629	0.3483
0.8601	0.0984	0.0415	0.4972	0.1641	0.3388
0.9148	0.0625	0.0227	0.3987	0.1344	0.4669
0.9139	0.0631	0.0230	0.3983	0.1338	0.4679
0.9349	0.0471	0.0180	0.3459	0.1100	0.5441
0.9341	0.0476	0.0183	0.3447	0.1096	0.5456
0.9708	0.0174	0.0118	0.2403	0.0477	0.7120
0.9707	0.0174	0.0118	0.2370	0.0468	0.7161

\*Figure 46.



TABLE XXII

VAPOR PRESSURES FOR THE TERNARY SYSTEM SYSTEM:  
WATER-ACETIC ACID-DIETHYLKETONE

HAC	Weight Percent		Pressure Mm. Hg.		
	H <sub>2</sub> O	DEK	50°	60°	70°
6.1	47.6	46.3	188.9	299.8	464.1
11.5	44.8	43.6	184.0	294.7	451.1
16.3	42.4	41.3	174.8	282.3	438.4
20.6	40.2	39.1	174.3	281.6	433.2
24.5	38.2	37.2	170.2	273.7	427.1
28.5*	36.4	35.5	167.9	270.1	418.8

\*Single liquid-phase.

TABLE XXIII  
VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS  
SYSTEM: DIETHYLKETONE-WATER AT 50° C

$x_d$	$\gamma_d$	$\gamma_w$	$\ln \gamma_d$	$\ln \gamma_w$	$(\ln \gamma_d)^{1/2}$	$(\ln \gamma_w)^{1/2}$	$(\ln \gamma_d / \gamma_w)$
0.00871	100.6	1.00	4.61	0.000	2.15	0.000	4.61
0.0500	17.96	1.02	2.89	0.0202	1.70	0.141	2.88
0.1	8.09	1.08	2.19	0.0770	1.48	0.277	2.11
0.2	4.49	1.21	1.50	0.191	1.23	0.437	1.31
0.3	3.00	1.39	1.10	0.329	1.05	0.574	0.77
0.4	2.24	1.62	0.806	0.482	0.898	0.695	0.324
0.5	1.80	1.94	0.588	0.663	0.767	0.766	-0.075
0.6	1.50	2.43	0.404	0.888	0.636	0.934	-0.484
0.7	1.28	3.24	0.247	1.175	0.497	1.085	-0.928
0.8	1.12	4.86	0.113	1.580	0.336	1.258	-1.47
0.850	1.06	6.47	0.058	1.865	0.241	1.365	-1.80
0.9*	1.04	8.30	0.039	2.115	0.099	1.452	-2.08
1.0*	1.00	17.0	0.000	2.83	0.000	1.684	-2.83

\*Values extrapolated from graph of  $\ln(\gamma_d/\gamma_w)$  vs.  $x_d$ .

TABLE XXIV  
VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS  
SYSTEM: DIETHYLKETONE-WATER AT 60° C

$x_d$	$\gamma_d$	$\gamma_w$	$\ln \gamma_d$	$\ln \gamma_w$	$(\ln \gamma_d)^{1/2}$	$(\ln \gamma_w)^{1/2}$	$(\ln \gamma_d / \gamma_w)$
0.00909	96.8	1.00	4.57	0.0	2.135	0.0	4.57
0.1	8.98	1.09	2.19	0.086	1.481	0.293	2.11
0.2	4.99	1.22	1.608	0.199	1.268	0.446	1.41
0.3	2.99	1.40	1.095	0.336	1.048	0.580	0.76
0.4	2.25	1.64	0.811	0.495	0.901	0.704	0.315
0.5	1.80	1.96	0.585	0.673	0.766	0.822	-0.087
0.6	1.49	2.45	0.399	0.895	0.632	0.946	-0.495
0.7	1.27	3.26	0.239	1.181	0.489	1.086	-0.963
0.8	1.12	4.90	0.1132	1.589	0.336	1.261	-1.474
0.8456	1.06	6.34	0.058	1.848	0.241	1.360	-1.790
0.9*	1.02	8.4	0.0198	2.128	0.141	1.458	-2.11
1.0*	1.0	15.4	0.000	2.735	0.000	1.653	-2.73

\*Values extrapolated from graph of  $\ln(\gamma_d/\gamma_w)$  vs  $x_d$ .

TABLE XXV  
VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS  
SYSTEM: DIETHYLKETONE-WATER AT 70° C

$x_d$	$\gamma_d$	$\gamma_w$	$\ln \gamma_d$	$\ln \gamma_w$	$(\ln \gamma_d)^{1/2}$	$(\ln \gamma_w)^{1/2}$	$(\ln \gamma_d / \gamma_w)$
0.00985	92.9	1.00	4.44	0.0000	2.106	0.00	4.57
0.050	18.3	1.03	2.91	0.0247	1.705	0.1563	2.88
0.1	9.14	1.07	2.21	0.0676	1.487	0.260	2.14
0.2	4.57	1.20	1.519	0.1822	1.232	0.427	1.334
0.3	3.05	1.37	1.114	0.3145	1.054	0.561	0.798
0.4	2.29	1.60	0.828	0.470	0.910	0.686	0.358
0.5	1.83	1.92	0.604	0.652	0.778	0.808	-0.048
0.6	1.52	2.41	0.418	0.878	0.647	0.938	-0.461
0.7	1.31	3.21	0.270	1.167	0.520	1.081	-0.899
0.8	1.14	4.81	0.131	1.570	0.362	1.252	-1.438
0.820	1.11	5.34	0.117	1.672	0.342	1.292	-1.555
0.9*	1.05	8.35	0.049	2.120	0.221	1.456	-2.07
1.0*	1.00	15.5	0.000	2.740	0.000	1.655	-2.74

\*Values extrapolated from graph of  $\ln (\gamma_d / \gamma_w)$  vs  $x_d$ .

TABLE XXVI

VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS  
SYSTEM: WATER-ACETIC ACID AT 50° C

Pressure mm. Hg.	$x_w$	$y_w$	$\gamma_a$	$\gamma_w$	$\ln (\gamma_w / \gamma_a)$	$(\ln \gamma_a)^{1/2}$	$(\ln \gamma_w)^{1/2}$
59.8	0.034	0.058	.998	1.846	+.615	.0480	.7830
65.0	0.083	0.136	1.017	1.829	+.587	.1296	.7771
69.0	0.123	0.201	1.026	1.861	+.595	.1610	.7882
72.6	0.210	0.293	1.061	1.561	+.386	.2432	.6675
75.8	0.301	0.394	1.090	1.436	+.276	.2934	.6013
78.0	0.331	0.453	1.070	1.490	+.328	.2660	.6313
77.3	0.380	0.465	1.134	1.310	+.145	.3542	.5200
79.8	0.470	0.556	1.182	1.244	+.052	.4089	.4676
83.8	0.558	0.631	1.288	1.199	-.072	.5031	.4257
85.9	0.668	0.732	1.411	1.132	-.220	.5868	.3520
87.5	0.802	0.837	1.735	1.047	-.505	.7426	.2147
87.9	0.806	0.856	1.643	1.062	-.436	.7045	.2447
90.7	0.911	0.937	2.150	1.027	-.739	.8750	.1620

TABLE XXVII  
VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS  
SYSTEM: WATER-ACETIC ACID AT 60° C

Pressure mm. Hg.	$x_w$	$y_w$	$\gamma_a$	$\gamma_w$	$\ln (\gamma_w / \gamma_a)$	$(\ln \gamma_a)^{1/2}$	$(\ln \gamma_w)^{1/2}$
94.2	0.048	0.061	1.005	1.328	+ .278	.0737	.5324
102.9	0.094	0.143	1.021	1.642	+ .475	.1450	.7041
109.3	0.141	0.219	1.029	1.687	+ .495	.1685	.7233
115.4	0.221	0.318	1.047	1.550	+ .392	.2141	.6621
119.5	0.302	0.390	1.092	1.380	+ .234	.2972	.5675
125.0	0.387	0.485	1.127	1.323	+ .161	.3456	.5294
128.7	0.480	0.573	1.187	1.234	— .034	.4136	.4582
132.8	0.575	0.668	1.247	1.180	— .055	.4698	.4069
137.4	0.677	0.753	1.381	1.122	— .208	.5681	.3220
142.5	0.814	0.851	1.763	1.049	— .520	.7532	.2184
145.6	0.911	0.933	2.229	1.016	— .786	.8954	.1265

TABLE XXVIII  
VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS  
SYSTEM: WATER-ACETIC ACID AT 70° C

Pressure mm. Hg.	$x_w$	$y_w$	$\gamma_a$	$\gamma_w$	$\ln (\gamma_w / \gamma_a)$	$(\ln \gamma_a)^{1/2}$	$(\ln \gamma_w)^{1/2}$
143.1	0.040	0.059	1.001	1.502	+.406	.0363	.6379
158.9	0.096	0.153	1.025	1.677	+.492	.1587	.7190
168.3	0.153	0.239	1.032	1.639	+.463	.1777	.7031
179.1	0.246	0.346	1.064	1.464	+.319	.2495	.6176
187.4	0.335	0.443	1.096	1.362	+.217	.3023	.5557
193.1	0.404	0.511	1.134	1.289	+.128	.3544	.5037
200.3	0.489	0.599	1.175	1.237	+.052	.4013	.4613
208.5	0.594	0.683	1.289	1.161	-.104	.5037	.3866
215.9	0.704	0.777	1.437	1.103	-.265	.6023	.3132
223.6	0.814	0.862	1.707	1.058	-.478	.7312	.2378
228.6	0.913	0.936	2.220	1.019	-.779	.8929	.1372

TABLE XXIX  
VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS SYSTEM:  
DIETHYLKETONE-ACETIC ACID AT 50° C

Pressure mm. Hg.	$x_d$	$y_d$	$\gamma_a$	$\gamma_d$	$\ln (\gamma_d / \gamma_a)$	$(\ln \gamma_a)^{1/2}$	$(\ln \gamma_d)^{1/2}$
115.6	0.964	0.989	1.809	1.016	-.578	.7700	.1242
112.3	0.894	0.957	1.628	1.039	-.499	.6979	.1955
106.3	0.813	0.912	1.403	1.049	-.291	.5816	.2179
100.5	0.719	0.843	1.303	1.066	-.200	.5142	.2532
94.1	0.576	0.732	1.164	1.139	-.022	.3899	.3608
89.7	0.484	0.650	1.107	1.195	+.076	.3187	.4218
85.8	0.429	0.585	1.093	1.201	+.094	.2979	.4277
81.6	0.354	0.500	1.068	1.240	+.150	.2568	.4642
74.1	0.247	0.374	1.024	1.297	+.236	.1553	.5097
72.0	0.220	0.324	1.031	1.269	+.207	.1765	.4877
70.8	0.167	0.250	1.039	1.335	+.250	.1969	.5374
66.7	0.121	0.192	1.015	1.387	+.312	.1211	.5718
65.0	0.073	0.114	1.028	1.418	+.322	.1663	.5912
62.4	0.028	0.044	1.030	1.441	+.336	.1710	.6044



TABLE XXX  
VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS SYSTEM:  
DIETHYLKETONE-ACETIC ACID AT 60° C

Pressure mm. Hg.	$x_d$	$y_d$	$\gamma_a$	$\gamma_d$	$\ln(\gamma_d/\gamma_a)$	$(\ln \gamma_a)^{1/2}$	$(\ln \gamma_d)^{1/2}$
176.9	0.966	0.989	1.837	1.027	-.582	.7800	.1628
170.7	0.908	0.965	1.543	1.035	-.398	.6583	.1869
162.9	0.831	0.920	1.415	1.045	-.303	.5891	.2104
156.8	0.757	0.874	1.287	1.069	-.186	.5025	.2583
142.2	0.581	0.725	1.163	1.118	-.040	.3889	.3336
140.1	0.539	0.676	1.165	1.134	-.020	.3918	.3543
143.1	0.460	0.614	1.089	1.194	+.092	.2920	.4206
127.3	0.379	0.528	1.057	1.235	+.155	.2369	.4596
116.7	0.260	0.384	1.026	1.301	+.237	.1613	.5132
115.1	0.241	0.347	1.038	1.280	+.210	.1936	.4972
109.6	0.178	0.266	1.022	1.338	+.269	.1483	.5393
104.4	0.133	0.195	1.018	1.313	+.254	.1344	.5216
99.3	0.078	0.119	1.007	1.374	+.310	.0886	.5634
95.3	0.030	0.052	1.002	1.574	+.452	.0461	.6736

TABLE XXXI

VAPOR-LIQUID EQUILIBRIA AND ACTIVITY COEFFICIENTS SYSTEM:  
DIETHYLKETONE-ACETIC ACID AT 70° C

Pressure mm. Hg.	$x_d$	$y_d$	$\gamma_a$	$\gamma_d$	$\ln(\gamma_d/\gamma_a)$	$(\ln \gamma_a)^{1/4}$	$(\ln \gamma_d)^{1/2}$
259.5	0.964	0.987	1.821	1.022	-.577	.7741	.1488
247.7	0.911	0.964	1.543	1.006	-.422	.6542	.0771
245.2	0.863	0.936	1.481	1.038	-.355	.6269	.1937
242.1	0.839	0.921	1.435	1.043	-.319	.6012	.2051
232.2	0.760	0.868	1.317	1.062	-.216	.5250	.2447
216.6	0.606	0.751	1.159	1.131	-.024	.3836	.3506
211.3	0.561	0.715	1.122	1.152	+.027	.3391	.3763
203.5	0.473	0.630	1.088	1.208	+.104	.2911	.4345
194.2	0.410	0.570	1.049	1.239	+.166	.2196	.4633
178.1	0.302	0.422	1.043	1.241	+.174	.2041	.4644
173.8	0.250	0.364	1.029	1.304	+.237	.1696	.5151
166.9	0.191	0.276	1.031	1.320	+.246	.1758	.5266
160.1	0.140	0.206	1.024	1.342	+.270	.1552	.5426
152.9	0.090	0.148	1.002	1.492	+.398	.0473	.6324
144.6	0.031	0.049	1.009	1.445	+.359	.0943	.6065

TABLE XXXII:

TERNARY ACTIVITY DATA FROM THE VAN LAAR EQUATION SYSTEM:  
WATER-ACETIC ACID-DIETHYLKETONE AT 50° C

$a_a$	$a_d$	$a_w$	P mm. Hg.	
			Calc.	Exp.
.13664*	.43450	.94850	146.45	169
.14642**	.76217	1.29038	216.98	
.13749*	.44215	.95008	147.54	169
.14696	.75793	1.27098	214.72	
.10606*	.23541	.93340	120.00	173
.12719	.80624	2.23865	308.75	
.10595*	.23572	.93346	120.03	173
.12802	.80566	2.25062	309.84	
.07395*	.14170	.94574	108.33	177
.09841	.80906	4.31568	499.57	
.07400*	.14156	.94572	108.31	177
.09849	.80903	4.31410	499.42	
.05815*	.10918	.95443	104.41	184
.08236	.81247	6.56944	707.54	
.05605*	.10356	.95576	103.76	184
.08161	.81273	6.68550	718.26	
.02209*	.06647	.97665	99.40	190
.03687	.84599	19.69843	1923.40	
.02254*	.06666	.97638	99.42	190
.03630	.84623	19.79859	1932.66	
	$A_{dw} = 4.65$		$A_{wd} = 2.82$	
	$A_{aw} = 0.62$		$A_{wa} = 0.39$	
	$A_{ad} = 1.09$		$A_{da} = 0.63$	

\*Water-rich phase.

\*\*DEK-rich phase.

TABLE XXXIII

TERNARY ACTIVITY DATA FROM THE VAN LAAR EQUATION SYSTEM:  
WATER-ACETIC ACID-DIETHYLKETONE AT 60° C

$a_a$	$a_d$	$a_w$	P mm. Hg.	
			Calc.	Exp.
.08504*	.24349	.93346	190.21	281
.09704**	.79735	1.84703	425.59	
.08683*	.25263	.93303	191.92	281
.09198	.80143	2.21995	481.55	
.08861*	.26555	.93279	194.33	281
.09484	.79960	2.01317	450.60	
.06061*	.14220	.94512	171.83	282
.07894	.80514	3.49179	671.00	
.06075*	.14338	.94500	172.03	282
.07788	.80532	3.68915	700.42	
.06364*	.14923	.94336	173.09	282
.07750	.80534	3.81685	719.46	
.04769*	.10830	.95376	165.96	295
.06606	.80924	5.38788	953.79	
.04747*	.10897	.95384	166.06	295
.06425	.81010	5.75850	1009.14	
.04923*	.11266	.95262	166.70	295
.06356	.81022	5.73064	1004.93	
.01820*	.05911	.97663	157.99	300
.03007	.83699	16.06838	2250.85	
.01837*	.06024	.97636	158.16	300
.02920	.83715	16.17192	2566.27	
.01883*	.06177	.97586	158.40	300
.02935	.83710	16.14705	2562.56	
	$A_{dw} = 4.56$		$A_{wd} = 2.74$	
	$A_{aw} = 1.08$		$A_{wa} = 0.42$	
	$A_{ad} = 0.63$		$A_{da} = 0.37$	

\*Water-rich phase.

\*\*DEK-rich phase.

TABLE XXXIV

TERNARY ACTIVITY DATA FROM THE VAN LAAR EQUATION SYSTEM:  
WATER-ACETIC ACID-DIETHYLKETONE AT 70° C

$a_a$	$a_d$	$a_w$	P mm. Hg.	
			Calc.	Exp.
.07953*	.25495	.81953	292.25	431
.08170**	.76118	1.61749	587.43	
.08089*	.25999	.91877	293.57	431
.08228	.75938	1.56504	574.79	
.05735*	.14372	.93800	264.54	438
.06896	.77715	2.63329	827.22	
.05779*	.14570	.93756	265.02	438
.06857	.77737	2.64573	830.13	
.04461*	.11128	.94920	256.96	451
.05908	.78634	3.88307	1120.32	
.04500*	.11308	.94875	257.37	451
.05900	.78651	3.91397	1127.58	
.01728*	.06693	.97443	247.53	465
.03061	.82270	10.68808	2716.18	
.01738*	.06698	.97434	247.54	465
.03032	.82401	10.97762	2784.15	
$A_{dw} = 4.34$		$A_{wd} = 2.74$		
$A_{aw} = 0.94$		$A_{wa} = 0.35$		
$A_{ad} = 0.56$		$A_{da} = 0.43$		

\*Water-rich phase.

\*\*DEK-rich phase.

TABLE XXXV

TERNARY ACTIVITY DATA FROM THE BLACK EQUATION (2) (A-20)  
 SYSTEM: WATER-ACETIC ACID-DIETHYLKETONE AT 50° C

$a_a$	$a_d$	$a_w$	P mm. Hg.	
			Calc.	Exp.
.17243*	.44299	.9915	154.19	169
.22018**	.43159	1.04450	159.80	
.17325*	.44166	1.00036	154.19	169
.21887	.42934	1.04559	159.56	
.14790*	.46704	.97429	153.29	173
.24160	.54778	.92727	163.78	
.14780*	.46781	.97430	153.38	173
.24272	.54862	.92411	163.66	
.11939*	.50175	.96903	155.22	177
.20983	.69514	.77105	164.74	
.11945*	.50112	.96902	155.15	177
.20993	.69505	.77101	164.74	
.10197*	.51891	.97006	156.32	184
.17816	.77055	.69260	164.49	
.09944*	.51507	.97039	155.76	184
.17661	.77336	.69001	164.48	
.04785*	.62436	.98010	166.47	190
.07827	.89454	.59616	164.32	
.04869*	.62104	.97992	166.11	190
.07721	.89509	.59679	164.38	
$A_{dw}^2 = 3.37$		$A_{wd}^2 = 1.59$	$C_{wd} = 1.24$	
$A_{aw}^2 = 0.87$		$A_{wa}^2 = 0.68$	$C_{aw} = 0.42$	
$A_{ad}^2 = 0.73$		$A_{da}^2 = 0.43$	$C_{ad} = 0.11$	

\*Water-rich phase.

\*\*DEK-rich phase.

TABLE XXXVI

TERNARY ACTIVITY DATA FROM THE BLACK EQUATION (2) (A-20)  
 SYSTEM: WATER-ACETIC ACID-DIETHYLKETONE AT 60° C

$a_a$	$a_d$	$a_w$	P mm. Hg.	
			Calc.	Exp.
.13394*	.30966	1.00823	217.54	281
.21823**	.50207	.94242	249.39	
.13572*	.30814	1.00984	217.67	281
.21642	.55277	.89202	250.65	
.13760*	.30849	1.01184	218.20	281
.21806	.52607	.91817	249.99	
.10860*	.33388	.99080	216.89	282
.19894	.66387	.78511	252.70	
.10877*	.33469	.99092	217.07	282
.19664	.67568	.77263	252.71	
.11187*	.32625	.99229	216.07	282
.19548	.68275	.76437	252.62	
.09238*	.35920	.98542	219.16	295
.17275	.74872	.71035	254.12	
.09302*	.36227	.98537	219.67	295
.16852	.75981	.70062	254.24	
.09524*	.35724	.98595	219.07	295
.16780	.75921	.70372	254.53	
.04597*	.48086	.98367	236.06	300
.08639	.87893	.63554	258.05	
.04634*	.48543	.98356	236.88	300
.08458	.87963	.63797	258.37	
.04729*	.48832	.98339	237.46	300
.08491	.87948	.63760	258.32	
$A_{dw}^2 = 3.53$		$A_{wd}^2 = 1.69$	$C_{wd} = 1.04$	
$A_{aw}^2 = 0.96$		$A_{wa}^2 = 0.60$	$C_{aw} = 0.30$	
$A_{ad}^2 = 0.89$		$A_{da}^2 = 0.31$	$C_{ad} = 0.18$	

\*Water-rich phase.

\*\*DEK-rich phase.

TABLE XXXVII

TERNARY ACTIVITY DATA FROM THE BLACK EQUATION (2) (A-20)  
 SYSTEM: WATER-ACETIC ACID-DIETHYLKETONE AT 70° C

$a_a$	$a_d$	$a_w$	P mm. Hg.	
			Calc.	Exp.
.15747*	.40309	.96813	352.94	431
.22766**	.53927	.92216	387.34	
.15914*	.39967	.96842	352.35	431
.22801	.53029	.93008	386.90	
.12624	.42007	.96498	352.31	438
.20229	.66049	.82237	392.07	
.12691*	.42040	.96495	352.48	438
.20160	.66157	.82226	392.23	
.10646*	.44418	.96711	356.34	451
.17210	.73775	.75911	393.22	
.10716*	.44559	.96699	356.78	451
.17162	.73913	.75762	393.17	
.05088*	.53268	.97867	374.40	465
.08119	.86902	.67032	394.08	
.05113*	.53178	.97861	374.19	465
.07974	.87119	.66753	393.79	
$A_{dw}^2 = 3.37$		$A_{wd}^2 = 1.69$	$C_{wd} = 1.06$	
$A_{aw}^2 = 0.94$		$A_{wa}^2 = 0.57$	$C_{aw} = 0.25$	
$A_{ad}^2 = 0.74$		$A_{da}^2 = 0.36$	$C_{ad} = 0.10$	

\*Water-rich phase.

\*\*DEK-rich phase.



TABLE XXXVIII

CALCULATION OF ACTIVITY COEFFICIENTS FOR THE DIETHYLKETONE-ACETIC ACID SYSTEM AT 70° C  
(Associated Molecular Weight Basis)

$x_{d(60)}$	$y_{d(60)}$	P mm. Hg.	$p_{la}^o$ mm. Hg.	$\frac{M_{a(\alpha)}}{M_{a(60)}}$	$x_{d(\alpha)}$	$y_{d(\alpha)}$	$\gamma_{a(\alpha)}$	$\gamma_{d(\alpha)}$
0.00	0.00	138.2	39.00	1.739				
0.031	0.049	144.6	39.96	1.739	0.053	0.083	1.012	0.869
0.090	0.148	152.9	41.22	1.752	0.148	0.234	0.995	0.927
0.140	0.206	160.1	42.35	1.761	0.226	0.317	1.022	0.863
0.191	0.276	166.9	43.38	1.762	0.294	0.402	1.021	0.875
0.250	0.346	173.8	44.38	1.770	0.369	0.484	1.028	0.875
0.302	0.422	178.1	45.00	1.778	0.436	0.565	0.994	0.887
0.410	0.570	194.2	47.23	1.791	0.555	0.704	0.934	0.946
0.473	0.630	203.5	48.45	1.796	0.617	0.754	0.946	0.956
0.561	0.715	211.3	49.50	1.801	0.697	0.819	0.913	0.952
0.606	0.751	216.6	50.20	1.805	0.736	0.845	0.921	0.955
0.760	0.868	323.2	52.13	1.815	0.851	0.922	0.880	0.966
0.839	0.921	242.1	53.31	1.822	0.904	0.956	0.804	0.983
0.863	0.936	245.2	53.72	1.822	0.921	0.963	0.831	0.985
0.911	0.964	245.7	53.74	1.824	0.949	0.979	0.731	0.973
0.964	0.987	259.5	55.40	1.835	0.979	0.993	0.626	1.010
1.000	1.000	260.3						

$$\gamma_{a(\alpha)} = \frac{p_{y_{a(\alpha)}}}{p_a^o x_{a(\alpha)}}$$

$$\gamma_{d(\alpha)} = \frac{p_{y_{d(\alpha)}}}{p_d^o x_{d(\alpha)}}$$

TABLE XXXIX

CALCULATION OF ACTIVITY COEFFICIENTS FOR THE WATER-ACETIC ACID SYSTEM AT 70° C  
(Associated Molecular Weight Basis)

$x_{w(60)}$	$y_{w(60)}$	P mm. Hg.	$p_{1a}^o$ mm. Hg.	$\frac{M_{a(\alpha)}}{M_{a(60)}}$	$x_{w(\alpha)}$	$y_{w(\alpha)}$	$\gamma_{a(\alpha)}$	$\gamma_{w(\alpha)}$
0.00	0.00	138.2	39.00	1.739				
0.040	0.059	143.1	39.72	1.745	0.068	0.099	1.001	0.892
0.096	0.153	158.9	42.12	1.760	0.158	0.242	1.034	1.040
0.153	0.239	168.3	43.58	1.766	0.242	0.357	1.032	1.062
0.246	0.346	179.1	45.11	1.778	0.367	0.485	1.053	1.013
0.335	0.443	187.4	46.30	1.783	0.473	0.579	1.081	0.981
0.404	0.511	193.1	47.08	1.790	0.548	0.652	1.075	0.983
0.489	0.599	200.3	48.00	1.794	0.632	0.728	1.071	0.989
0.594	0.683	208.5	49.11	1.800	0.724	0.795	1.120	0.981
0.704	0.777	215.9	50.10	1.804	0.810	0.862	1.133	0.969
0.814	0.862	223.6	51.08	1.810	0.888	0.919	1.168	0.989
0.913	0.936	228.6	51.73	1.813	0.950	0.964	1.190	0.993
1.000	1.000	233.7						

$$\gamma_{a(\alpha)} = \frac{Py_{a(\alpha)}}{p_a^o x_{a(\alpha)}}$$

$$\gamma_{w(\alpha)} = \frac{Py_{w(\alpha)}}{p_w^o x_{w(\alpha)}}$$

TABLE XL

CALCULATIONS FOR LIQUID-LIQUID EQUILIBRIUM TIE-LINES  
OF ACETIC ACID-DIETHYLKETONE-WATER AT 70° C

Column	1	2	3	4	5	6	7	8	9
Equil. Tie-Line	$x_a(60)$	$x_d(60)$	$x_w(60)$	$P_{\text{exp.}}$	$\frac{M_a(\alpha)}{M_a(60)}$	$\Sigma N_i(\alpha)$	$x_a(\alpha)$	$x_d(\alpha)$	$x_w(\alpha)$
I	0.0964	0.0406	0.8629	431	1.895	0.9544	0.0534	0.0425	0.9041
I <sub>d</sub> <sup>w</sup>	0.1629	0.3483	0.4889	431		0.9232	0.0930	0.3765	0.5305
II	0.0625	0.0227	0.9148	438	1.905	0.9703	0.0338	0.0234	0.9428
II <sub>d</sub> <sup>w</sup>	0.1344	0.4669	0.3987	438		0.9361	0.0755	0.499	0.426
III	0.0471	0.0180	0.9349	451	1.917	0.9774	0.0252	0.0184	0.9564
III <sub>d</sub> <sup>w</sup>	0.1100	0.5441	0.3459	451		0.9474	0.0606	0.5744	0.3650
IV	0.0174	0.0118	0.9708	465	1.925	0.9916	0.0091	0.0119	0.9790
IV <sub>d</sub> <sup>w</sup>	0.0477	0.7120	0.2403	465		0.9771	0.0254	0.7286	0.2460
V	0.00	0.00985	0.9901	462.5					
V <sub>d</sub> <sup>w</sup>	0.00	0.8200	0.1800	462.5					

Columns 1-3 represent the compositions of the coexisting phases when the molecular weight of acetic acid is taken as 60.05

Column 4 is the experimentally determined system pressure, mm. Hg.

Column 5 is the ratio of the associated molecular weight of acetic acid to 60.05.

Columns 7-9 represent the compositions of the coexisting phases adjusted to the associated molecular weight of acetic acid

TABLE XL (Continued)  
(Proposed Equation This Work)

Column	10	11	12	14	14	15	16	17	18	19
Equil. Tie-Line	$\gamma_a(\alpha)$	$\gamma_d(\alpha)$	$\gamma_w(\alpha)$	$a_a(\alpha)$	$a_d(\alpha)$	$a_w(\alpha)$	$p_a(\alpha)$	$p_d(\alpha)$	$p_w(\alpha)$	$p_{calc.}$
I	1.040	19.8	0.992	.0554	.841	.890	7.65	219	208	435
I <sub>d</sub> <sup>w</sup>	.564	2.25	1.680	.0509	.846	.891	7.04	220	208	435
II	1.113	36.7	0.980	.0376	.859	.922	5.19	224	215	444
II <sub>d</sub> <sup>w</sup>	.494	1.722	2.165	.0370	.858	.922	5.11	223	215	443
III	1.130	47.5	0.975	.0283	.874	.932	3.91	228	218	446
III <sub>d</sub> <sup>w</sup>	.480	1.521	2.560	.0291	.871	.933	4.01	227	218	445
IV	1.160	76.6	0.965	.0106	.911	.945	1.46	237	220	458
IV <sub>d</sub> <sup>w</sup>	.444	1.248	3.84	.0112	.909	.945	1.55	236	220	458
V <sub>w</sub>					.940	.930		237.5	225	462.5
					.940	.930		237.5	225	462.5

Columns 10-12, 13-15 are the activity coefficients and activities calculated with the correction term included.

Columns 16-18 represent the calculated partial pressures of the components, and the calculated total pressure of the system.

Column 19 can be compared with Column 4.

TABLE XL (Continued)  
(Colburn-Schoenborn (3) with Correction Term)

Column	10c	11c	12c	13c	14c	15c	16c	17c	18c	19c
Equil. Tie-Line	$\gamma_a(\alpha)$	$\gamma_d(\alpha)$	$\gamma_w(\alpha)$	$a_a(\alpha)$	$a_d(\alpha)$	$a_w(\alpha)$	$p_a(\alpha)$	$p_d(\alpha)$	$p_w(\alpha)$	$p_{calc.}$
I	1.028	18.4	1.000	.0548	.781	.909	7.56	203	212	423
I <sup>w</sup> <sub>d</sub>	.546	2.133	1.690	.0508	.804	.894	7.02	209	208	424
II	1.100	35.0	.984	.0372	.819	.928	5.14	213	217	435
II <sup>w</sup> <sub>d</sub>	.490	1.686	2.15	.0372	.840	.911	5.14	219	213	437
III	1.115	46.9	.983	.0282	.864	.941	3.90	225	220	449
III <sup>w</sup> <sub>d</sub>	.466	1.525	2.570	.0283	.874	.939	3.91	227	219	450
IV	1.159	76	.950	.0105	.904	.930	1.45	235	217	457
IV <sup>w</sup> <sub>d</sub>	.447	1.256	3.82	.0114	.914	.933	1.57	238	218	458

## APPENDIX C

### FIGURES

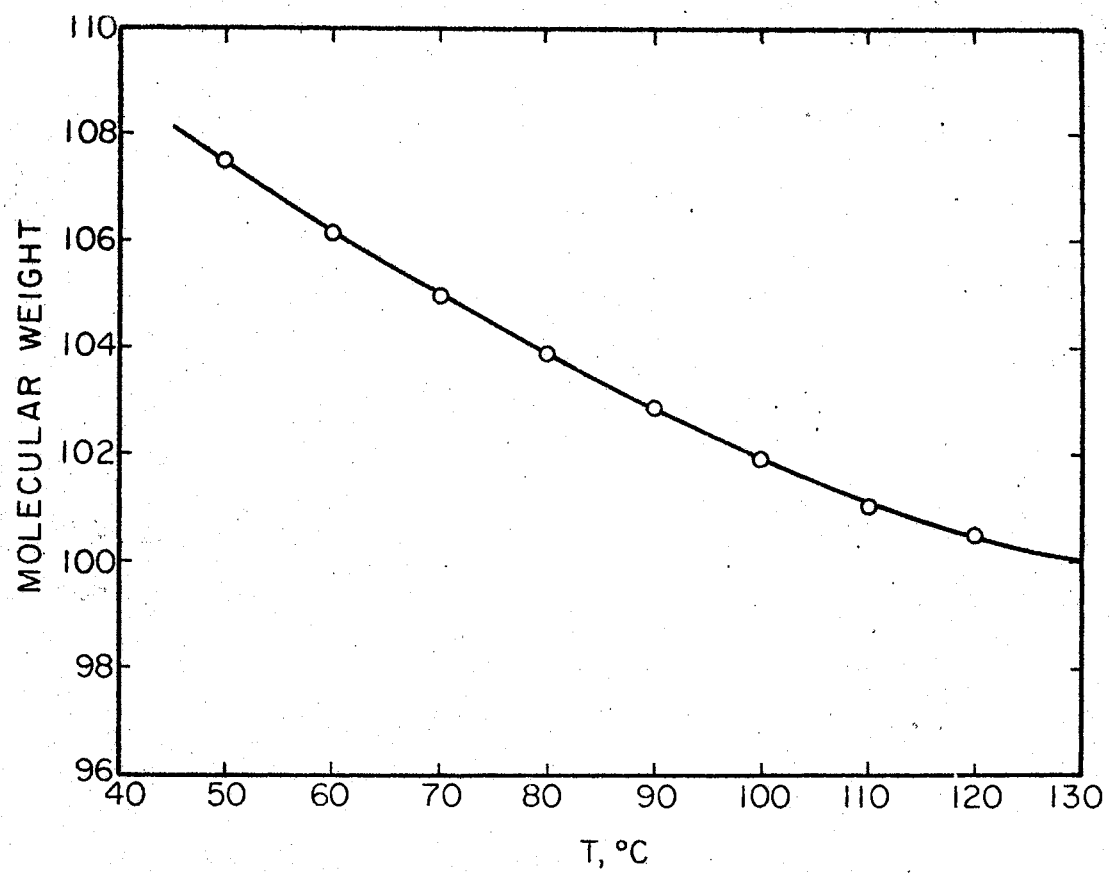


Figure 1. Molecular Weight of Acetic Acid at Saturation

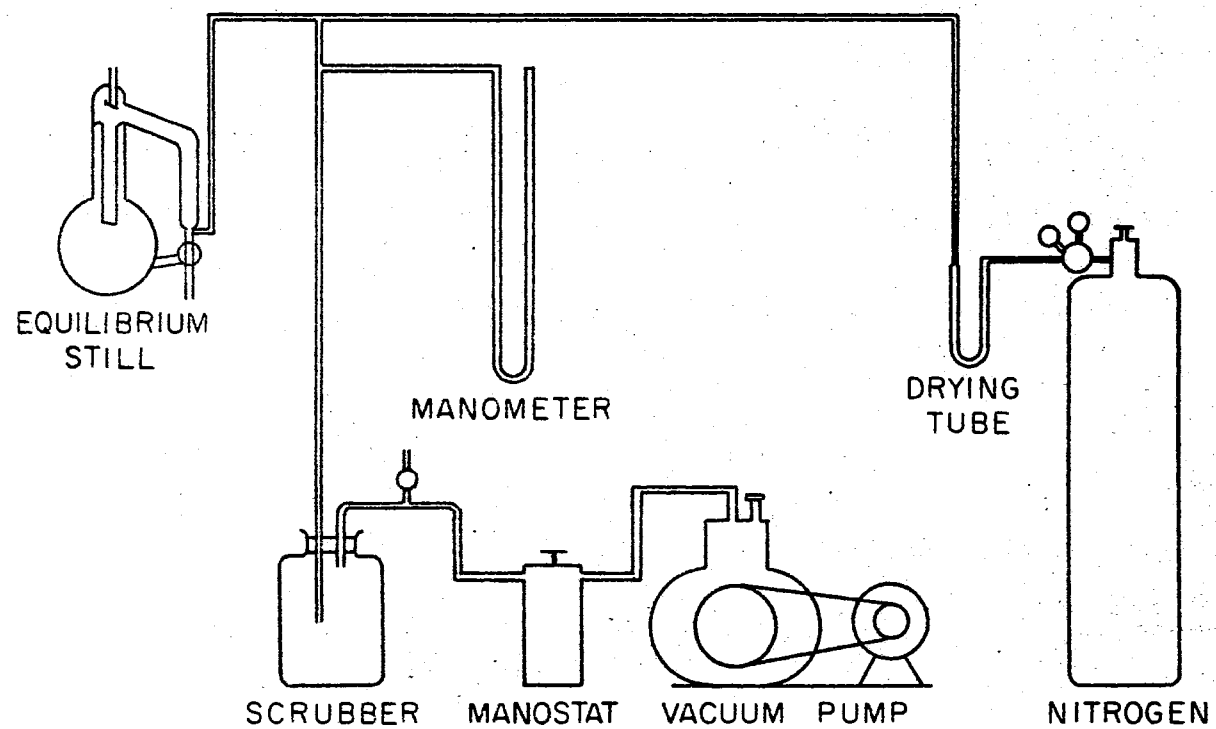


Figure 2. Experimental Apparatus for Vapor-Liquid Equilibrium Measurements



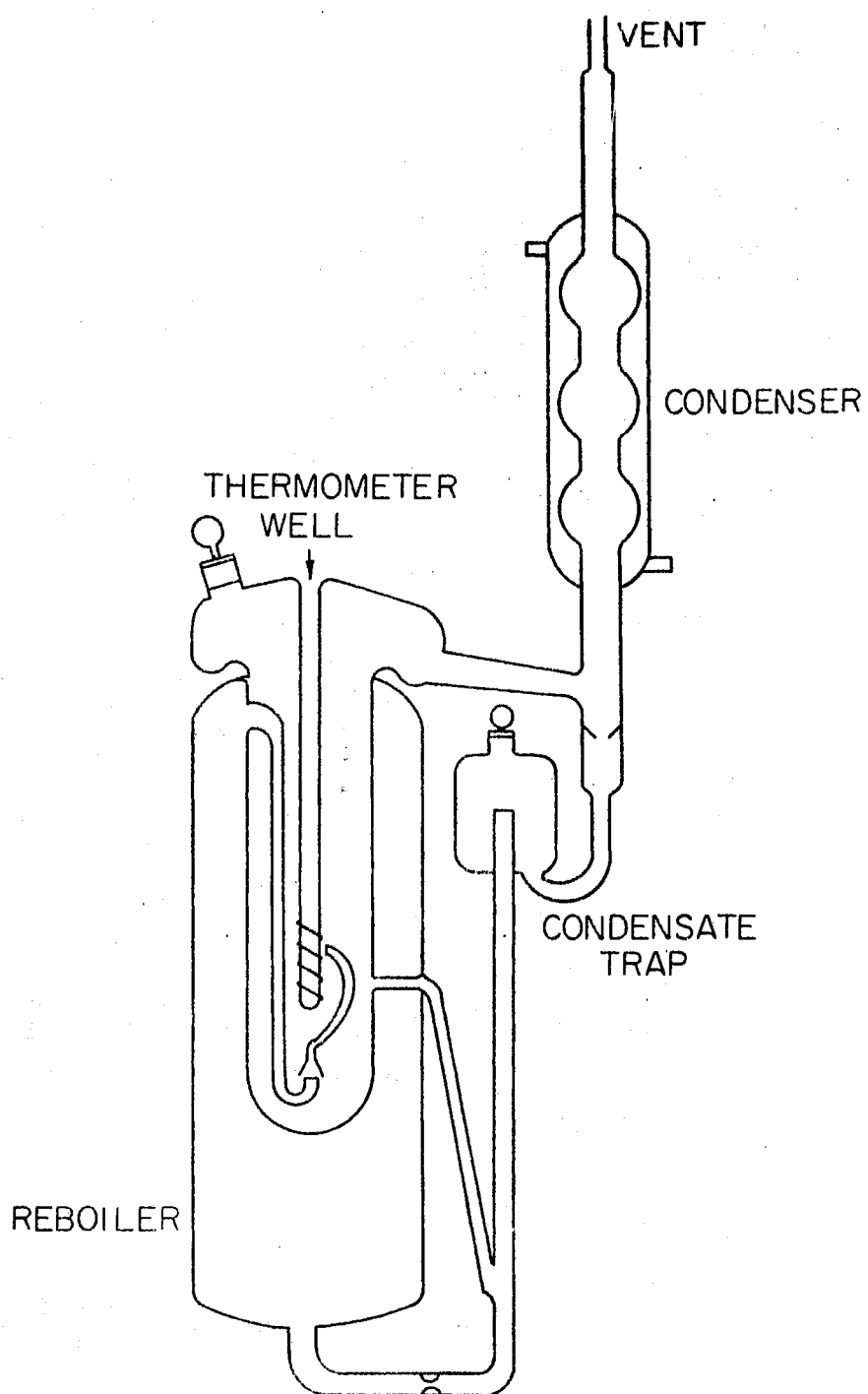


Figure 3. Modified Scatchard Equilibrium Still

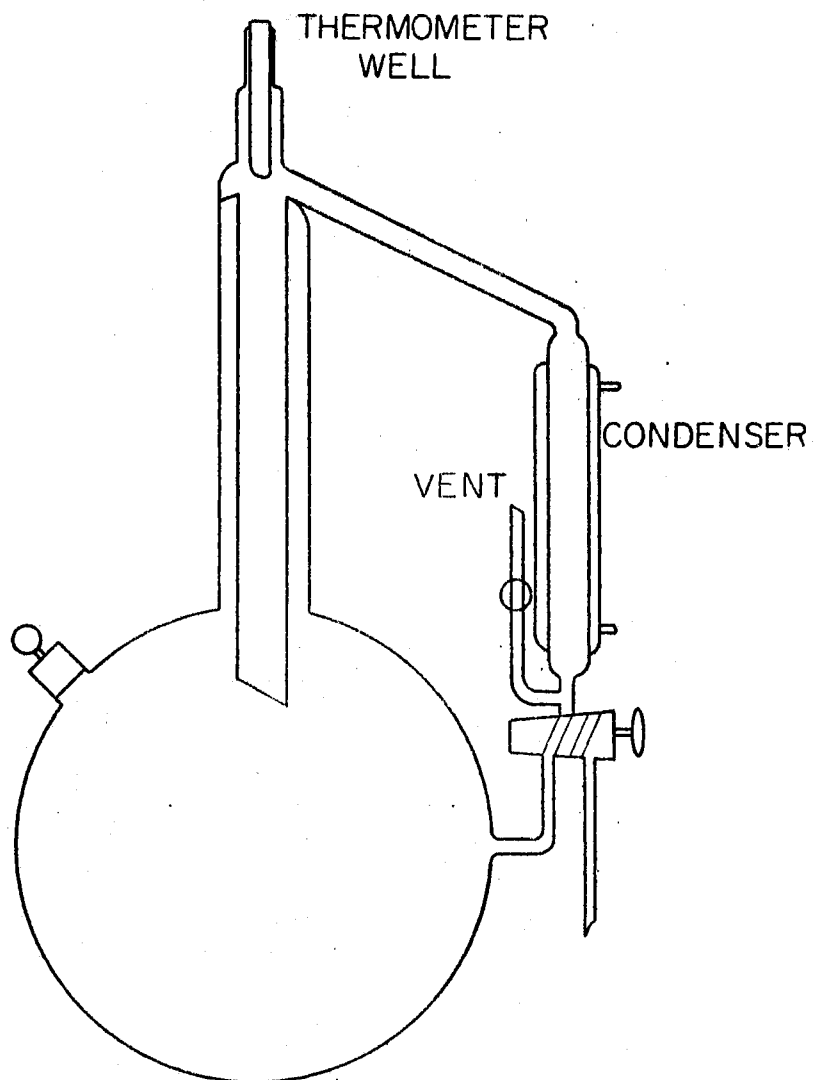


Figure 4. Hands and Norman Equilibrium Still

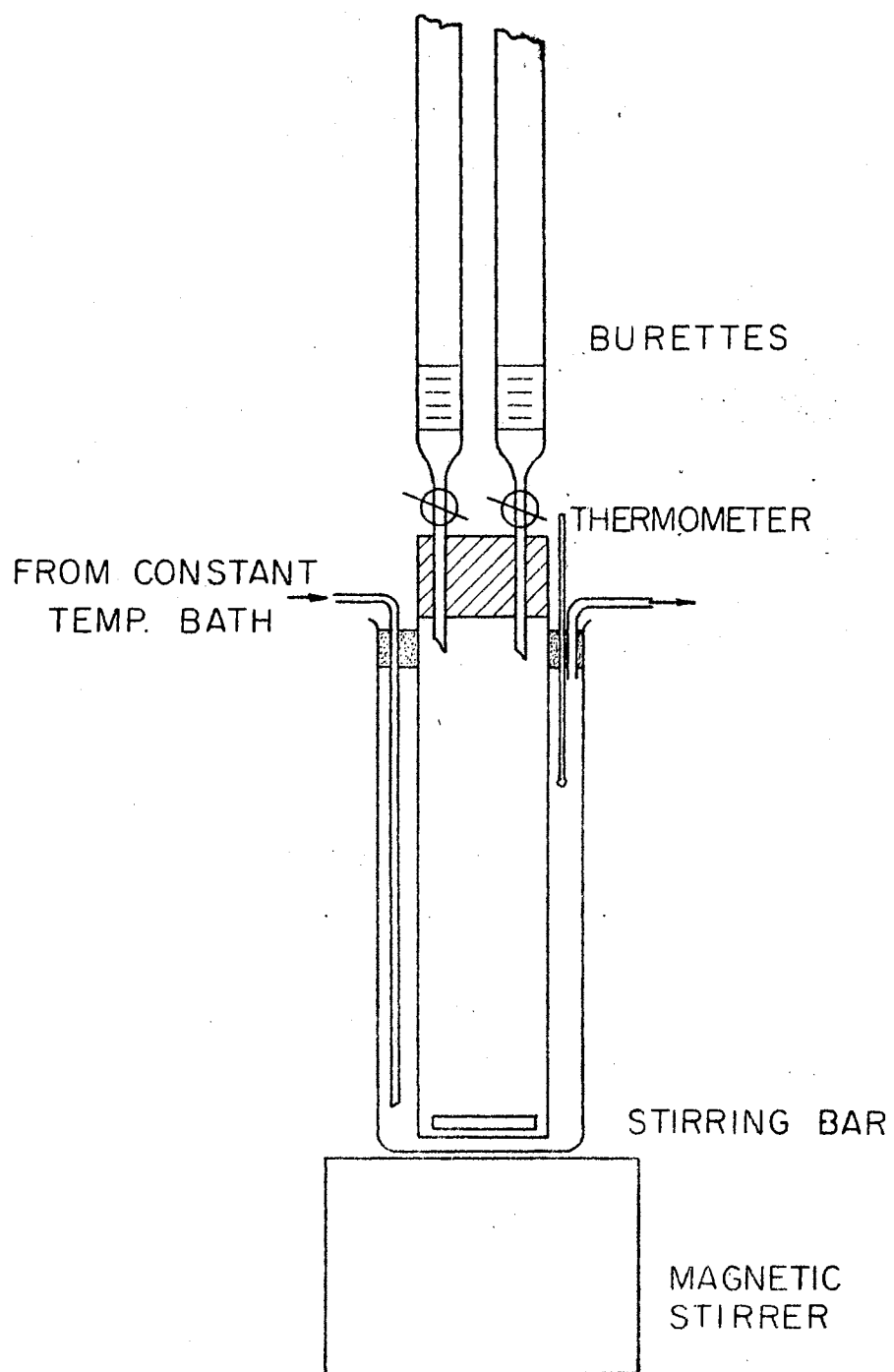


Figure 5. Cloud Point Titrator

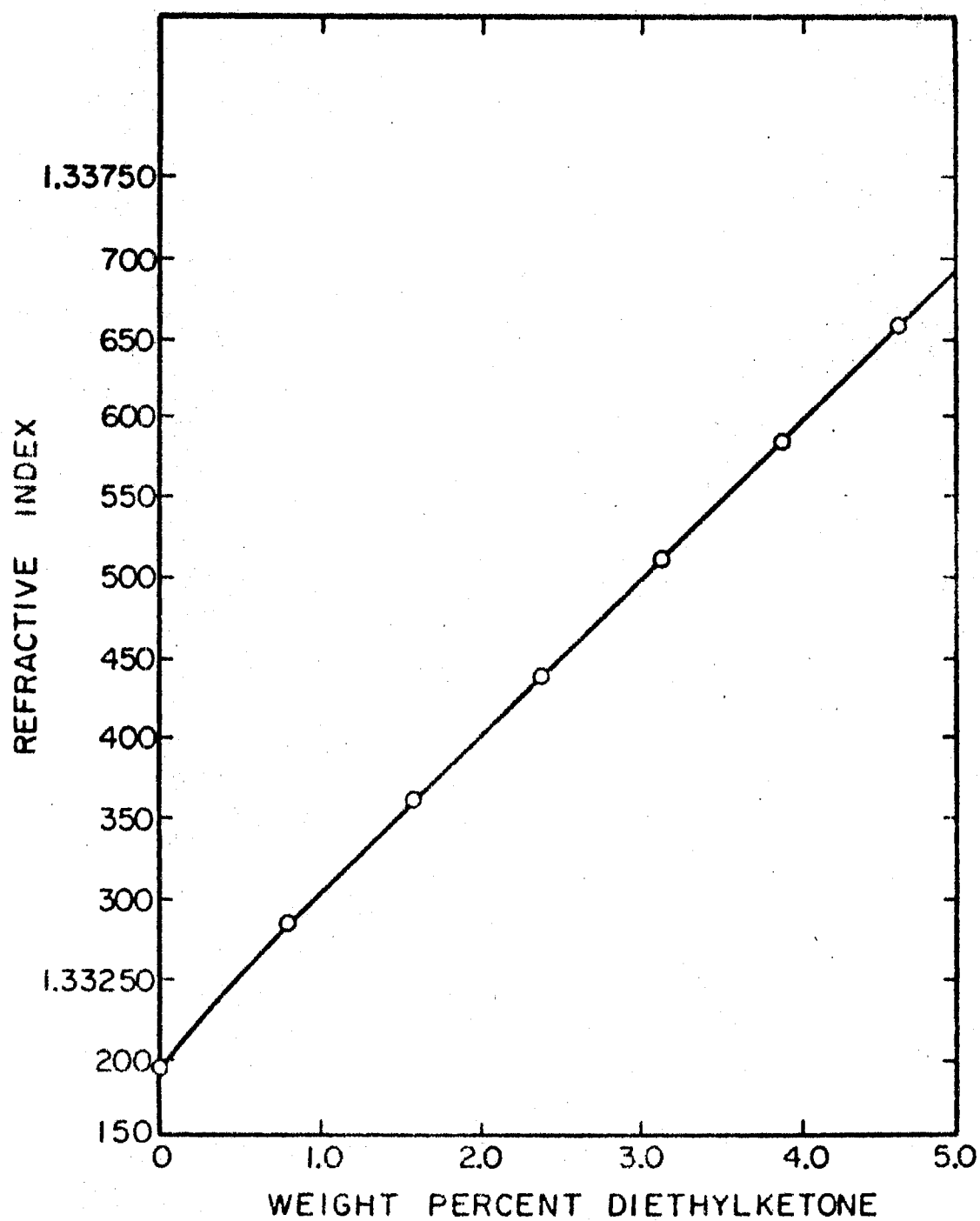


Figure 6. Refractive Index for Water Diethylketone System  
at 30° C

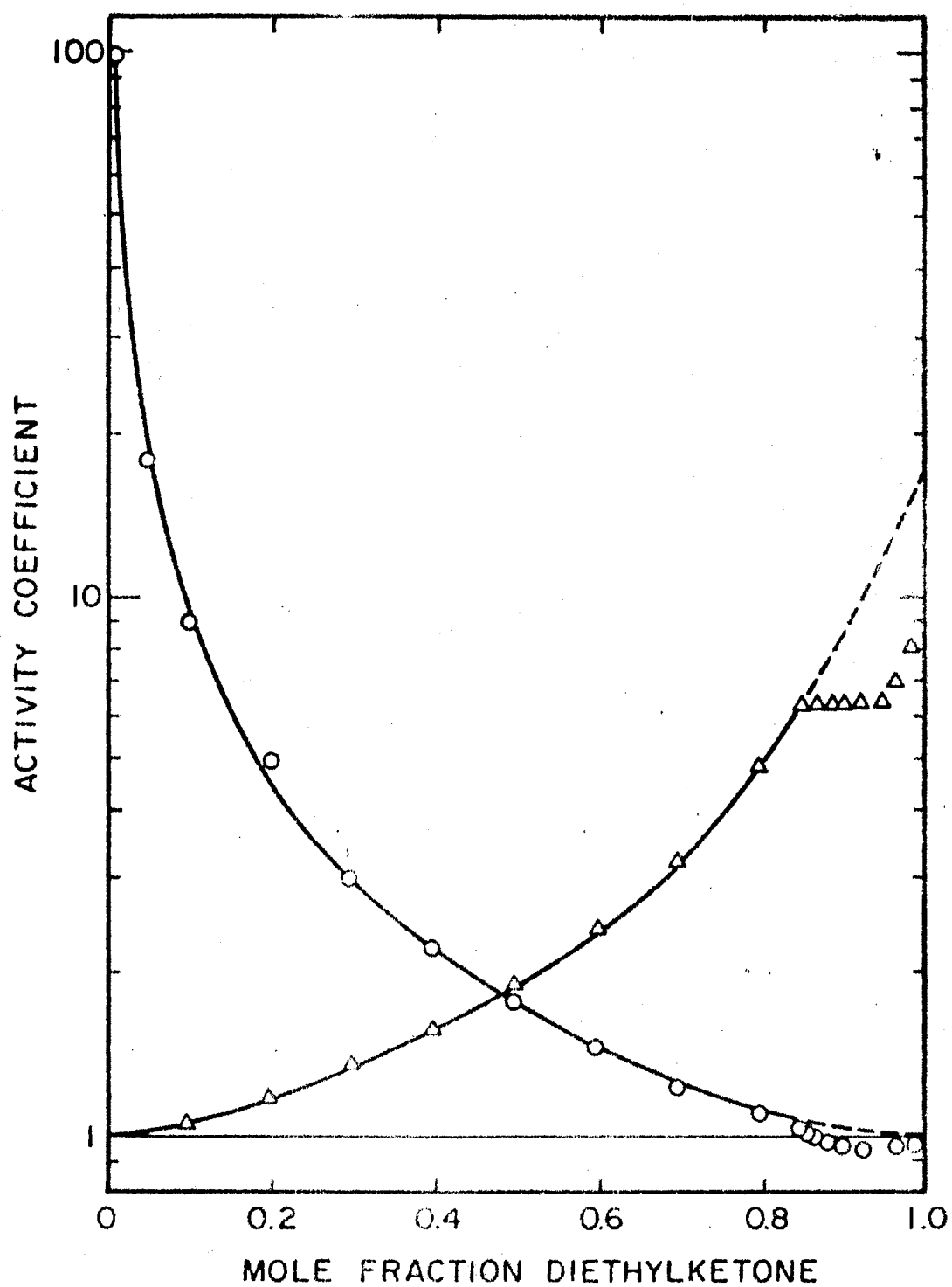


Figure 7. Activity Coefficient Versus Composition,  
Diethylketone-Water System at 50° C

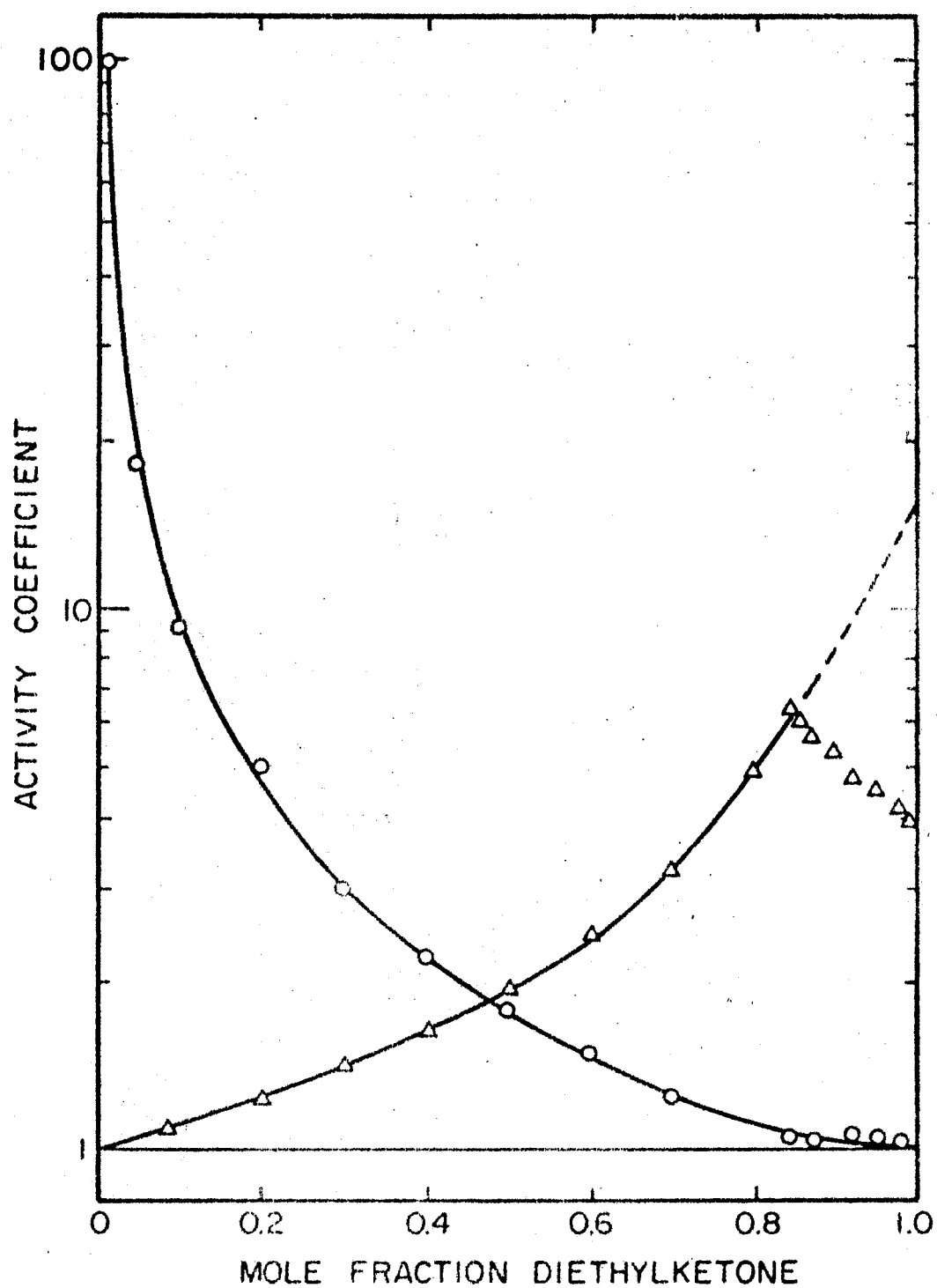


Figure 8. Activity Coefficient Versus Composition, Diethylketone-Water System at 60° C

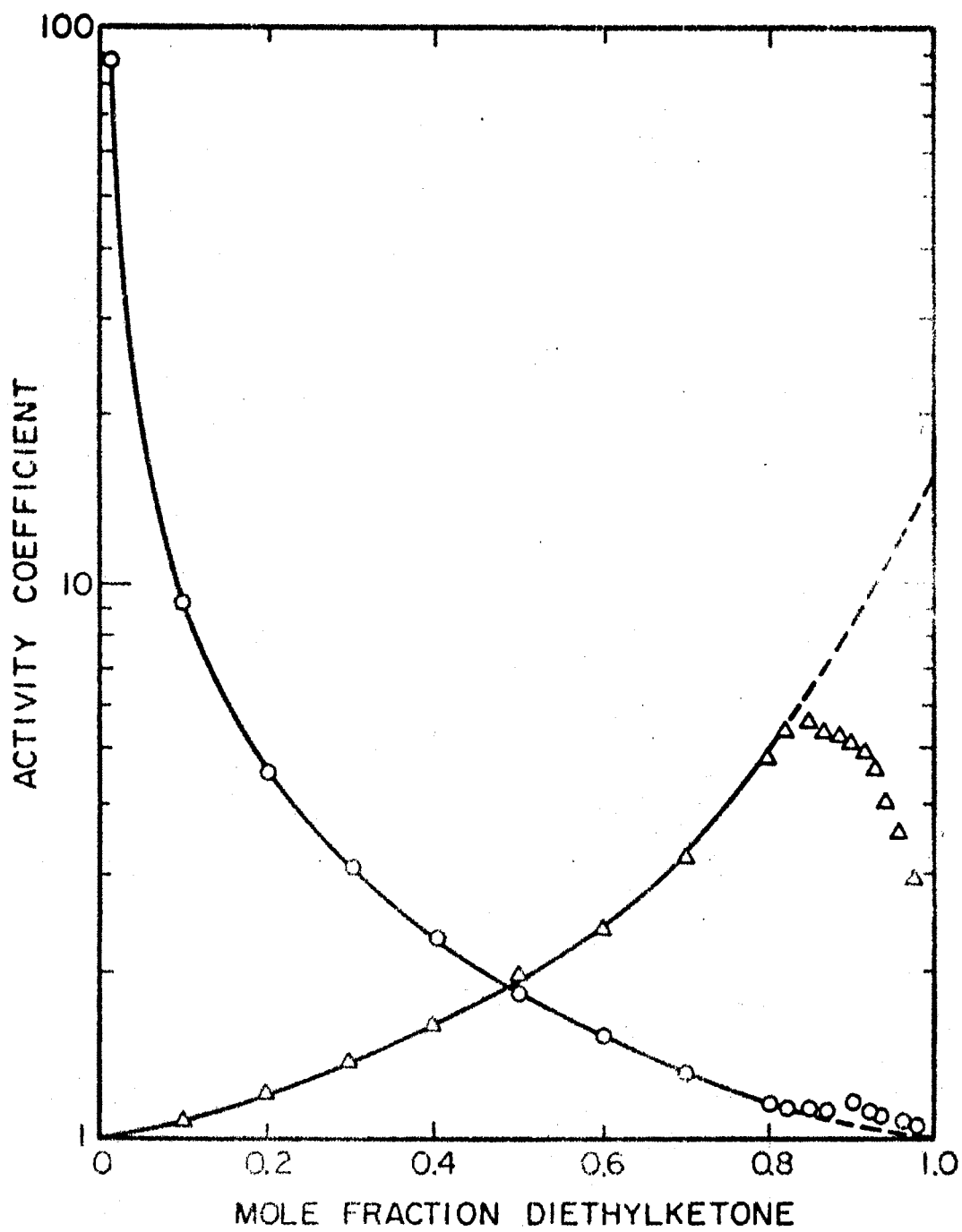


Figure 9. Activity Coefficient Versus Composition, Diethylketone-Water System at 70° C

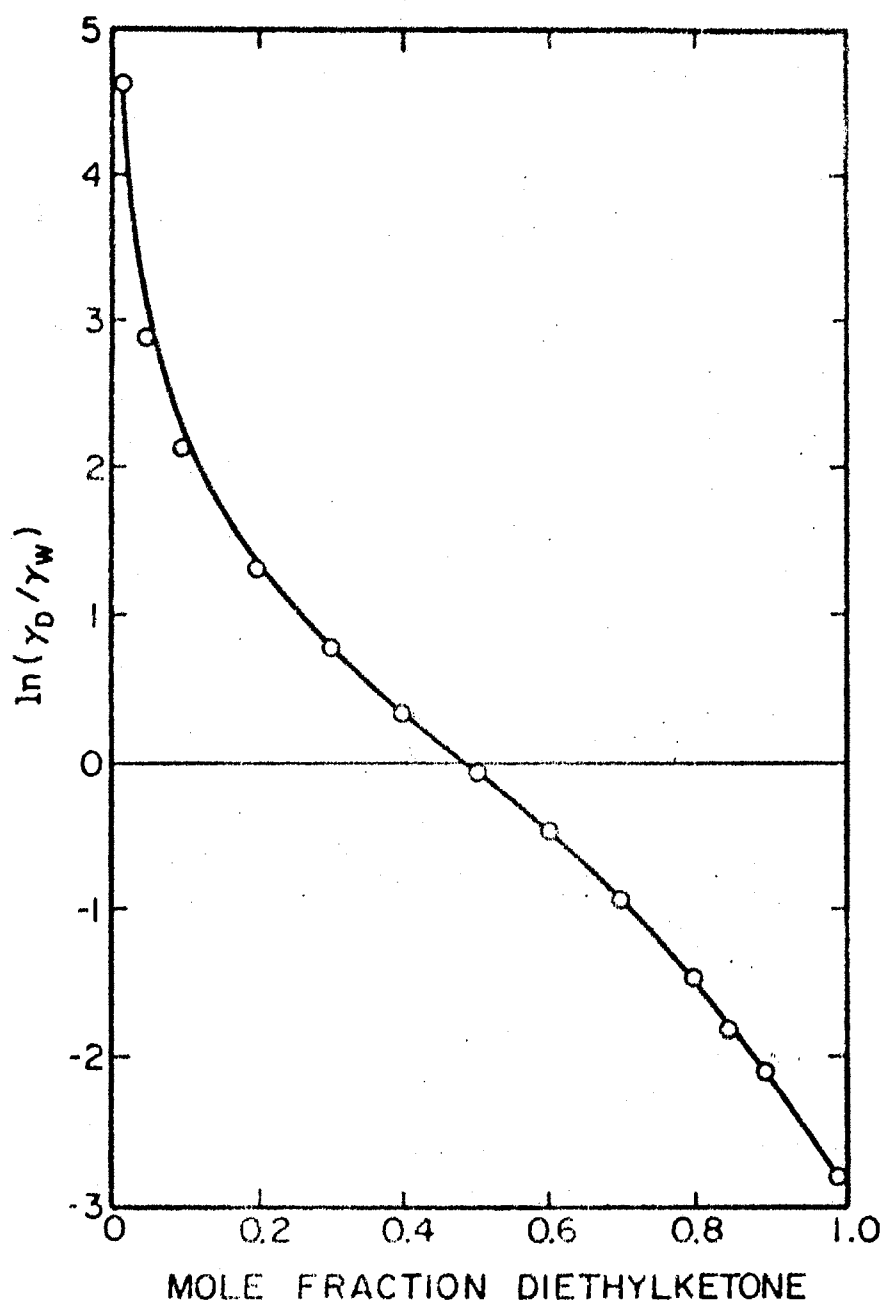


Figure 10.  $\ln(\gamma_D/\gamma_W)$  Versus Composition,  
Diethylketone-Water System  
at 50° C



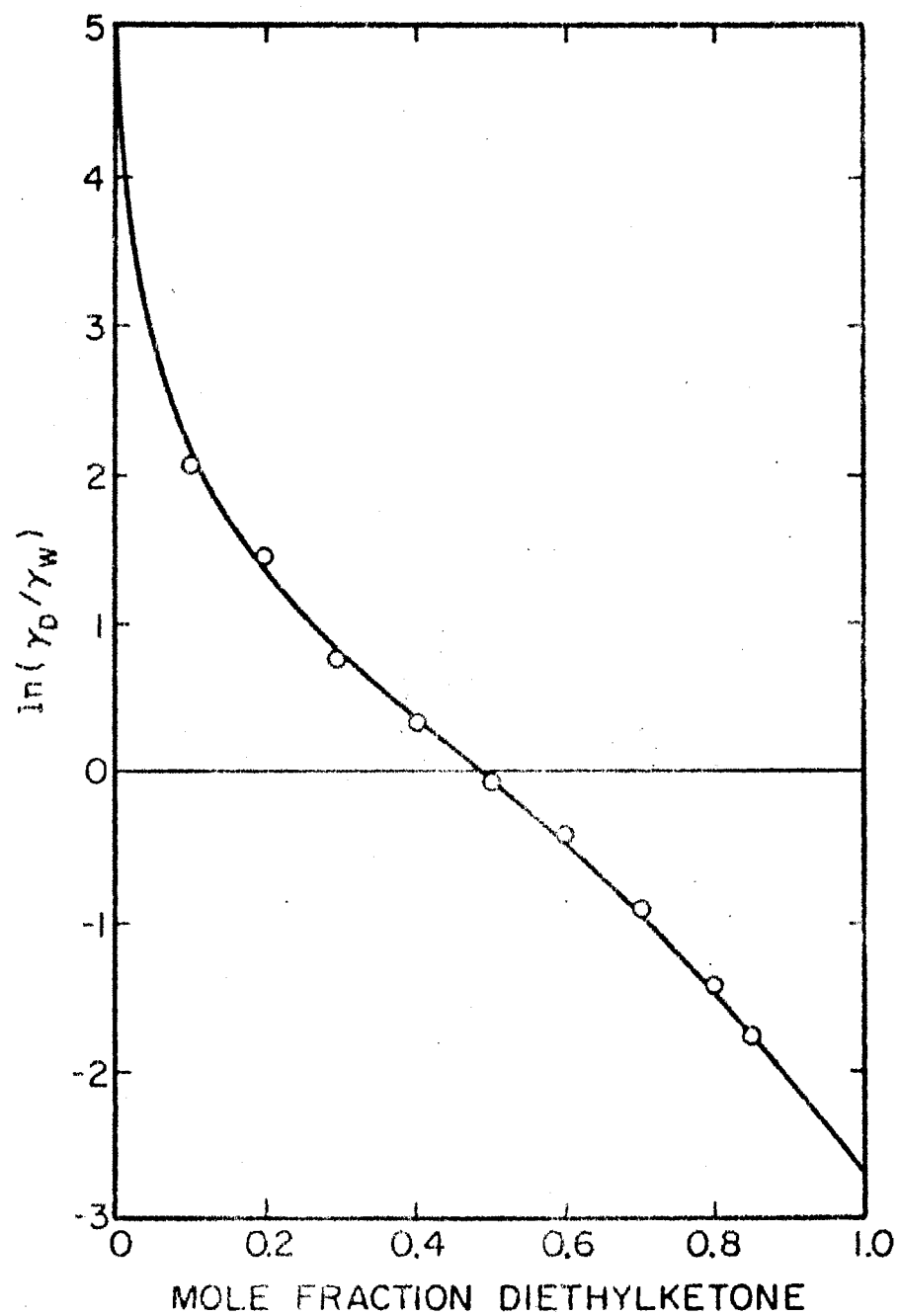


Figure 11.  $\ln(\gamma_D/\gamma_W)$  Versus Composition,  
Diethylketone-Water System  
at 60° C

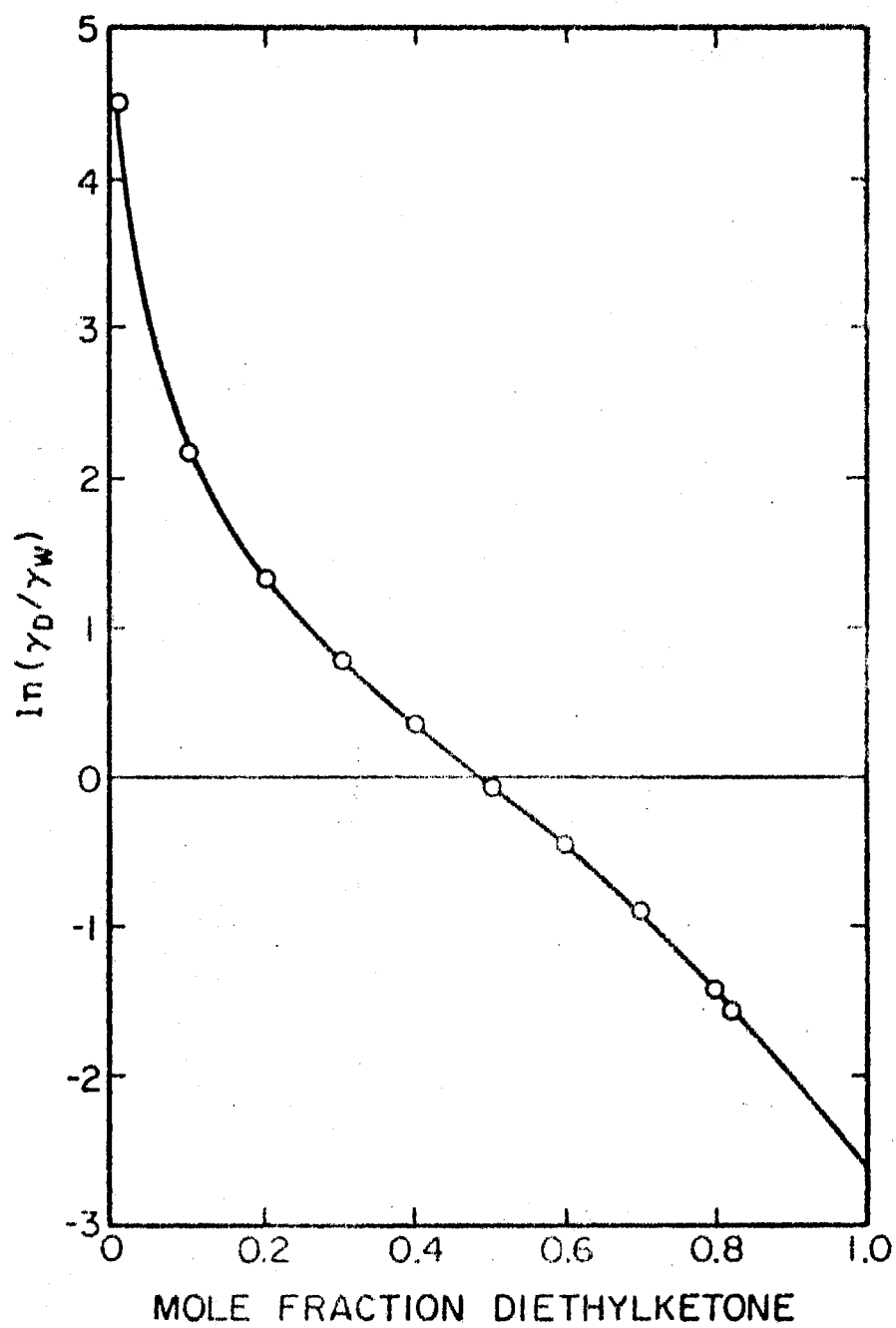


Figure 12.  $\ln(\gamma_D/\gamma_W)$  Versus Composition,  
Diethylketone-Water System at  
70° C

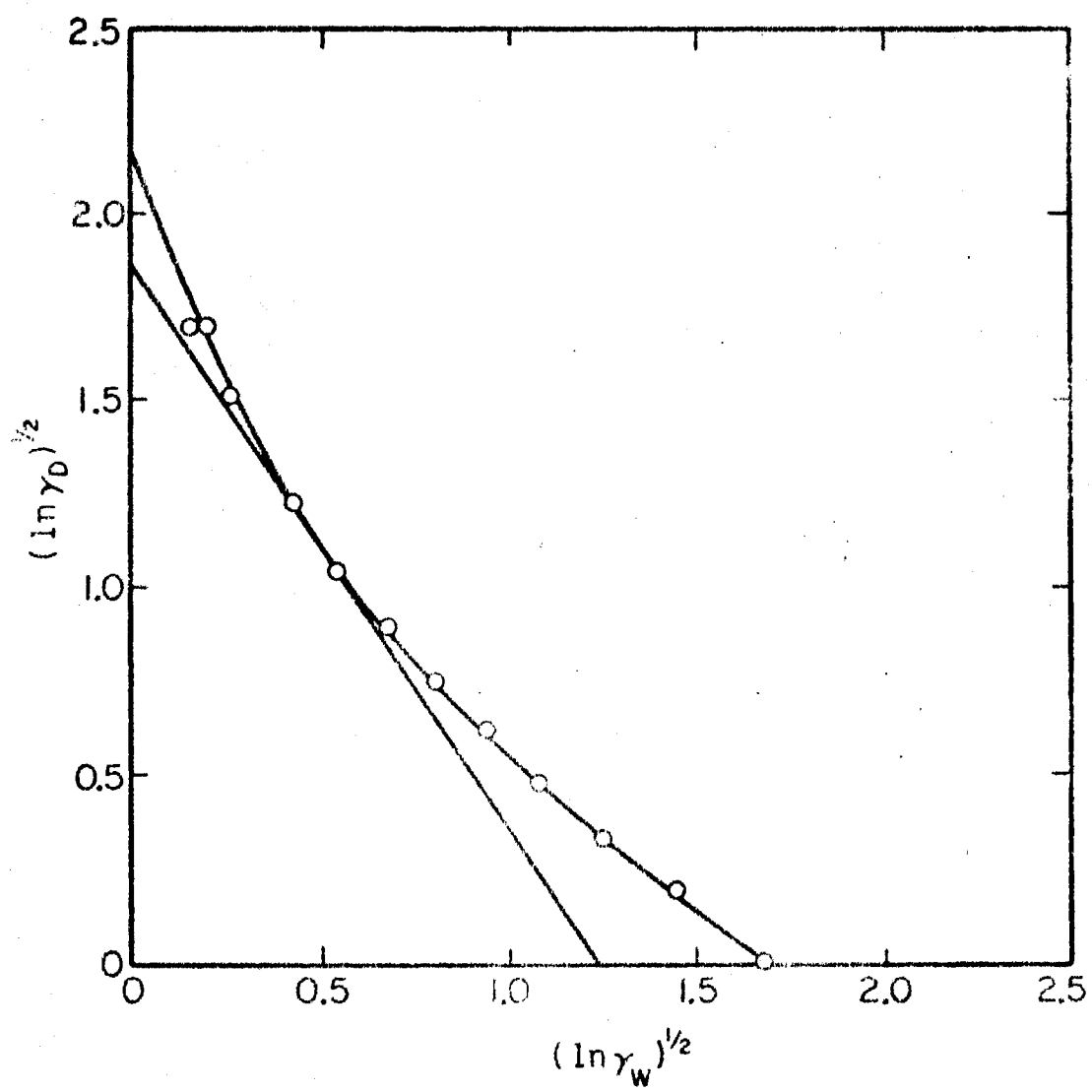


Figure 13.  $(\ln \gamma_D)^{1/2}$  Versus  $(\ln \gamma_W)^{1/2}$ , Diethylketone-Water System at 50° C

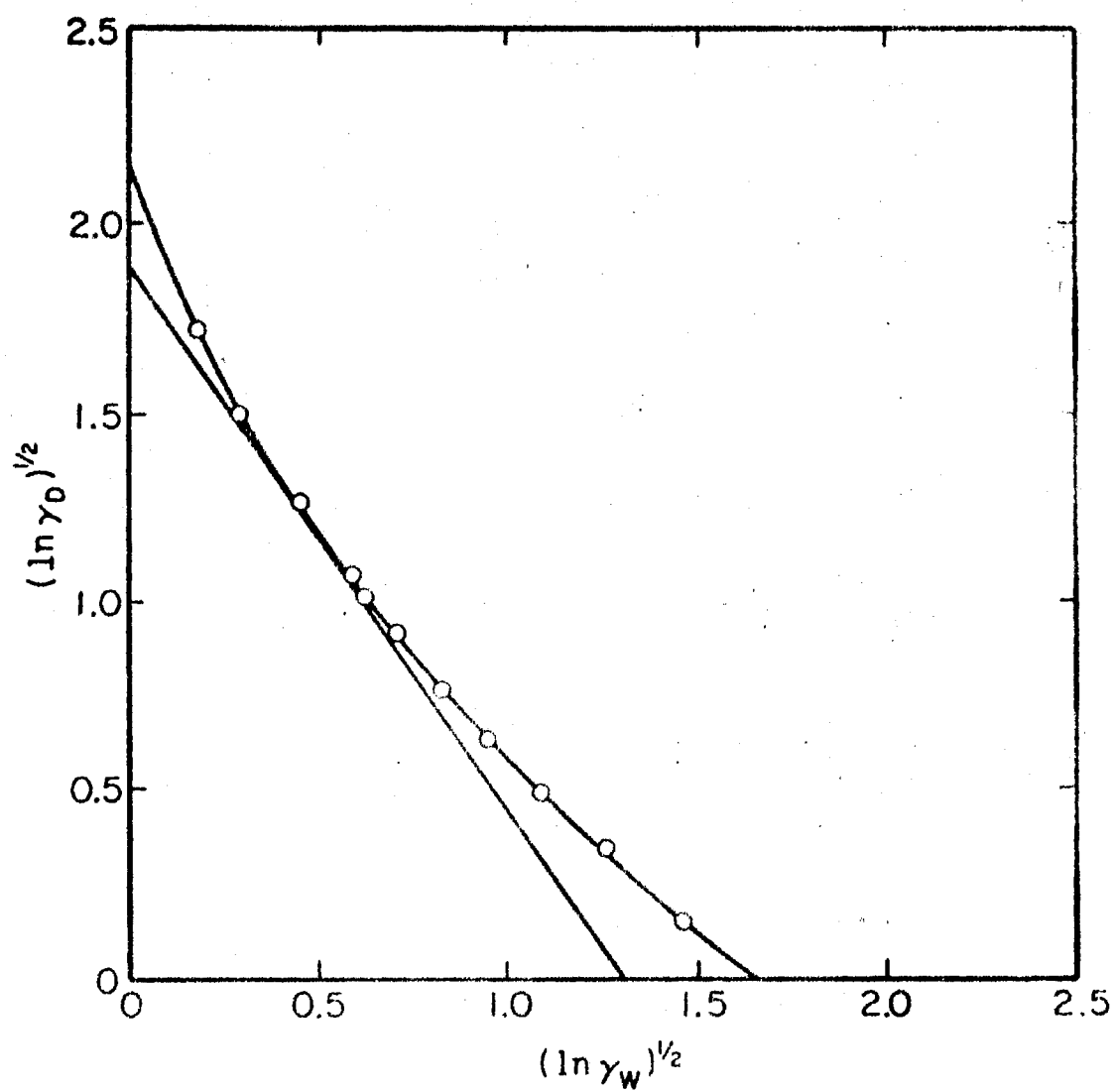


Figure 14.  $(\ln \gamma_D)^{1/2}$  Versus  $(\ln \gamma_W)^{1/2}$ , Diethylketone-Water System at 60° C

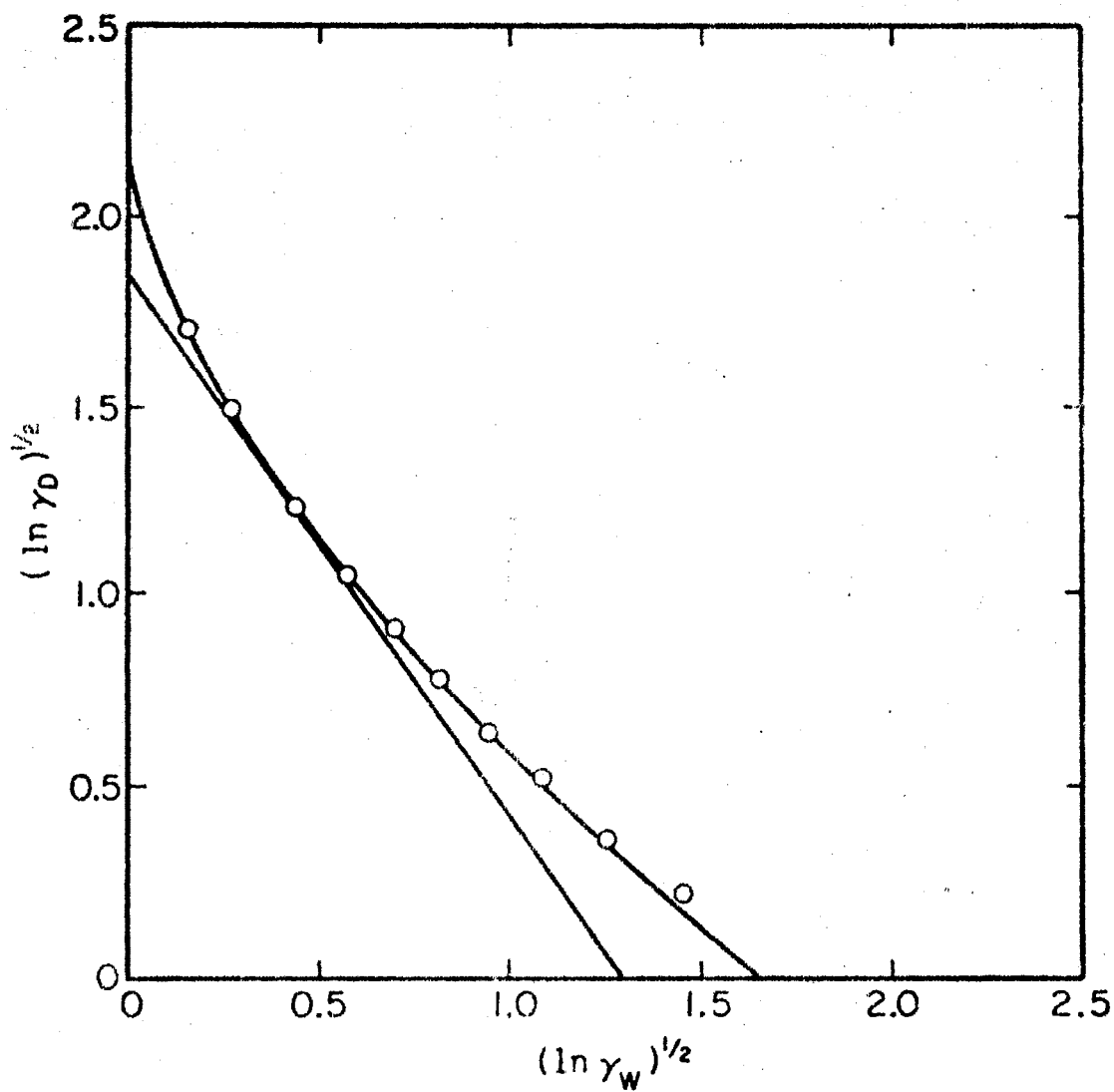


Figure 15.  $(\ln \gamma_D)^{1/2}$  Versus  $(\ln \gamma_W)^{1/2}$ , Diethylketone-Water System at 70° C

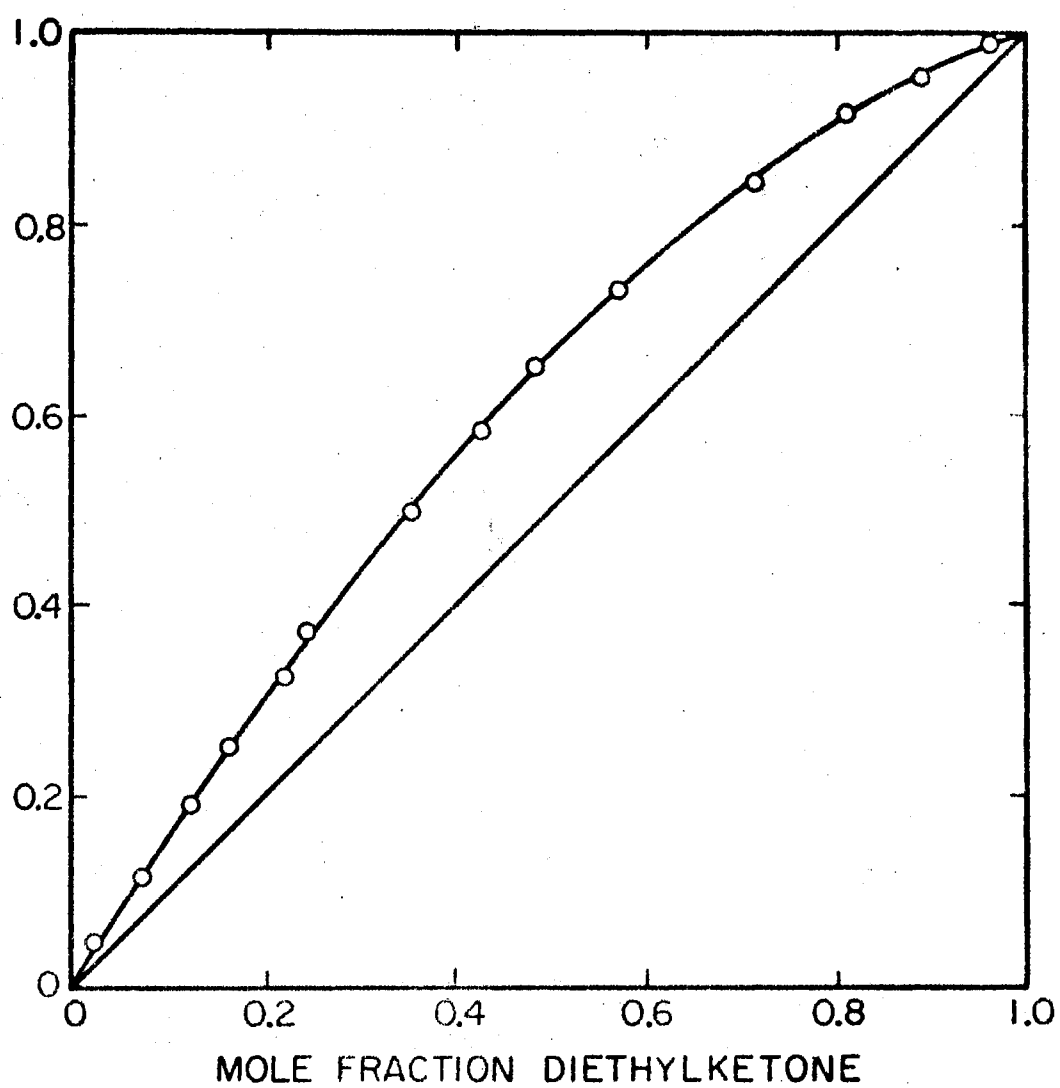


Figure 16. x-y Diagram Diethylketone-Acetic Acid System at 50° C

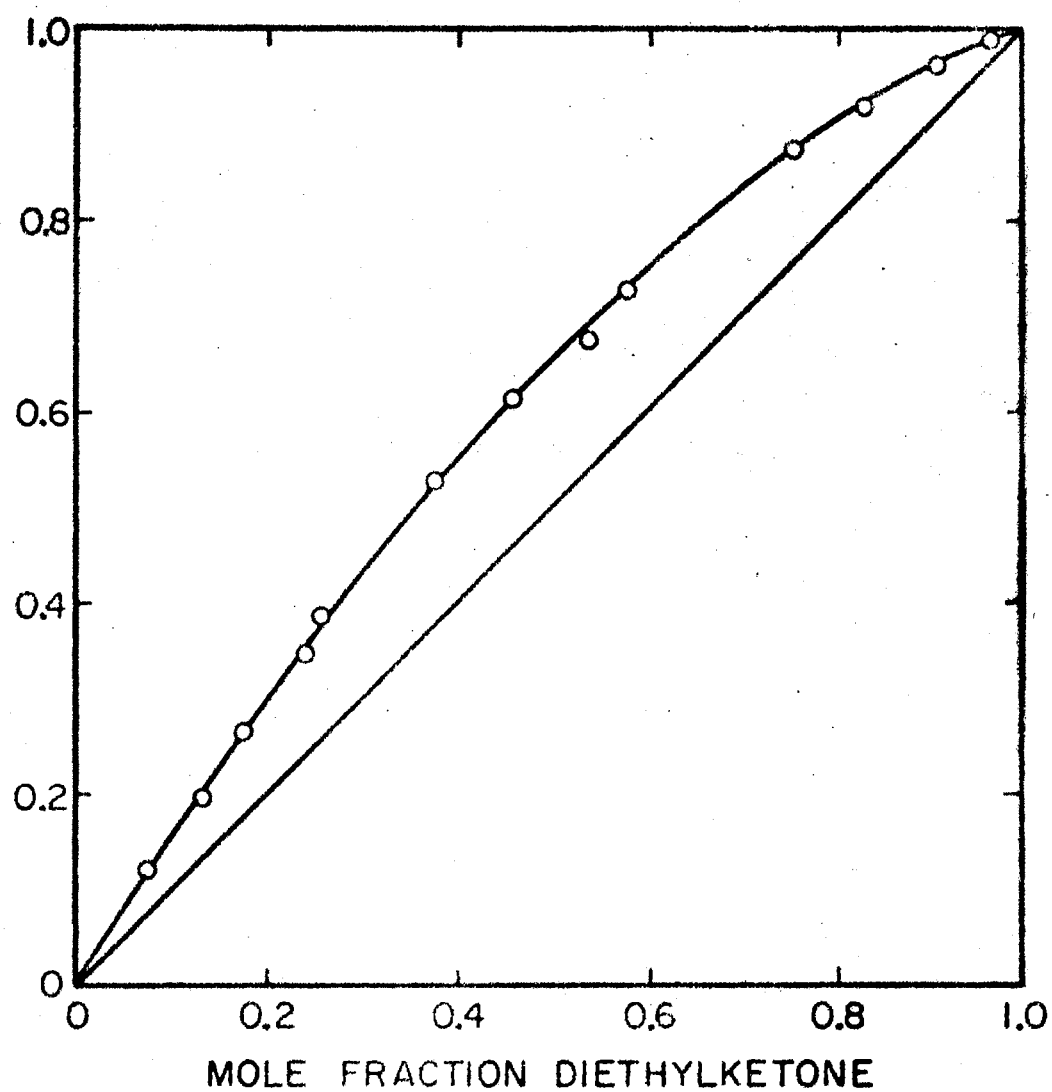


Figure 17. x-y Diagram Diethylketone-Acetic Acid System  
at 60° C

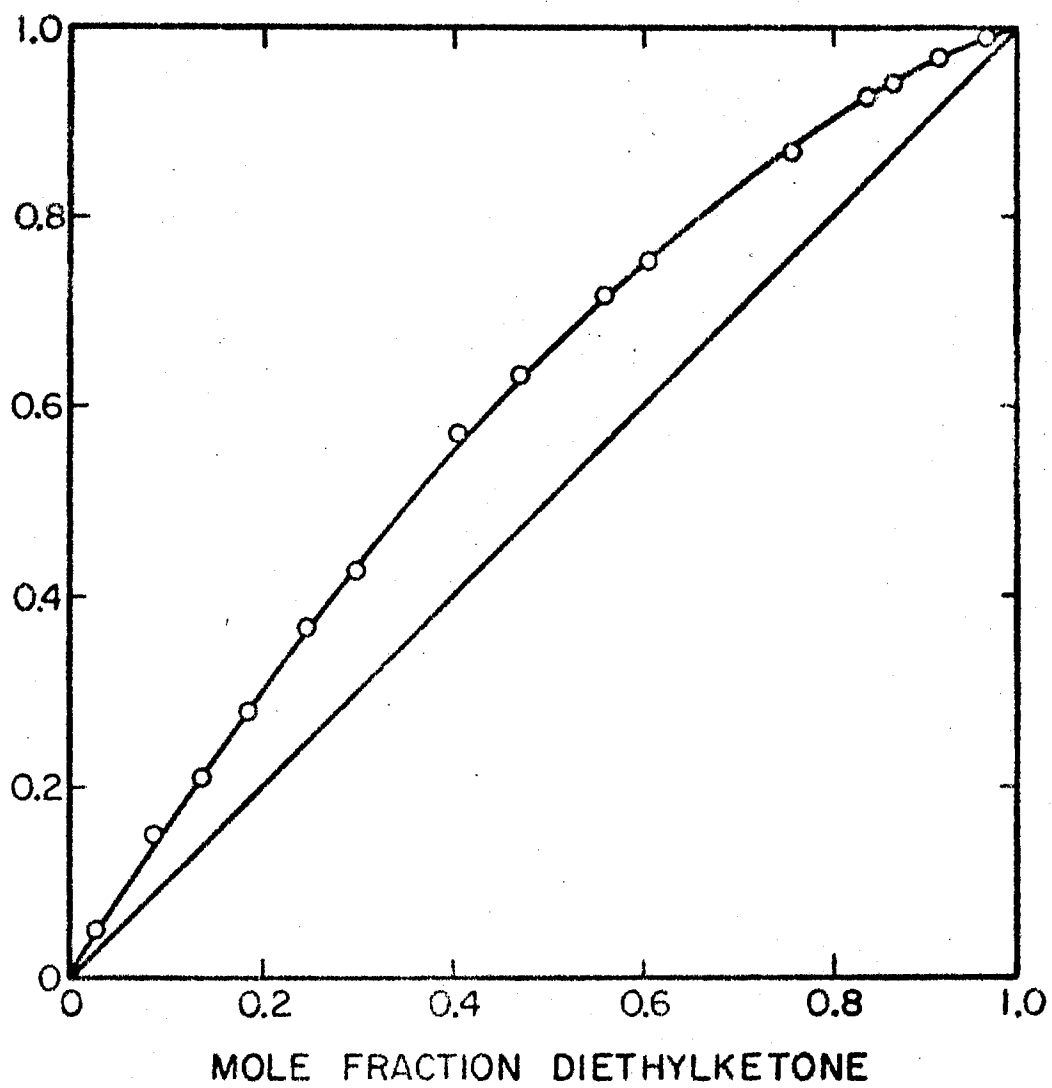


Figure 18. x-y Diagram Diethylketone-Acetic Acid System at 70°C



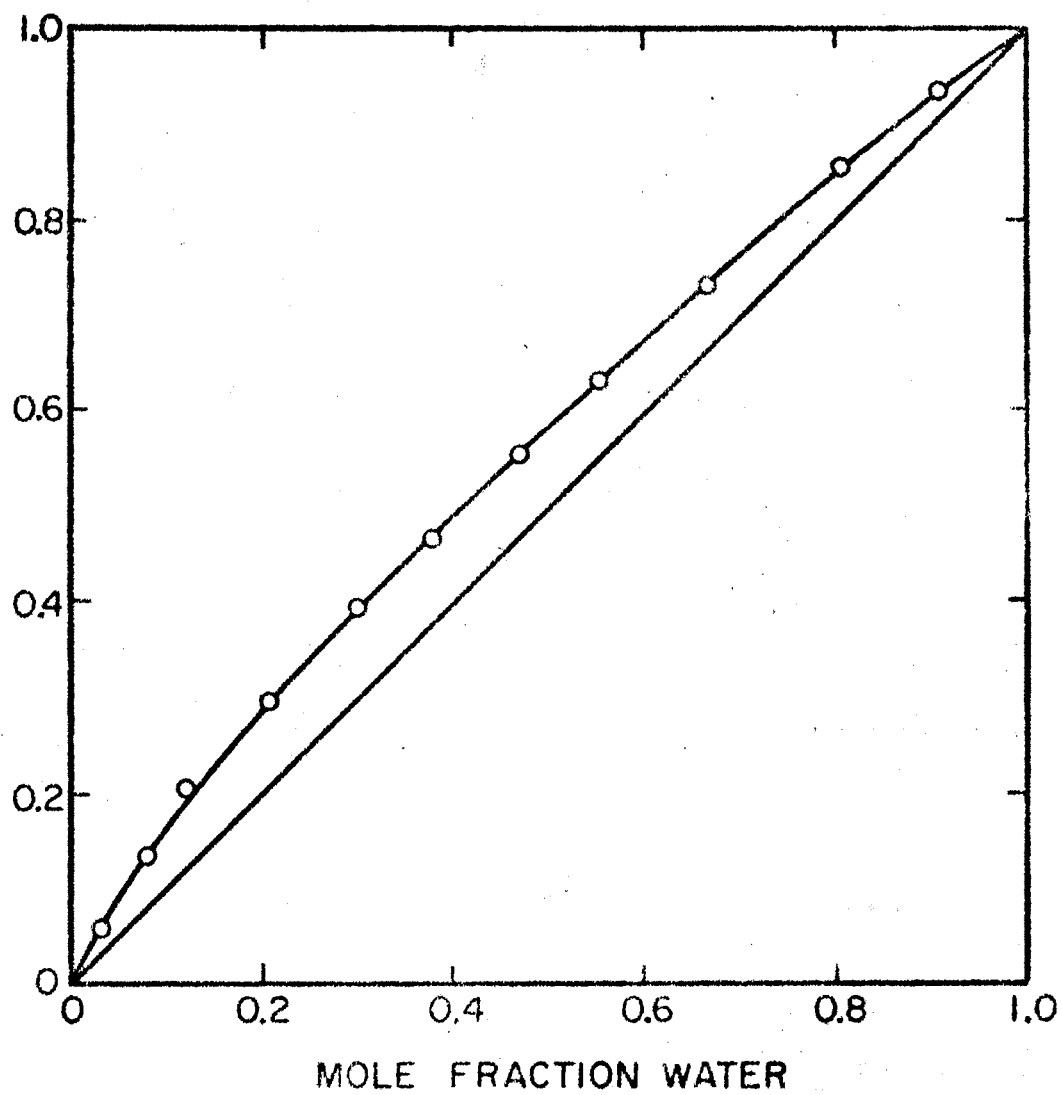


Figure 19. x-y Diagram Water-Acetic Acid System at 50° C

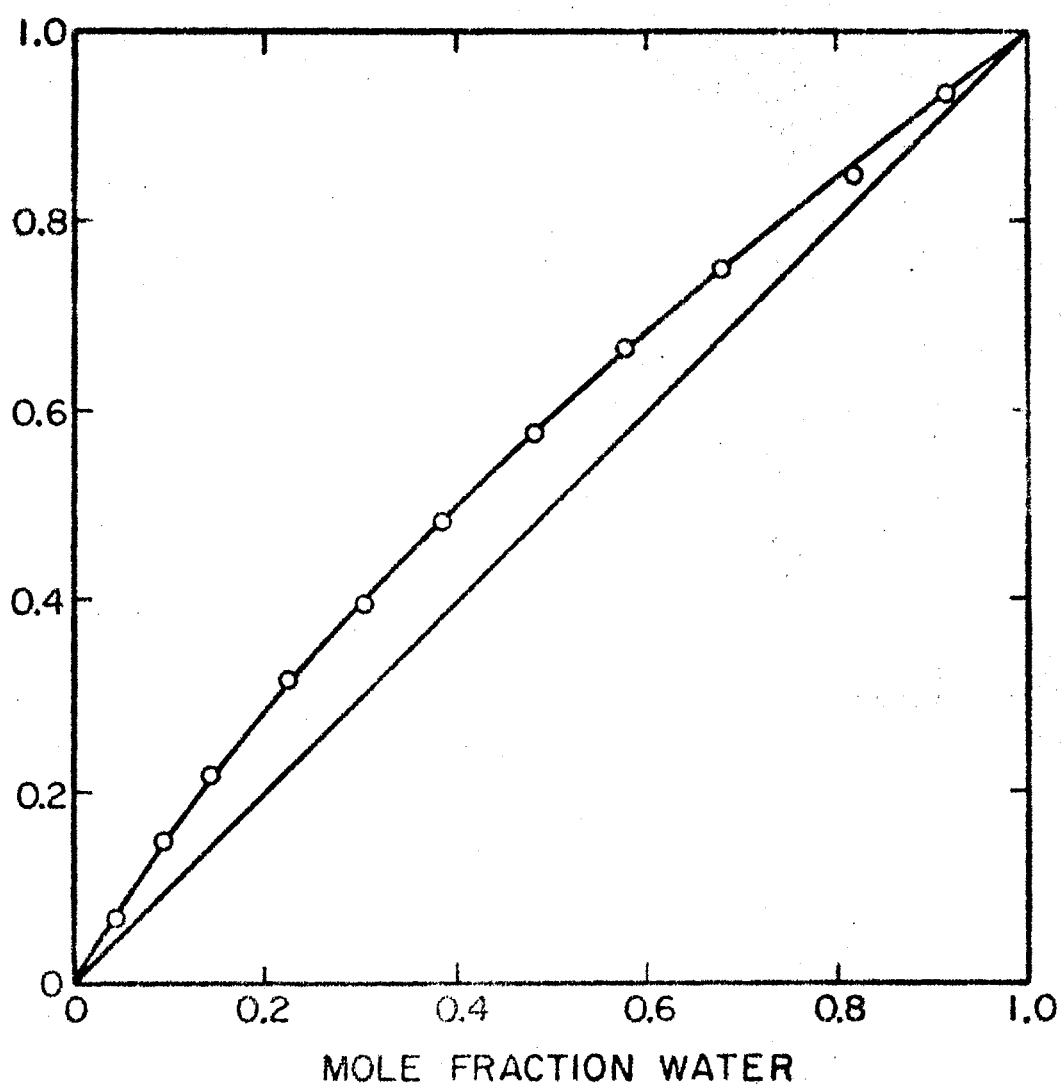


Figure 20. x-y Diagram Water-Acetic Acid System at 60° C

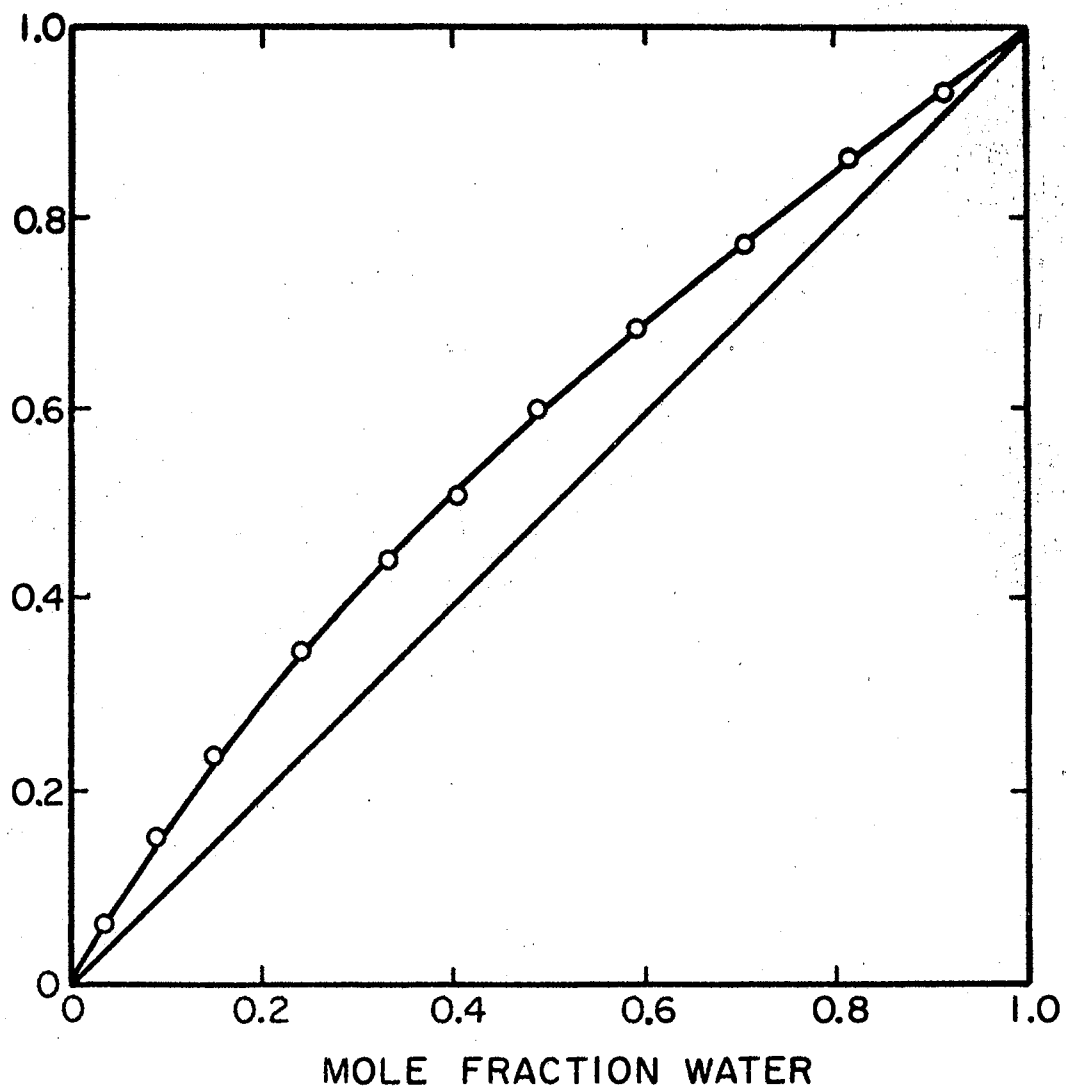


Figure 21. x-y Diagram Water-Acetic Acid System at 70° C

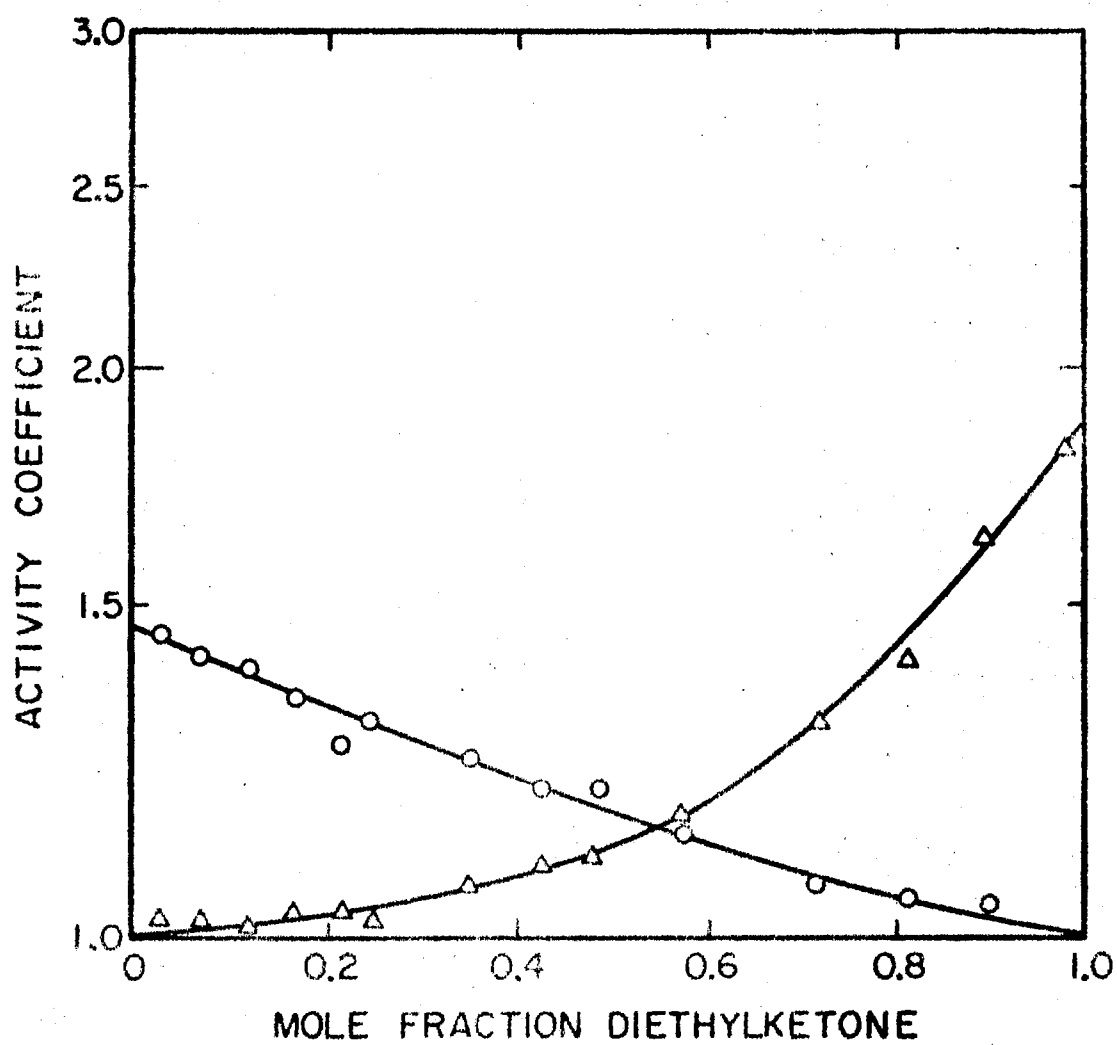


Figure 22. Activity Coefficient Versus Composition, Diethylketone Acetic Acid System at 50° C

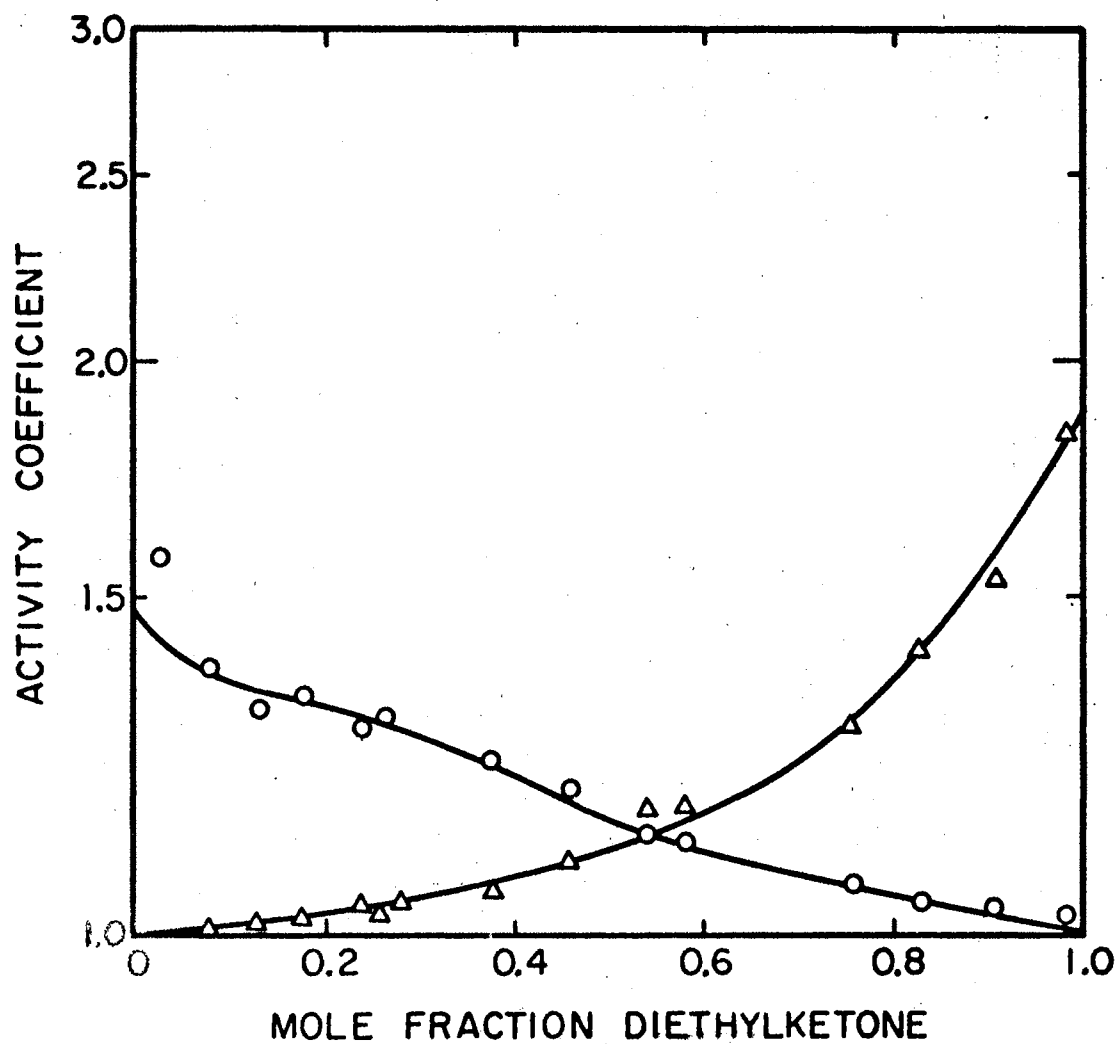


Figure 23. Activity Coefficient Versus Composition, Diethylketone Acetic Acid System at 60° C

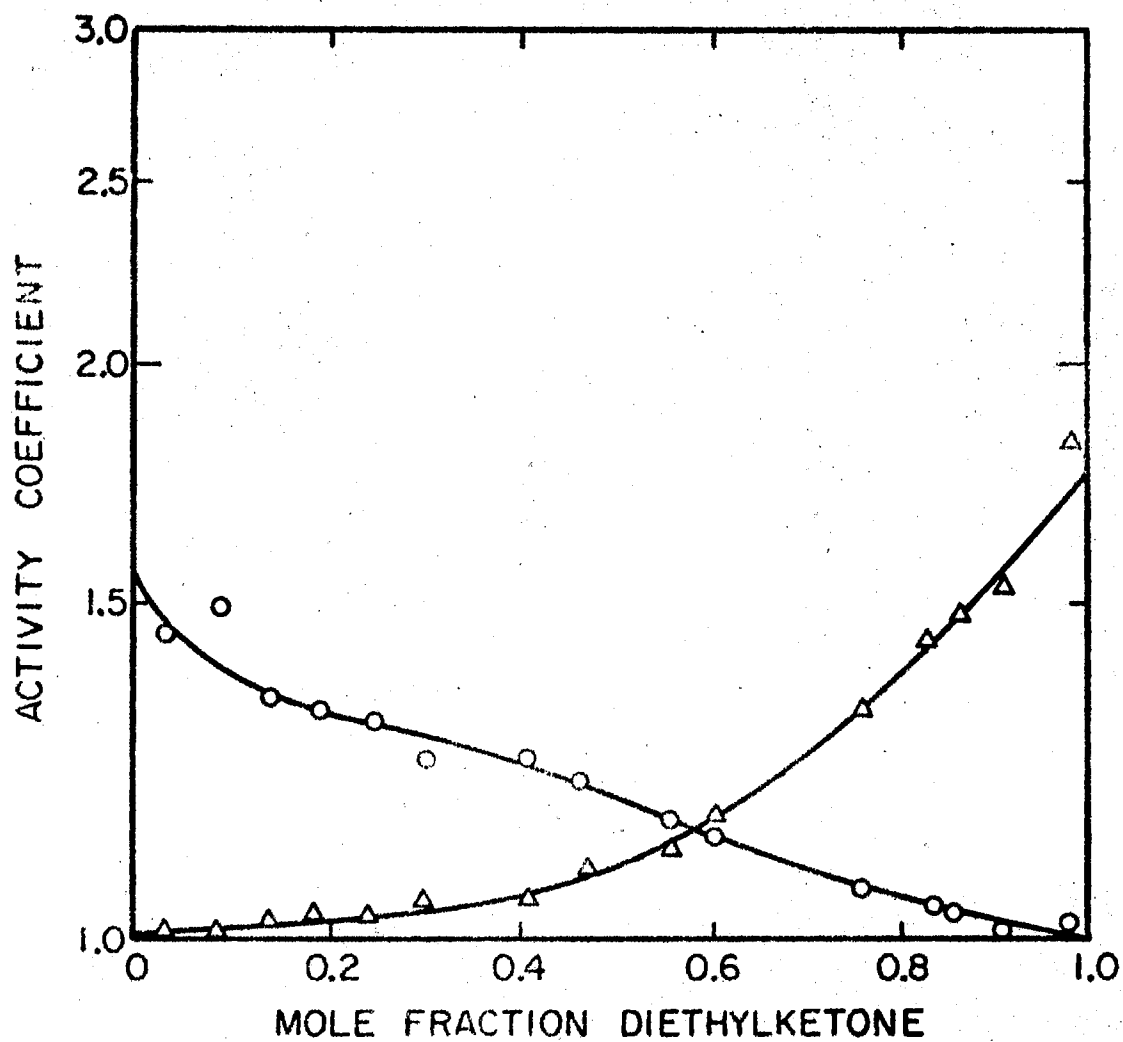


Figure 24. Activity Coefficient Versus Composition, Diethylketone Acetic Acid Systems at 70° C

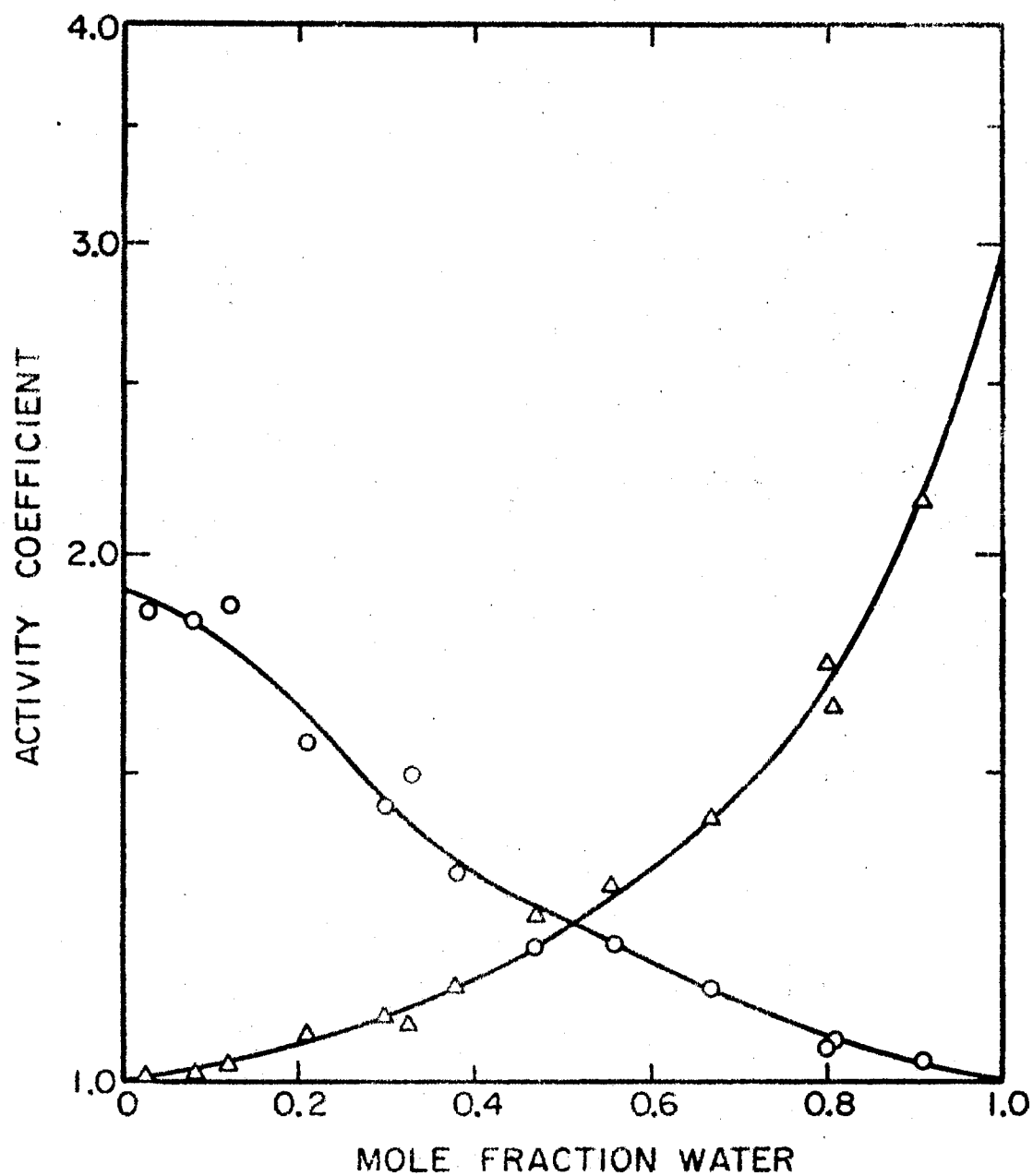


Figure 25. Activity Coefficient Versus Composition Water-Acetic Acid System at 50° C

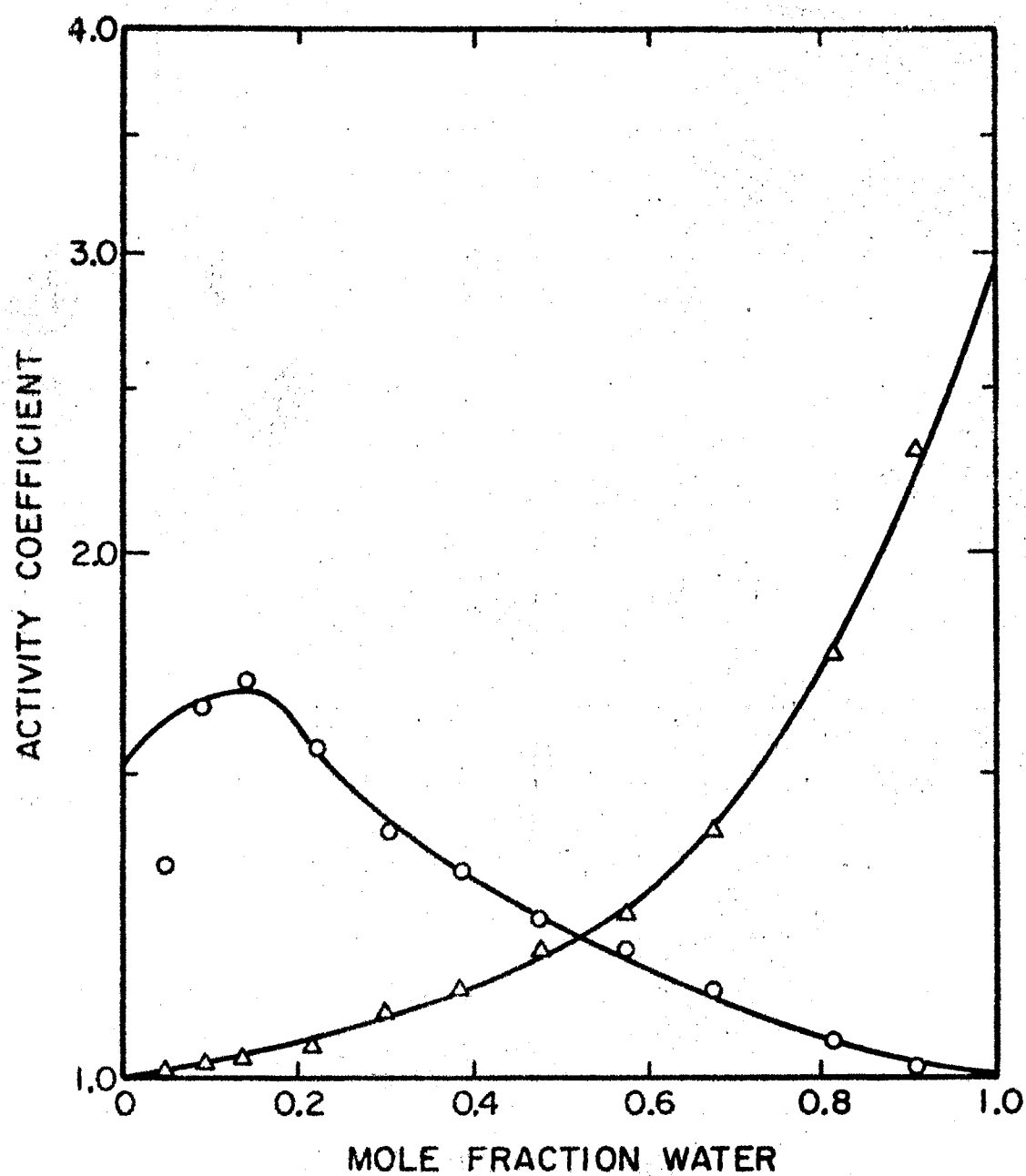


Figure 26. Activity Coefficient Versus Composition Water-Acetic Acid System at 60° C



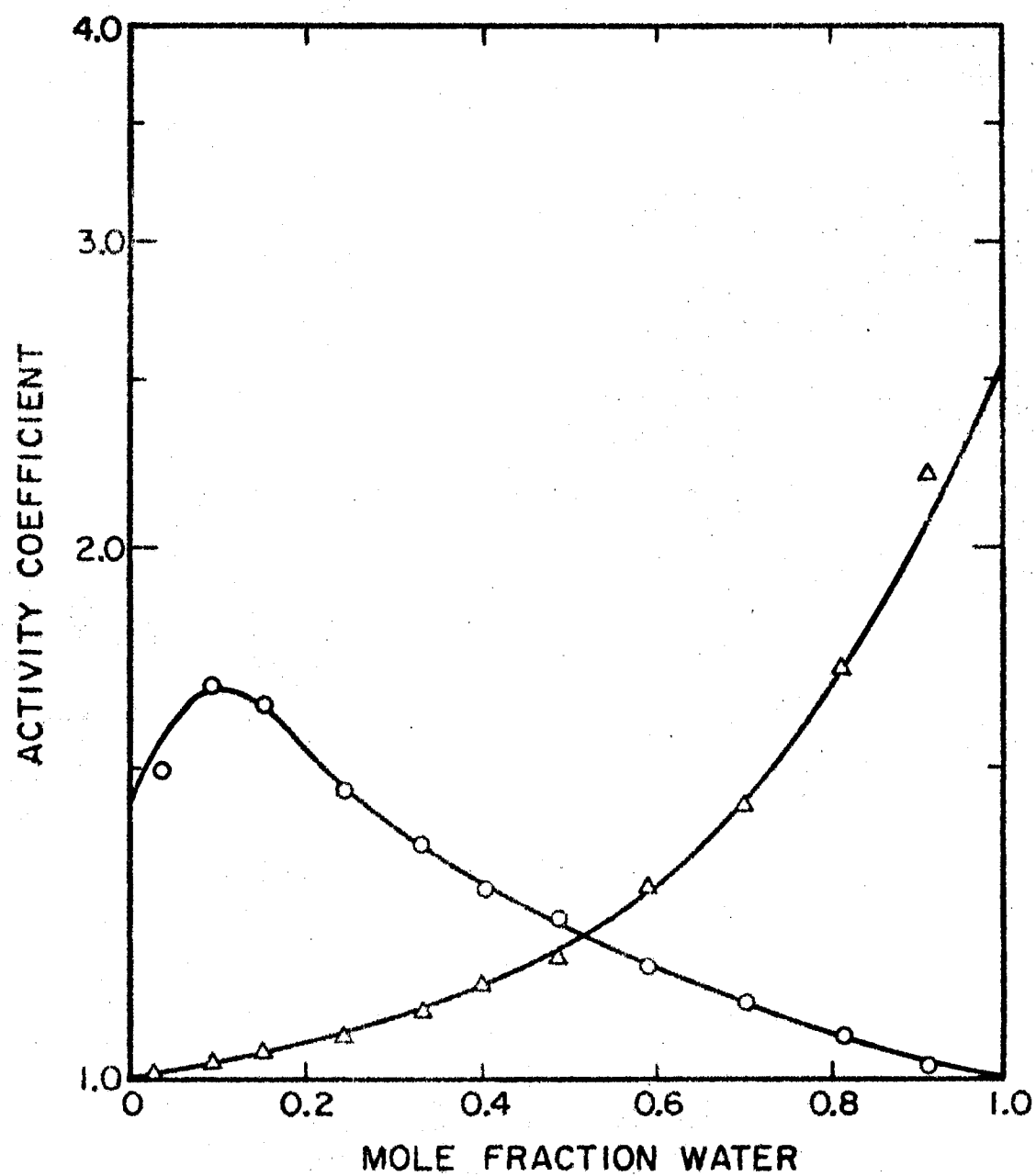


Figure 27. Activity Coefficient Versus Composition Water-Acetic Acid System at 70° C

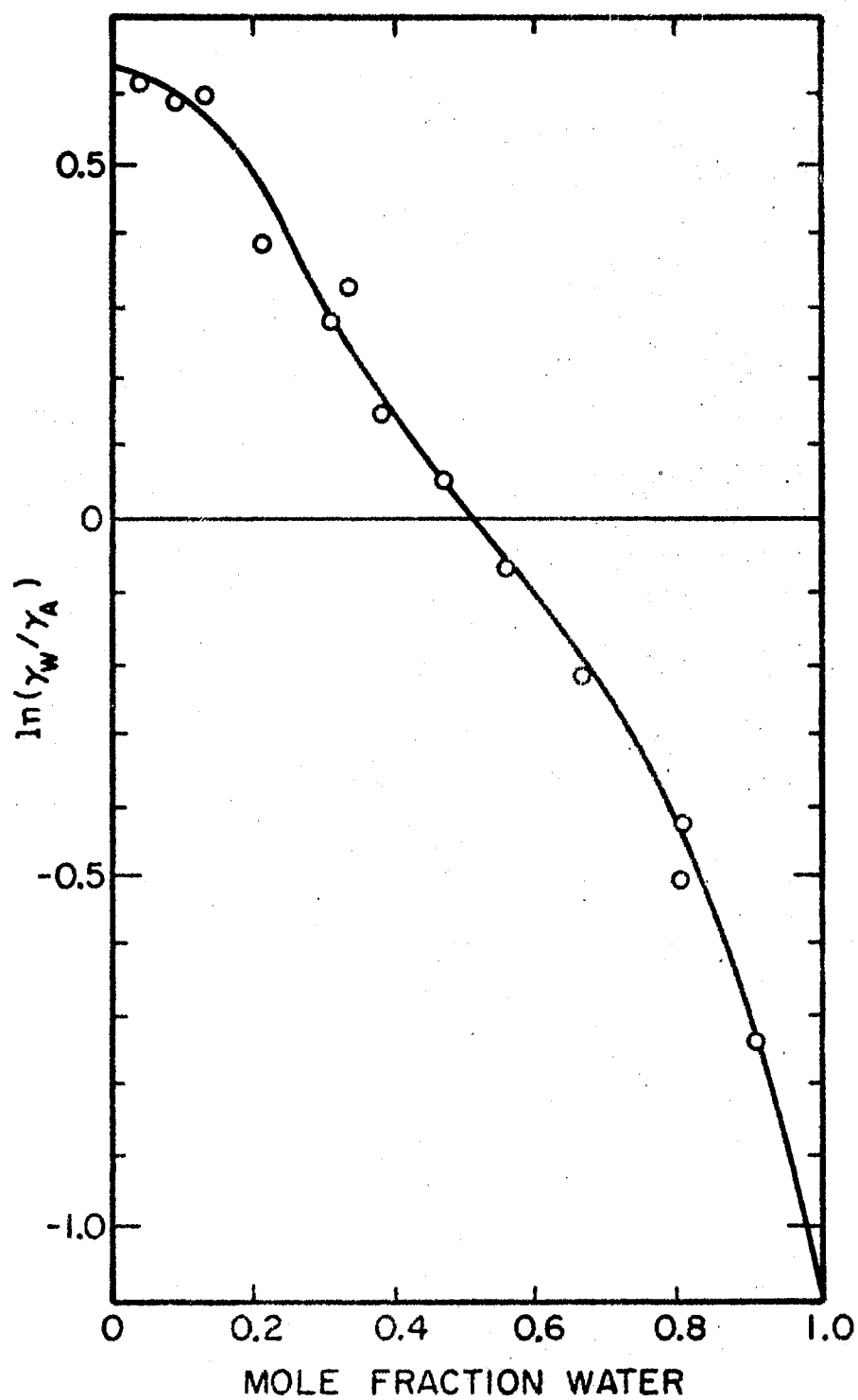


Figure 28.  $\ln(\gamma_W/\gamma_A)$  Versus Composition, Water-Acetic Acid System at 50° C

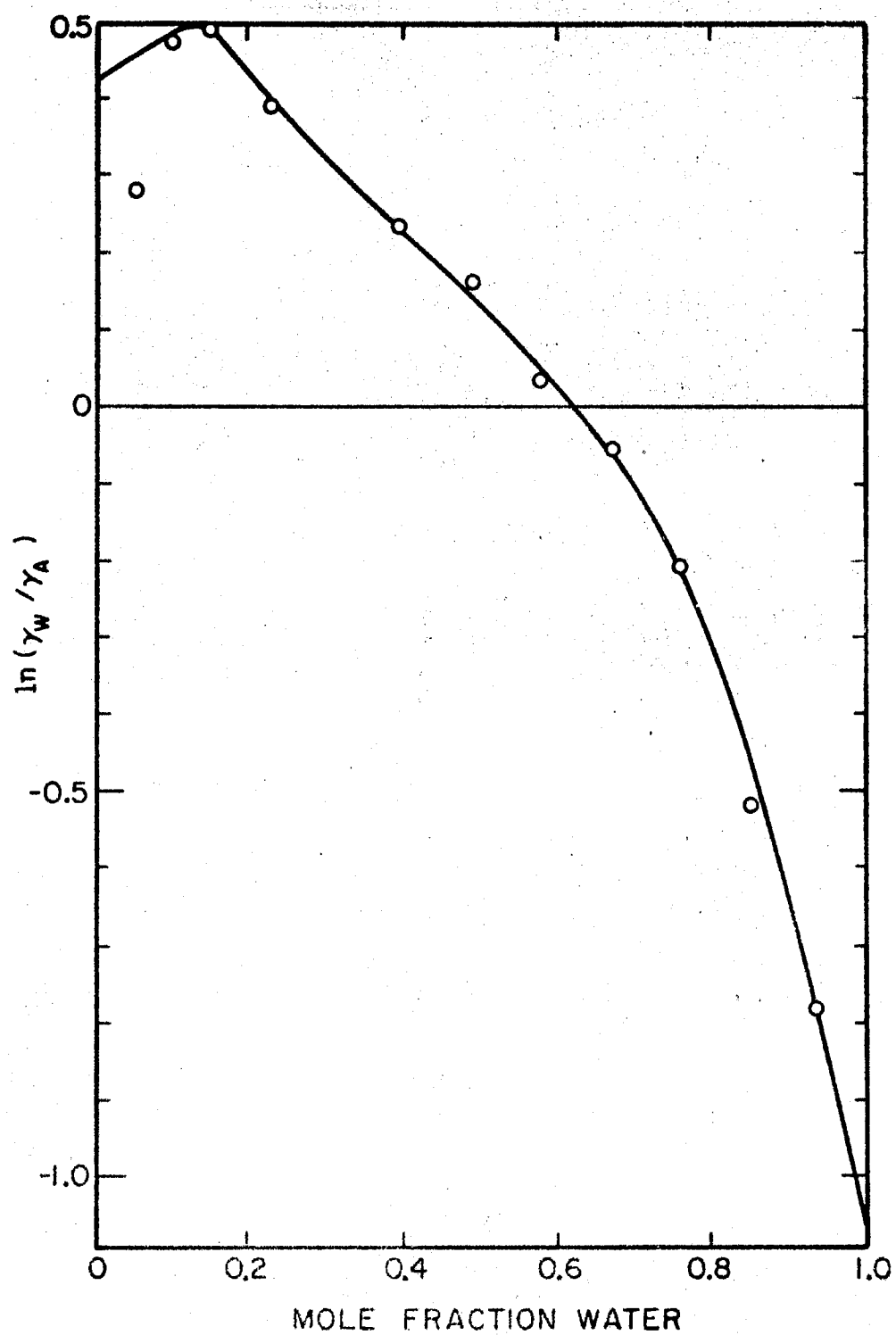


Figure 29.  $\ln(\gamma_W/\gamma_A)$  Versus Composition, Water-Acetic Acid System at 60° C

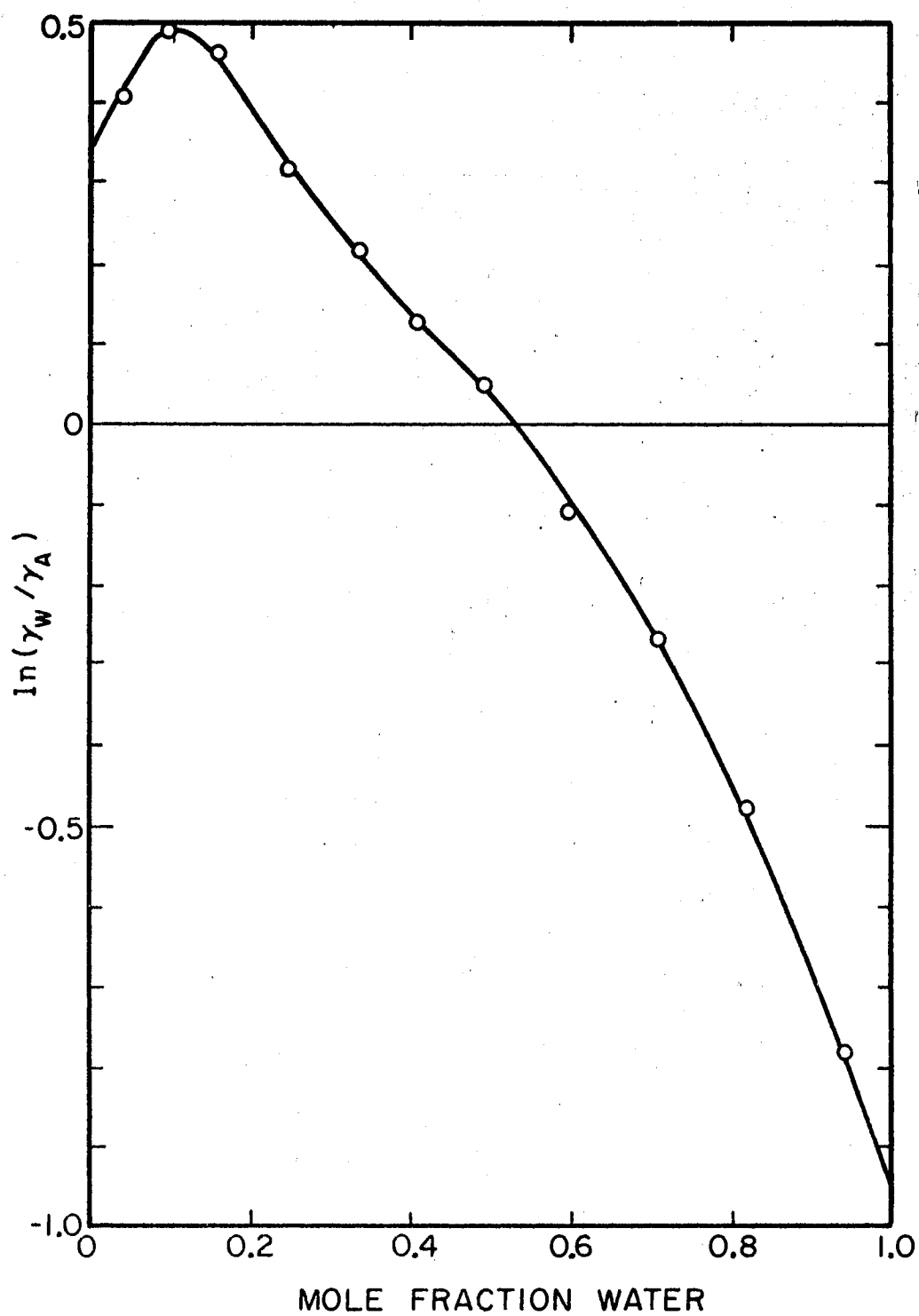


Figure 30.  $\ln(\gamma_W/\gamma_A)$  Versus Composition, Water-Acetic Acid System at 70° C

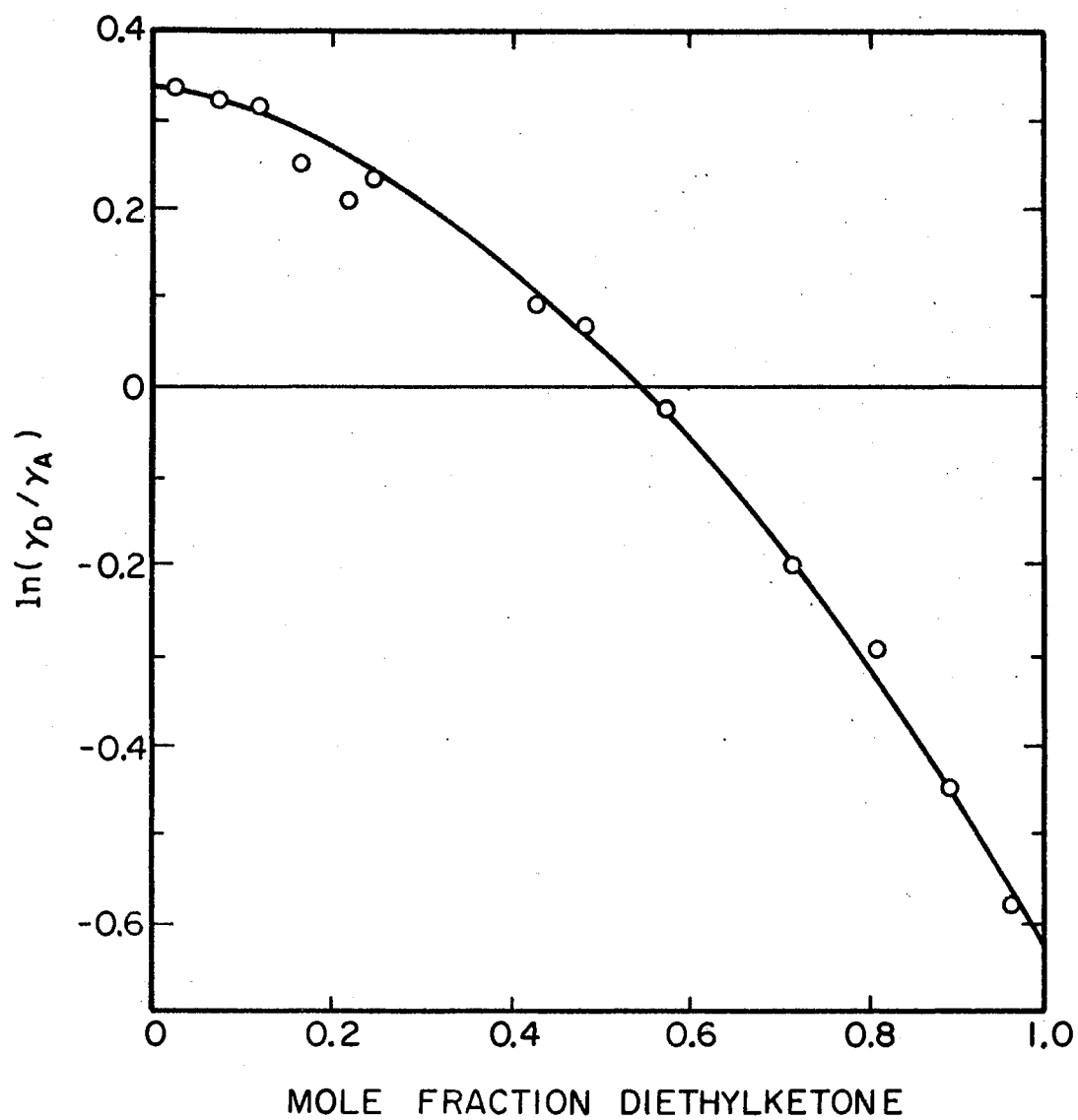


Figure 31.  $\ln(\gamma_D/\gamma_A)$  Versus Composition Diethylketone-Acetic Acid System at 50° C

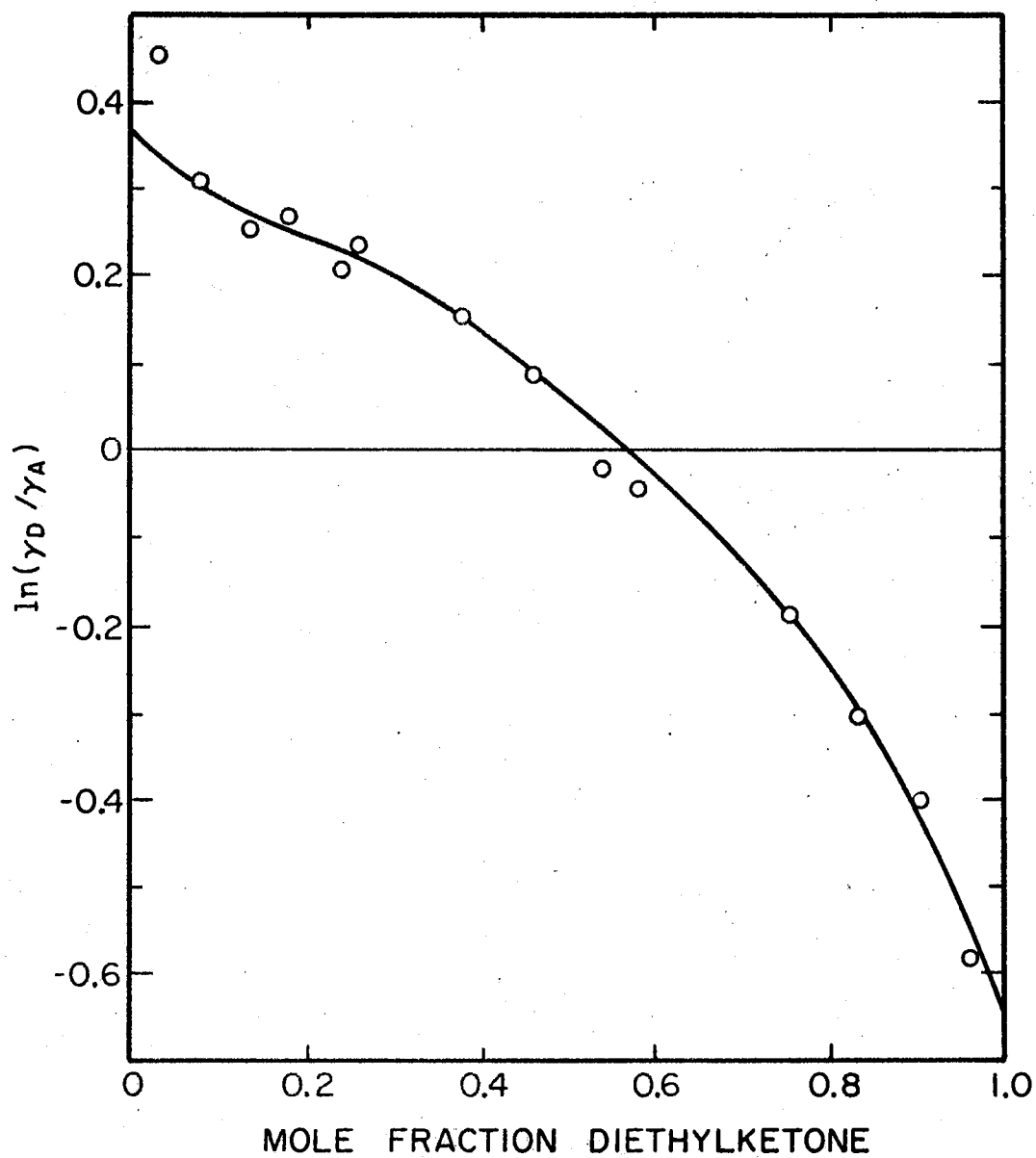


Figure 32.  $\ln(\gamma_D/\gamma_A)$  Versus Composition Diethylketone-Acetic Acid System at 60° C

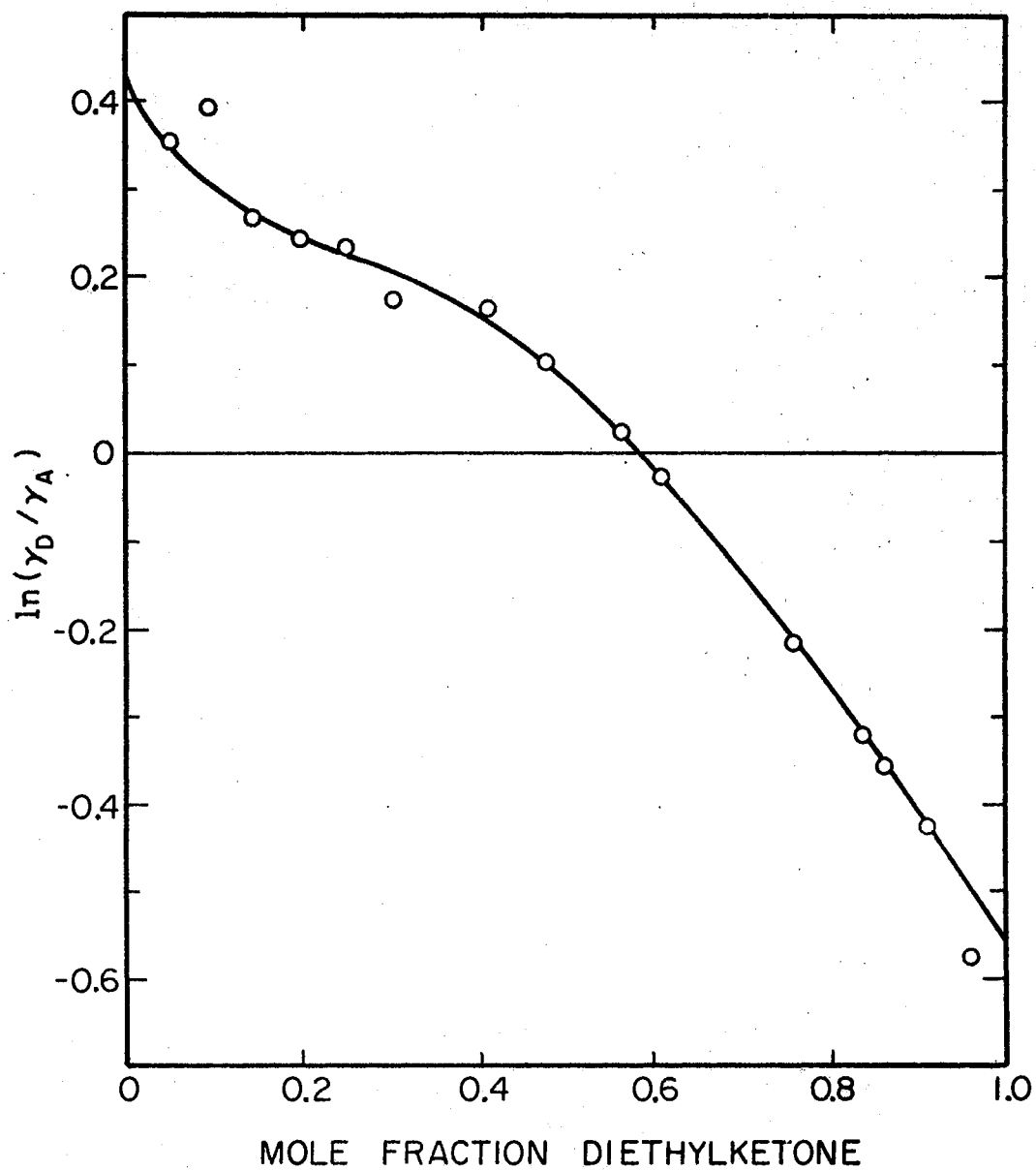


Figure 33.  $\ln(\gamma_D/\gamma_A)$  Versus Composition Diethylketone-Acetic Acid System at 70° C

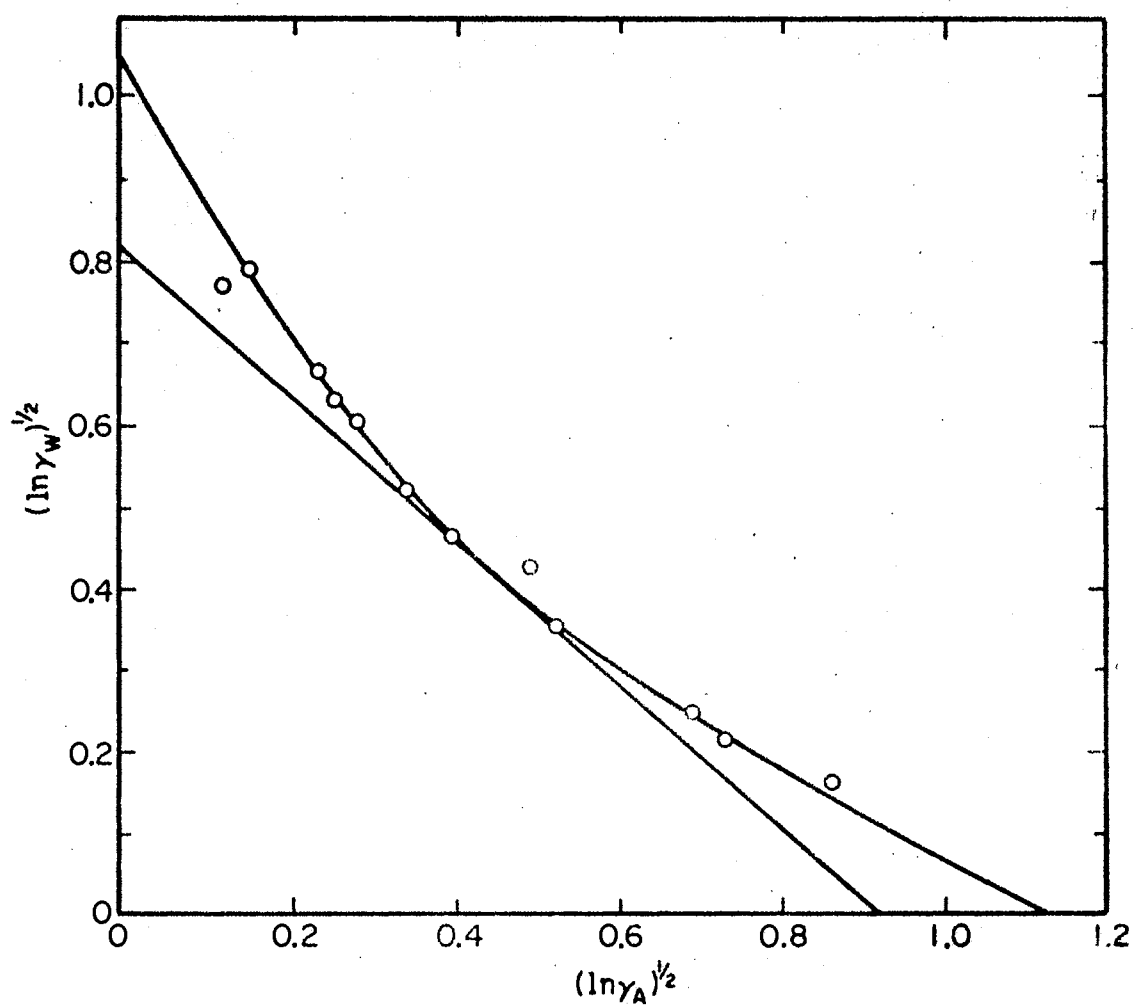


Figure 34.  $(\ln \gamma_W)^{1/2}$  Versus  $(\ln \gamma_A)^{1/2}$  Water-Acetic Acid System  
at 50° C



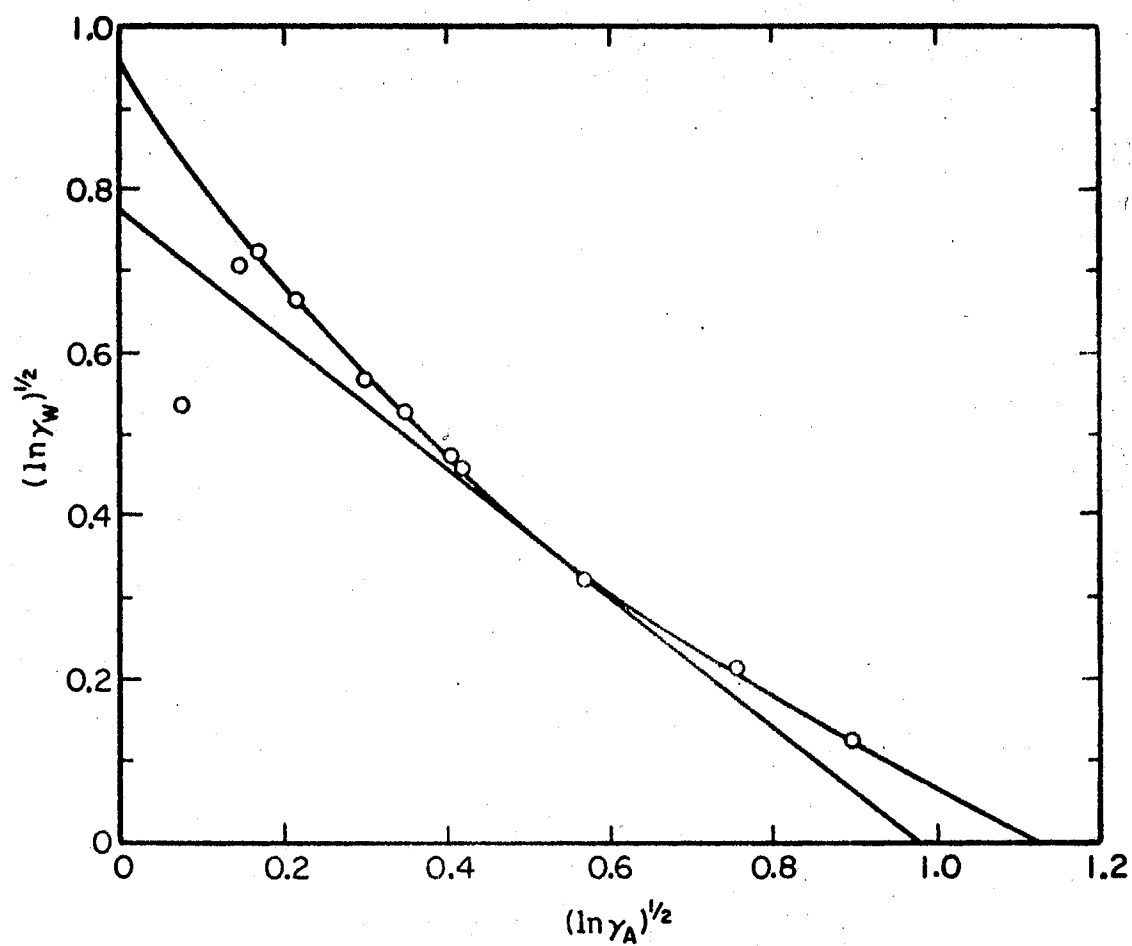


Figure 35.  $(\ln \gamma_W)^{1/2}$  Versus  $(\ln \gamma_A)^{1/2}$  Water-Acetic Acid System  
at 60° C

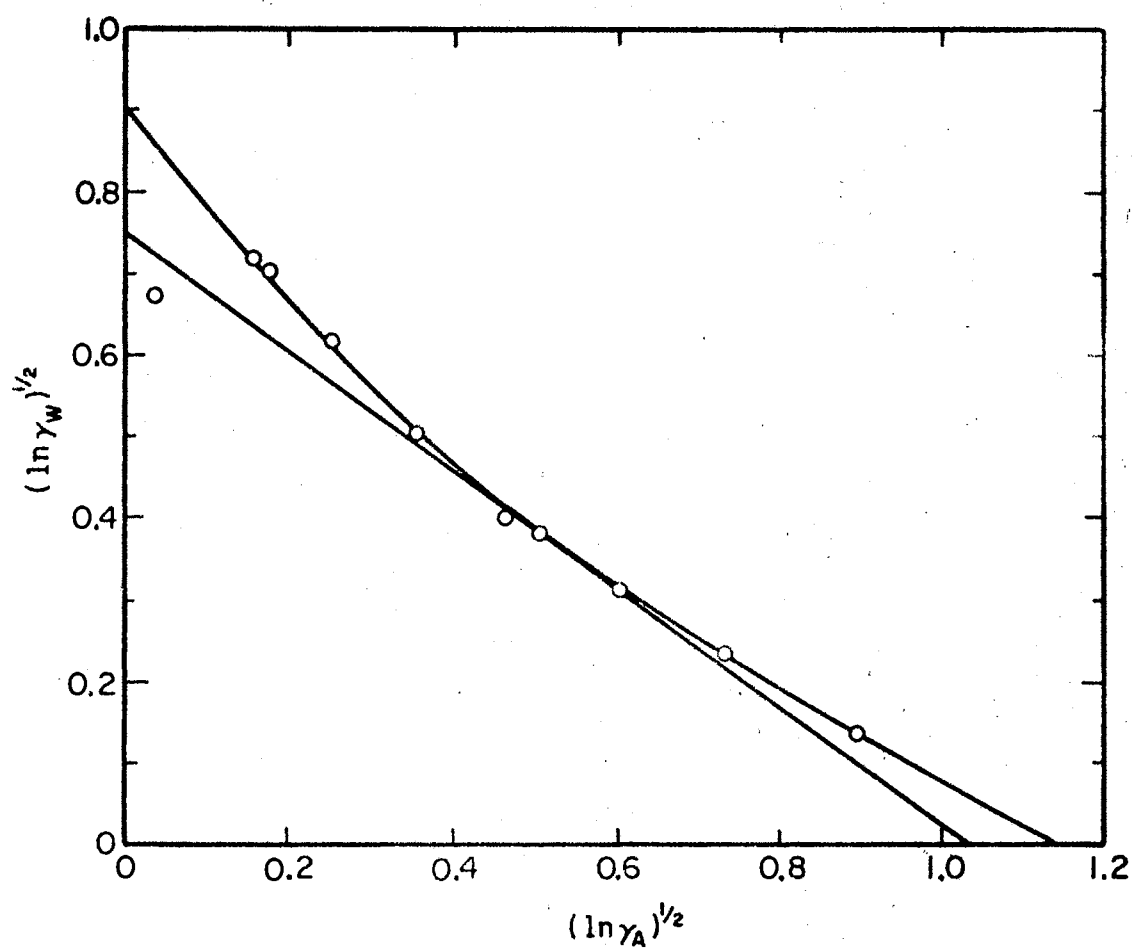


Figure 36.  $(\ln \gamma_W)^{1/2}$  Versus  $(\ln \gamma_A)^{1/2}$  Water-Acetic Acid System  
at 70°C

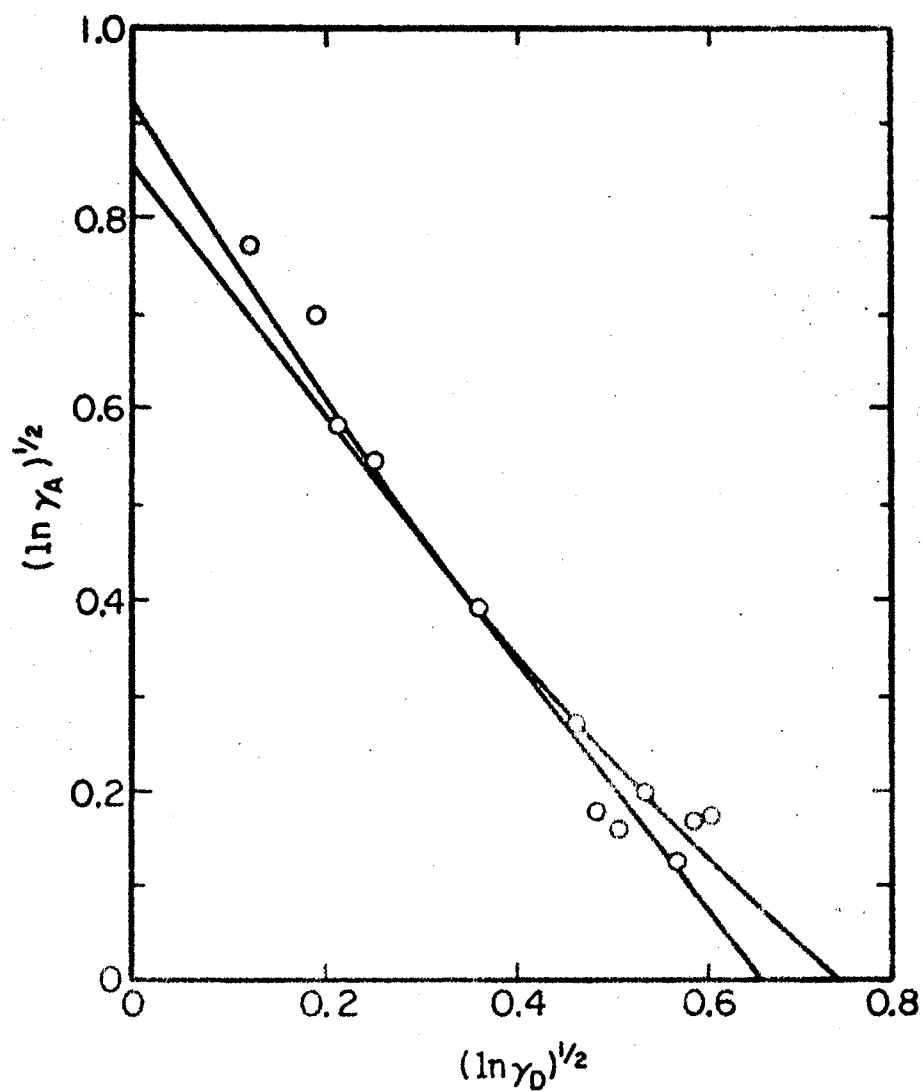


Figure 37.  $(\ln \gamma_D)^{1/2}$  Versus  $(\ln \gamma_A)^{1/2}$  Diethylketone-Acetic Acid System at 50°C

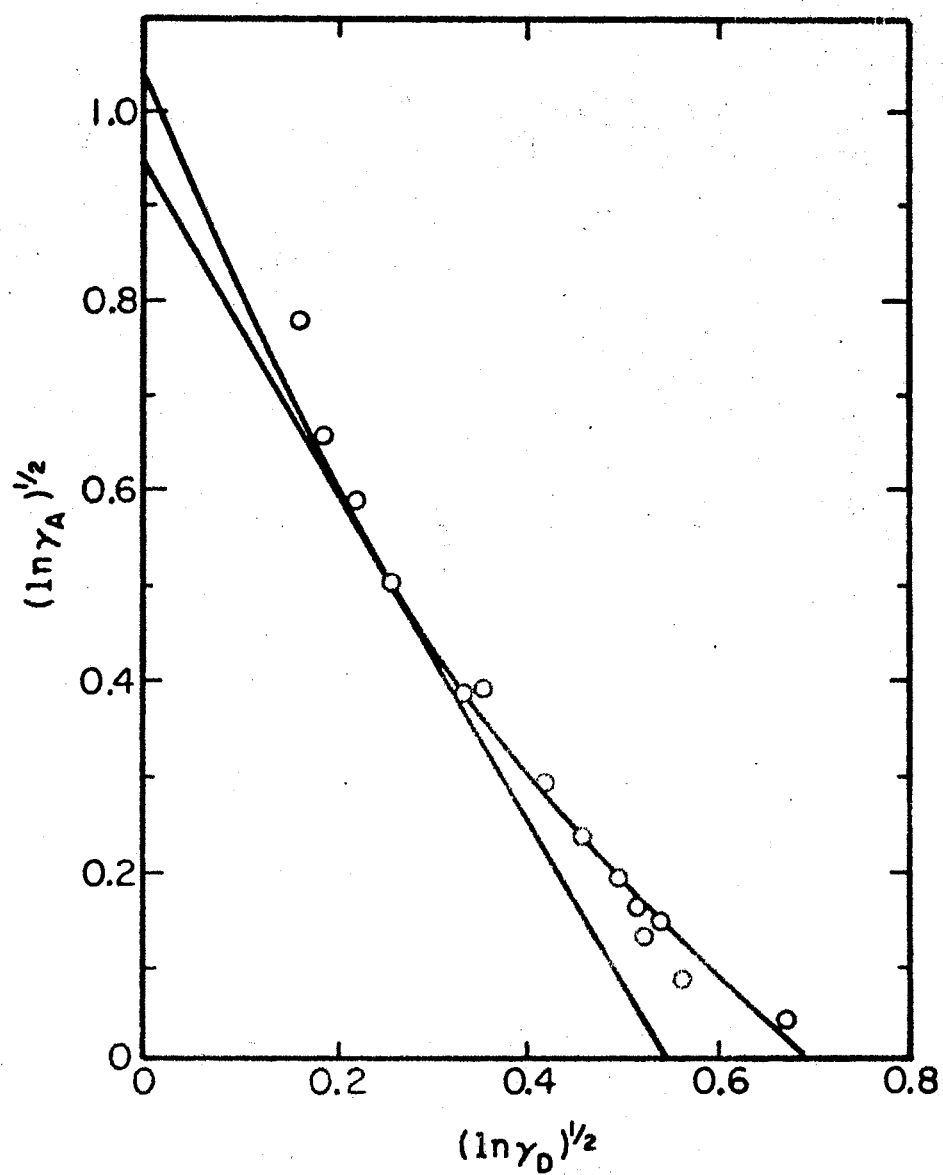


Figure 38.  $(\ln \gamma_D)^{1/2}$  Versus  $(\ln \gamma_A)^{1/2}$  Diethylketone-Acetic Acid System at 60°C

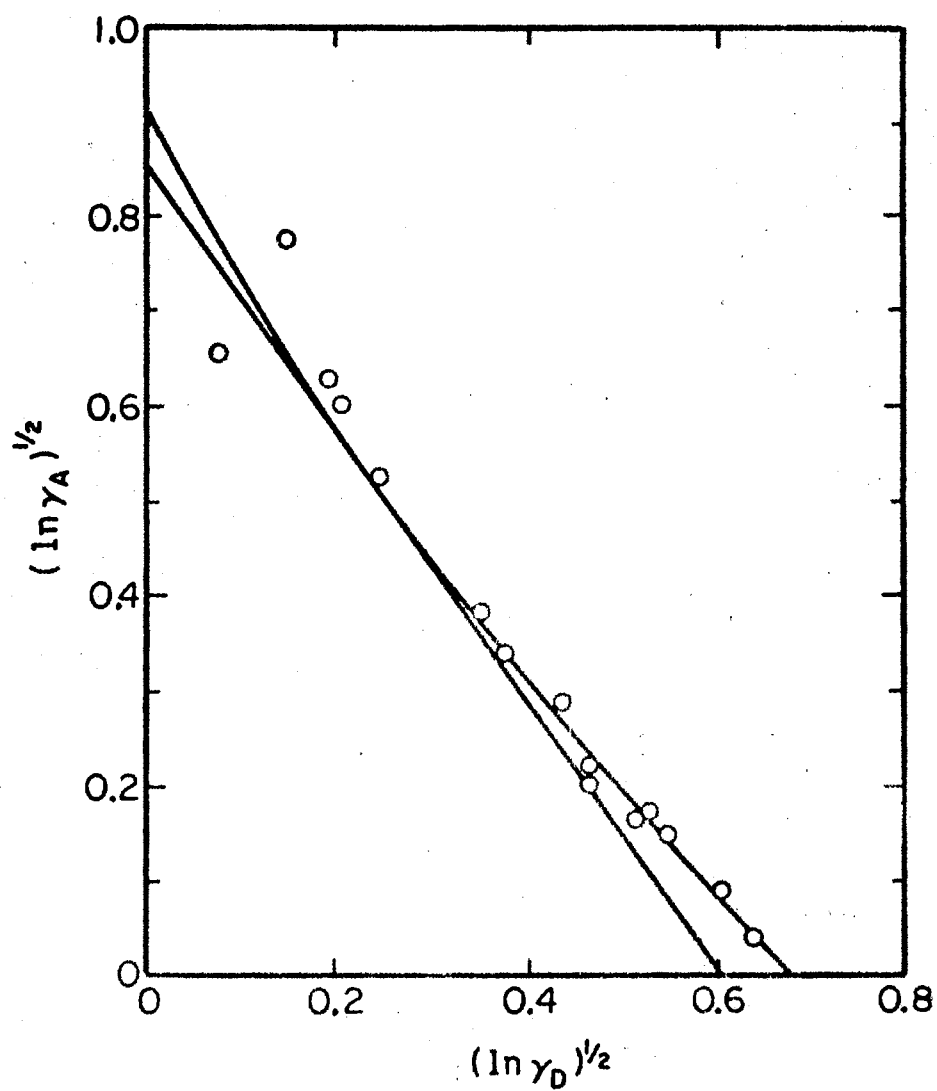


Figure 39.  $(\ln \gamma_D)^{1/2}$  Versus  $(\ln \gamma_A)^{1/2}$  Diethylketone-Acetic Acid System at 70°C

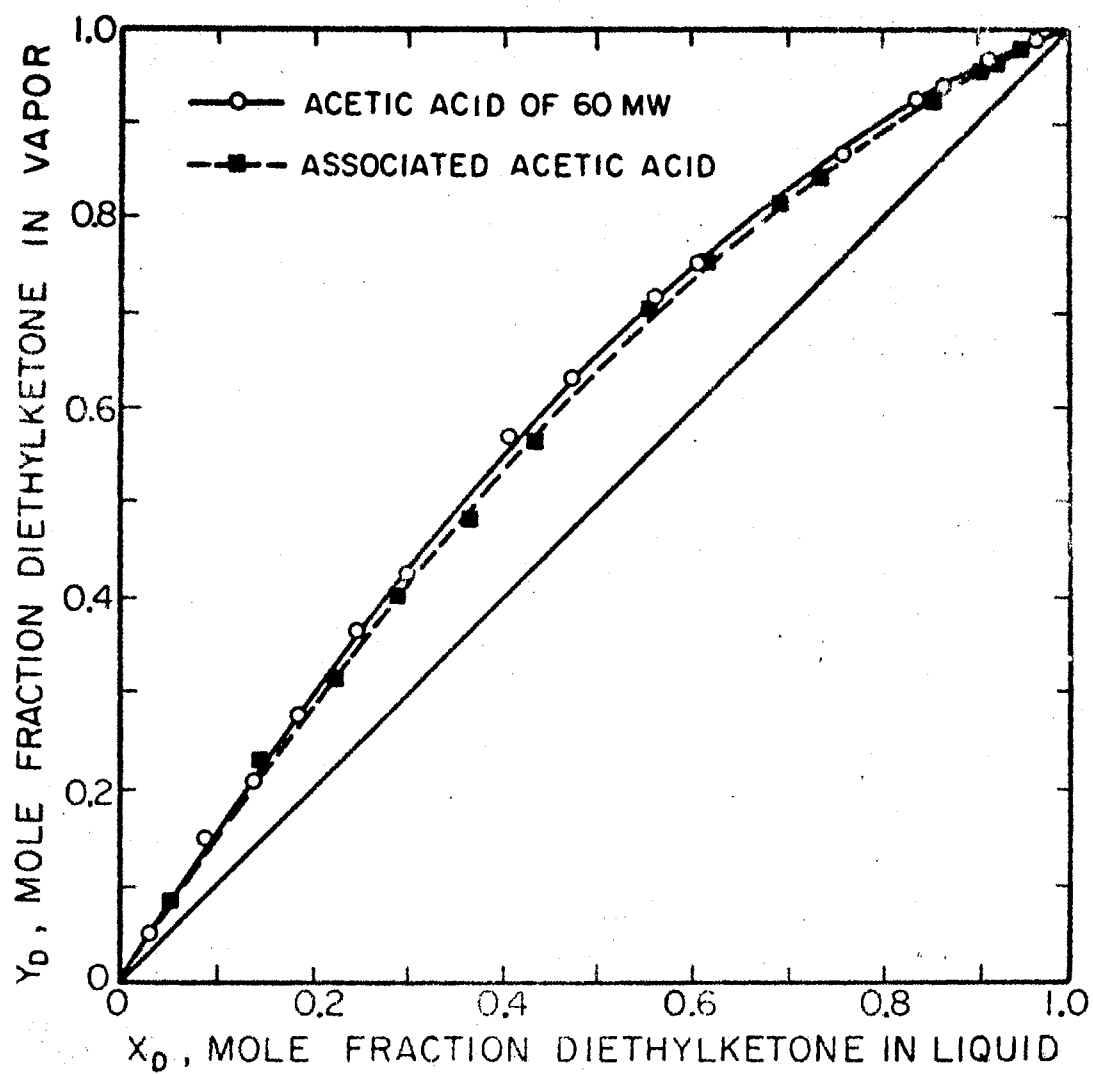


Figure 40. x-y Diagram Acetic Acid-Diethylketone System at 70° C (Associated Acetic Acid Molecular Weight Basis)

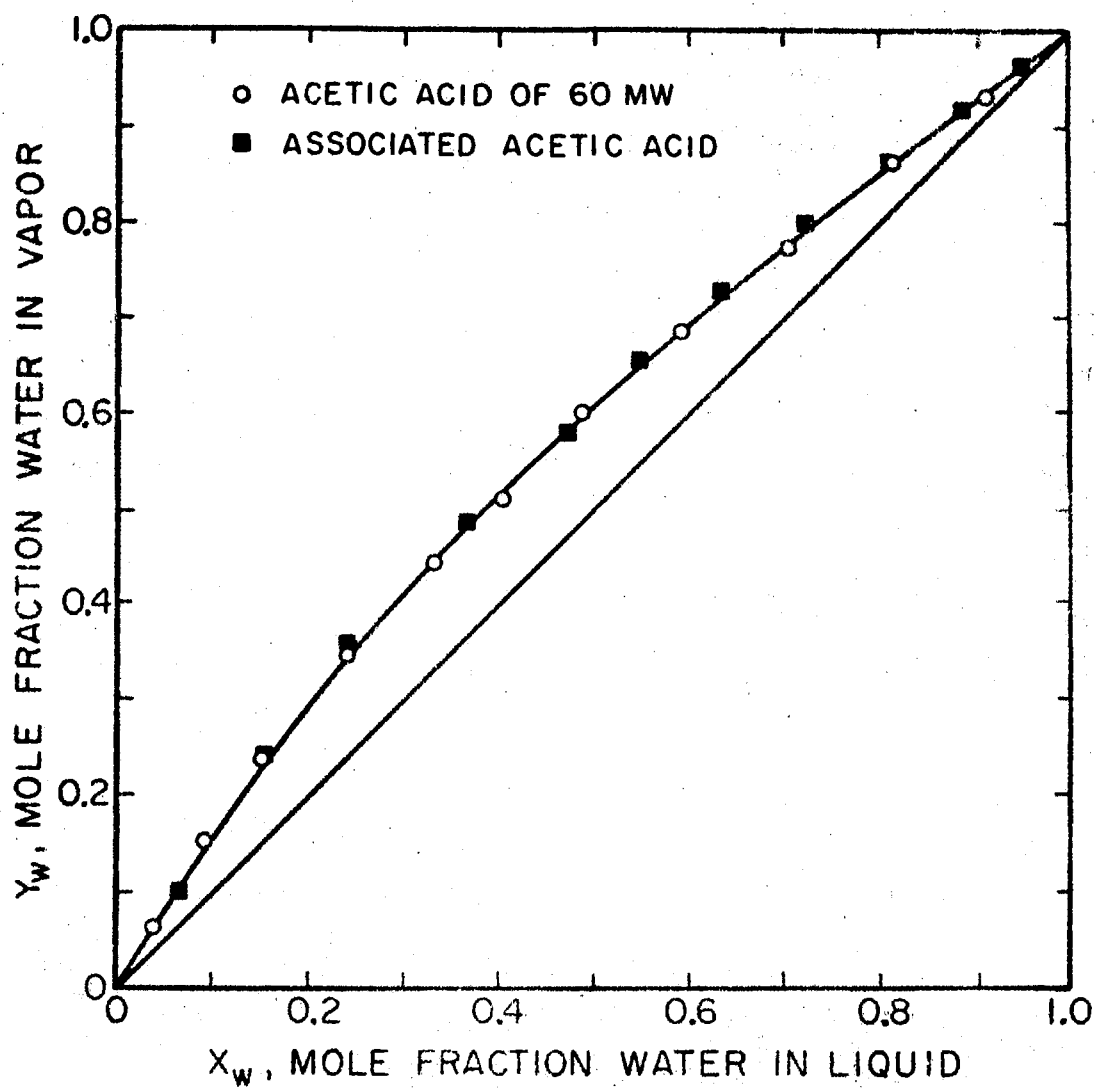


Figure 41. x-y Diagram Acetic Acid-Water System at 70° C  
(Associated Acetic Acid Molecular Weight Basis)

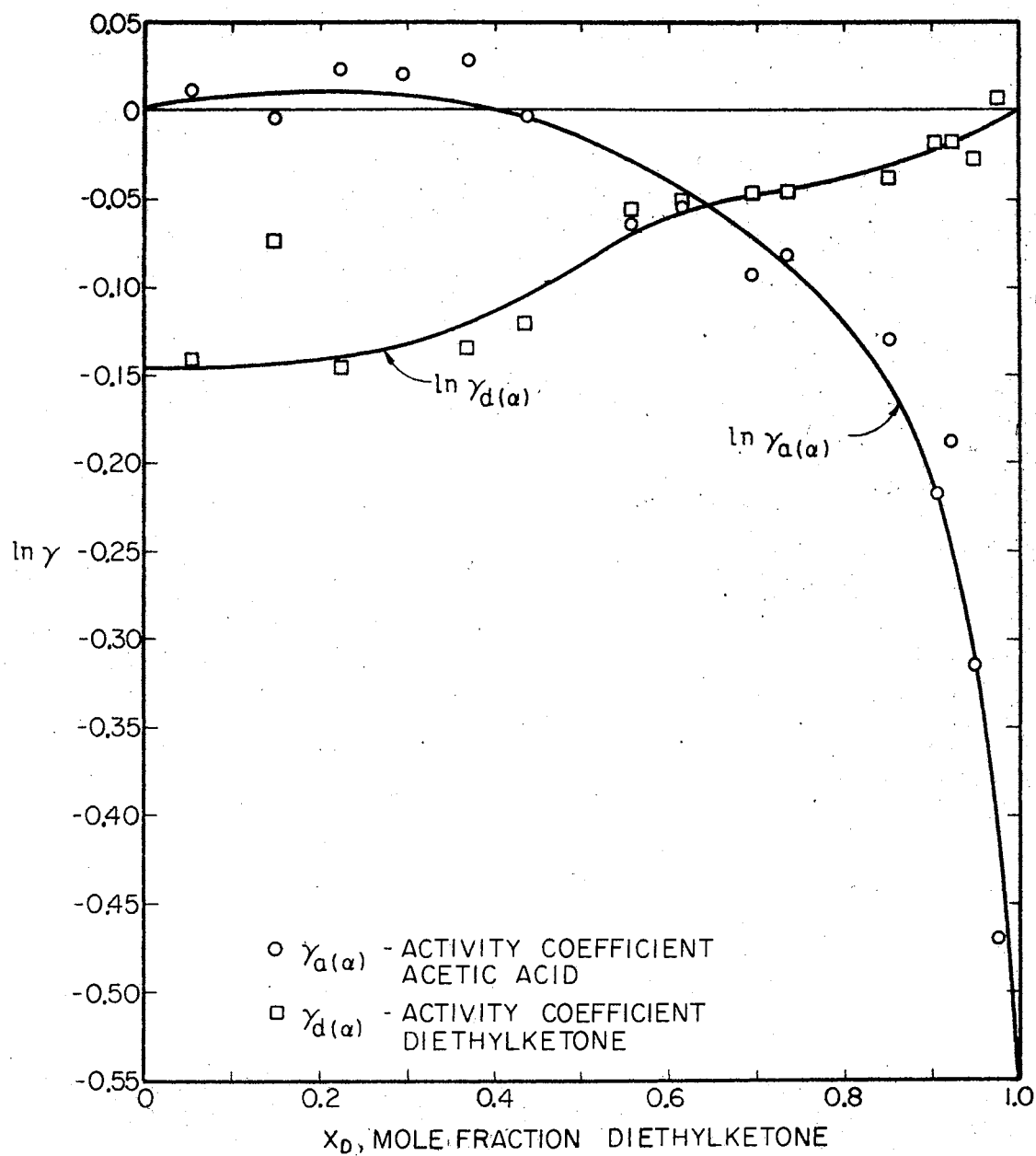


Figure 42. Activity Coefficient Versus Composition for Acetic Acid-Diethylketone System at 70° C (Associated Acetic Acid Molecular Weight Basis)



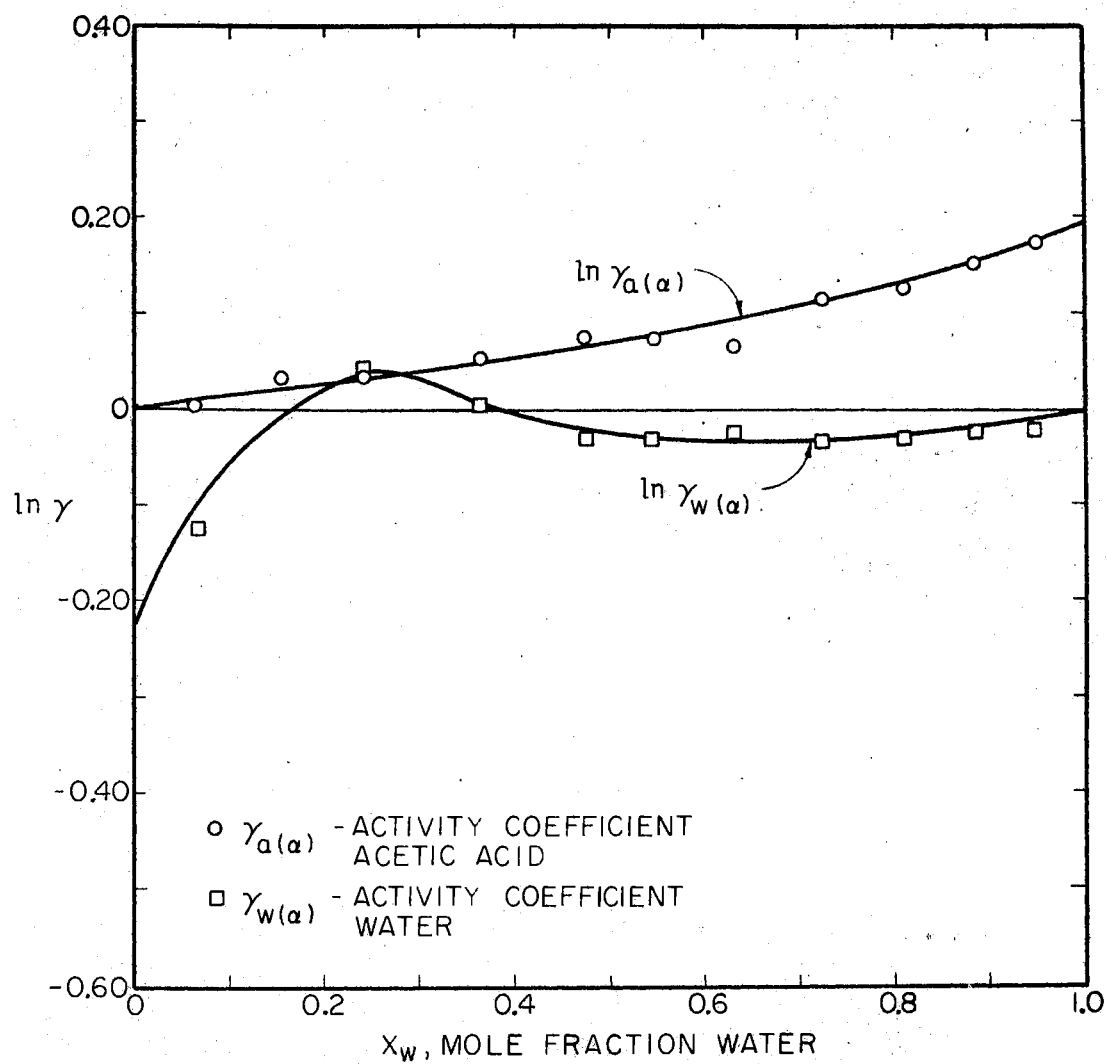


Figure 43. Activity Coefficient Versus Composition for Acetic Acid-Water System at 70° C (Associated Acetic Acid Molecular Weight Basis)

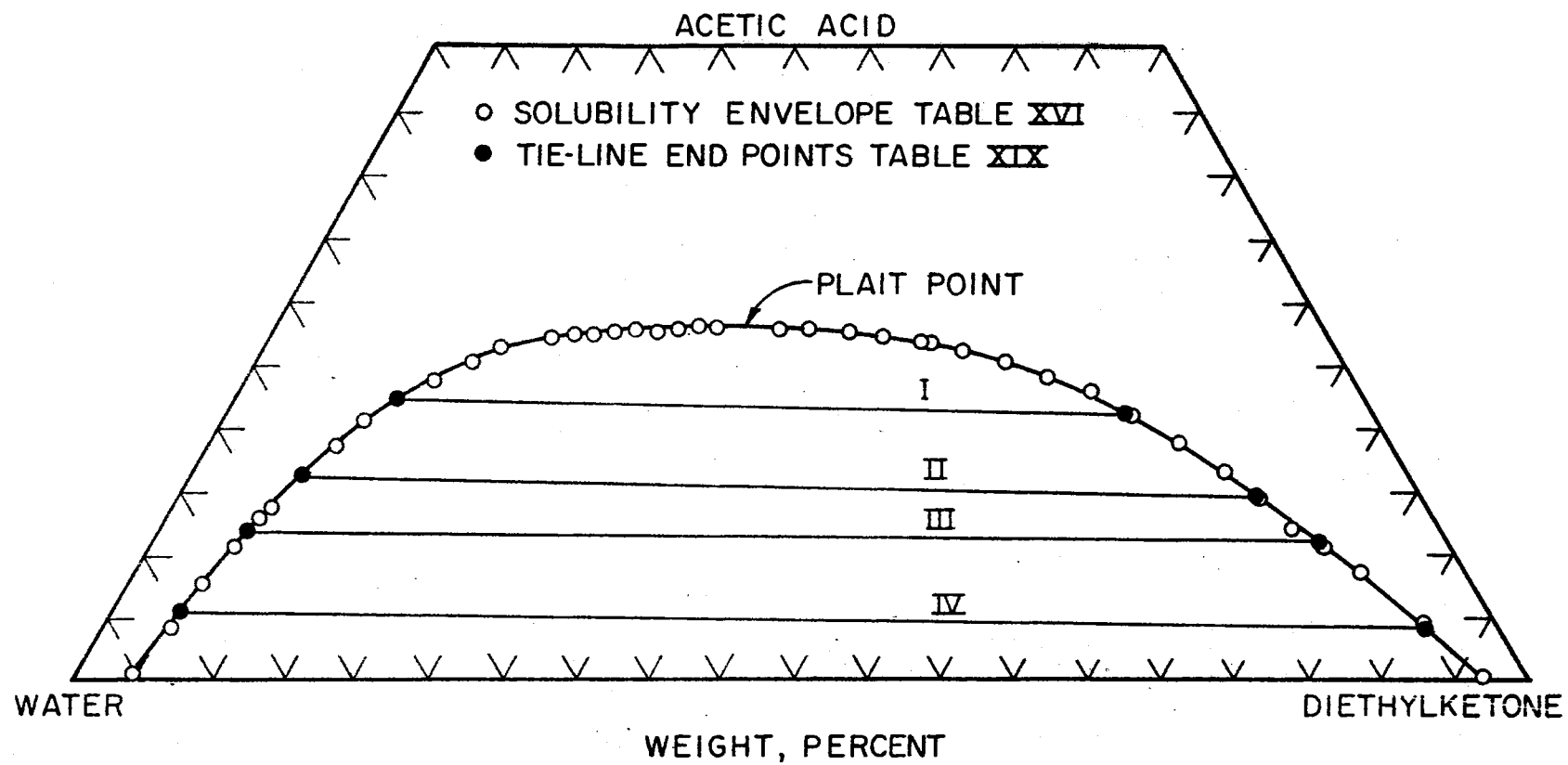


Figure 44. Composition Diagram Diethylketone-Water-Acetic Acid System at 50° C

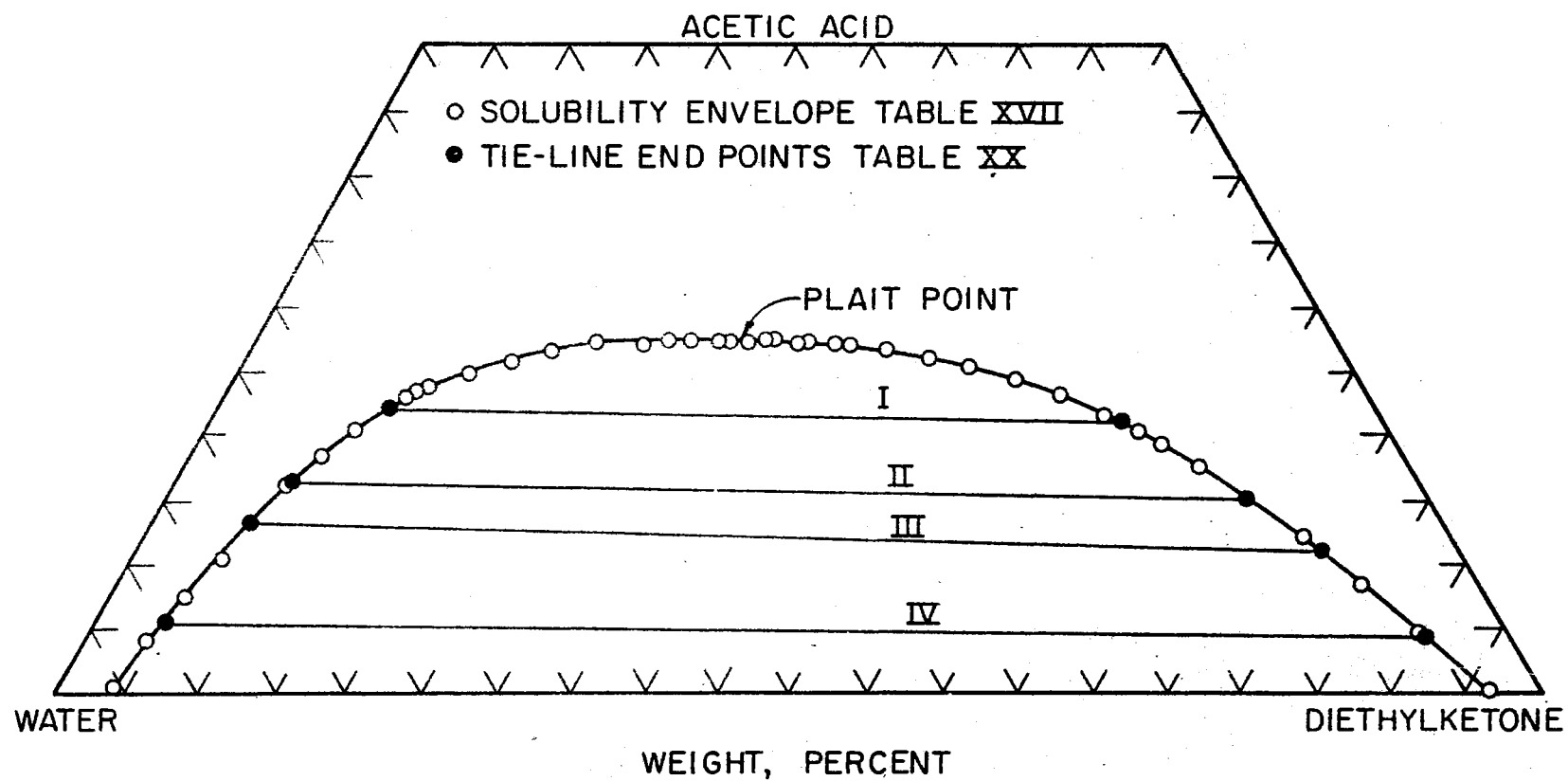


Figure 45. Composition Diagram Diethylketone-Water-Acetic Acid System at 60° C

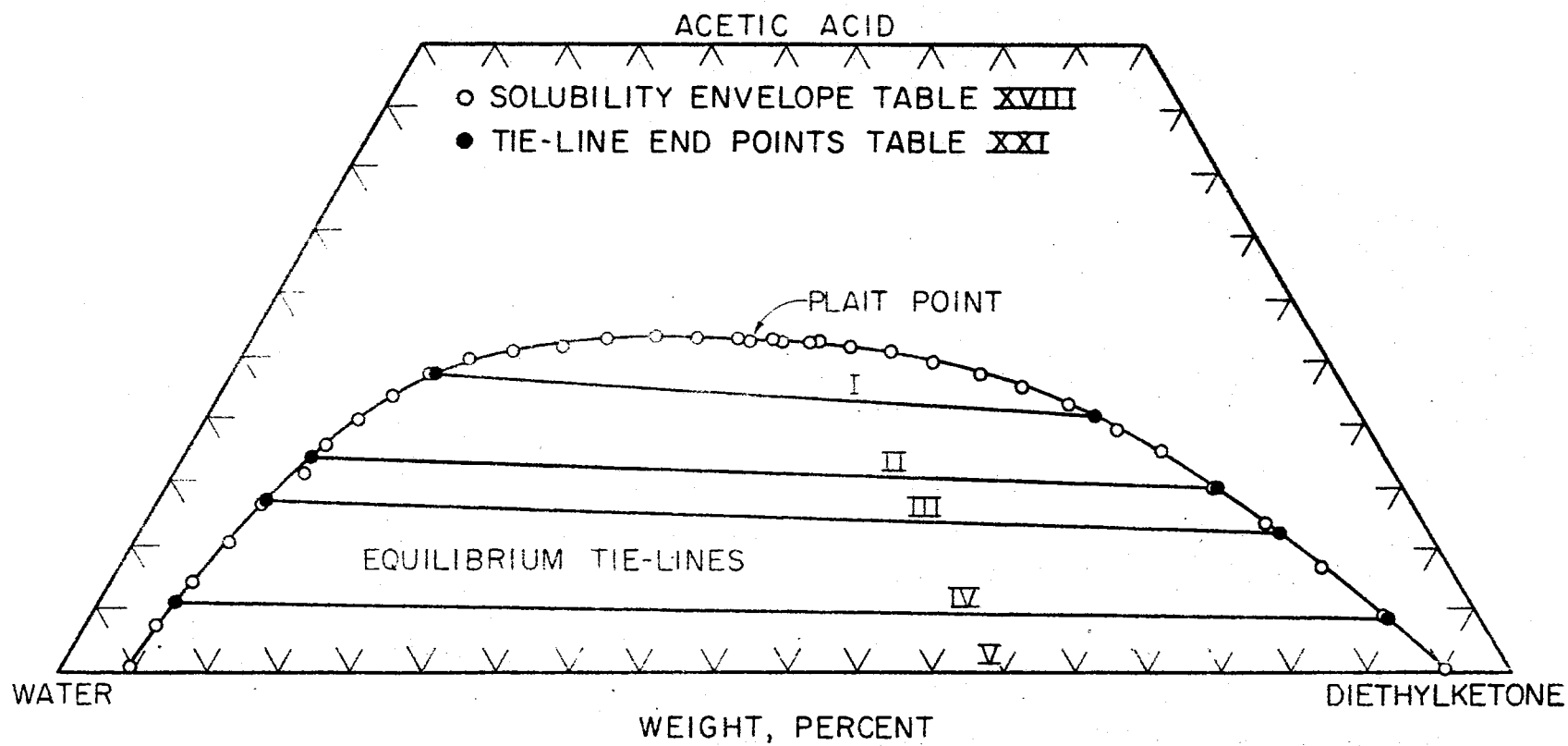


Figure 46. Composition Diagram Diethylketone-Water-Acetic Acid System at 70° C

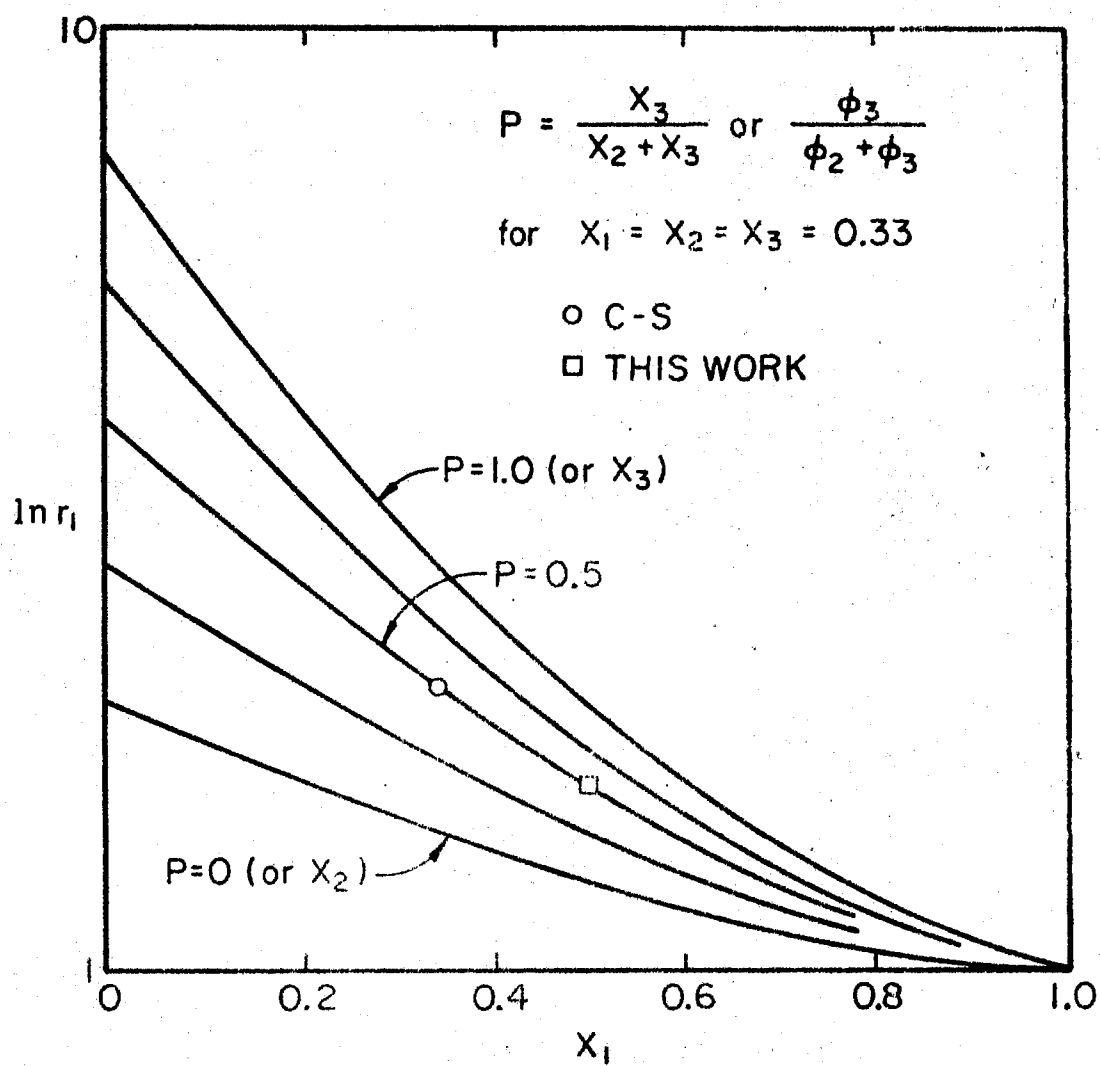


Figure 47. Comparison of Proposed Equation With Colburn Method

## VITA

Philip Otto Haddad

Candidate for the Degree of

Doctor of Philosophy

Thesis: PHASE EQUILIBRIA IN THE ACETIC ACID-DIETHYLKETONE-WATER SYSTEM

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Professional Experience: Employed in 1950 as engineering trainee by Deep Rock Oil Company, Cushing, Oklahoma; employed from 1951 to 1962 by Dow Chemical Company, Freeport, Texas in Magnesium Research and Magnesium Development, and worked in various capacities from Development Engineer to Production Specialist. Employed in 1962 by Standard Magnesium Corporation, Tulsa, Oklahoma as Director of Research and Development, and as a consultant. Entered Graduate College at Oklahoma State University in January, 1963. From October, 1965 until April, 1968 was engaged in developing a cell feed process for the newly formed American Magnesium Company. In June, 1968, rejoined the Dow Chemical Company as a Senior Production Specialist in the Magnesium Technology Center.