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THE EXPERIMENTAL DETERMINATION AND PREDICTION OF TERNARY-LIQUID EQUILIBRIA DATA

BY

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A

THESIS

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I. INTRODUCTION

Although the field of liquid extraction is of increasing importance in today's chemical industry, the ternary-liquid data so necessary to the design and study of extraction operations are available in the literature only to a limited extent. During the twentieth century, approximately 120 ternary-liquid systems have been studied. However, limiting solubility data have been reported for approximately one-third of these systems, and about 30 per cent of the equilibria data reported for the remainder of these systems are incomplete or inaccurate.

Within limits, liquid equilibria data may be calculated for a ternary system from the properties of its constituents which are readily available in the literature. As binary equilibria data are comparatively plentiful in the literature, it is clearly desirable to predict the ternary-liquid characteristics from this media. The proper choice of computational method is as inherent to the accuracy of equilibria prediction as the accuracy of the binary data used, and the physical properties of the ternary system itself.

A number of methods have been proposed in the past decade which could be useful in predicting the equilibria curves for ternary-liquid systems. It was believed that a comparison of the ternary-liquid equilibria data predicted for several systems by certain of these methods, with the experimental equilibria data obtained from the literature, would result in the development of rules governing the use and applicability of these prediction methods. Consequently, certain major prediction methods were chosen for study. These were: (1) the van Laar method, (2) the Margules method, (3) the van Laar and Margules methods modified by the use of the Colburn constant, (4) the van Laar and Margules methods as modified by Wohl, and (5) the Scheibel and Friedland method.

The purpose of this investigation was to determine experimentally the ternary-liquid solubility and equilibria data for a previously unreported ternary-liquid system, and to compare these data, along with the equilibria data obtained from the literature, for other ternary systems with those data approximated by five major prediction methods. The system chosen for experimental study consisted of methanol, water, and 1-nitropropane. Experimental systems reported in the literature and chosen for study were: (1) ethanol, ethyl acetate, water; (2) acetone, benzene, water; (3) acetic acid, benzene, water; (4) acetone, chloroform, water; and (5) cyclohexane, aniline, N-heptane. The results of this study were the formulation of a set of rules concerning the choice and application of methods for predicting ternary-liquid equilibria data.

II. LITERATURE REVIEW

The literature was reviewed for the purpose of (1) listing the major sources of ternary-liquid equilibria and solubility data, (2) studying the major methods in use for the prediction of ternary-liquid equilibria data, and (3) locating published systems for which the binary and ternary equilibria data were available so that the prediction methods could be compared with actual experimental results.

Sources of Ternary Equilibria Data

During this century, approximately 120 ternary-liquid systems have been studied. However, about one-third of the systems reported in the literature include only the limiting solubility data and much of the reported equilibrium data is incomplete or inaccurate.

In 1910 Bonner(6) made a list of all work done on ternary-liquid systems up to that time, and in 1929 the authors of the International Critical Tables(31) did essentially the same thing; but in neither case was any distinction made between the complete diagrams and those merely listing the solubility curve. Also, the data available in the International Critical Tables were so sketchy that all but four systems were presented graphically, and many of these were only partially complete.

As the extraction of liquids with other liquids became of great industrial importance, an interest in ternary-liquid equilibria data grew. Consequently, since 1929 a great deal of excellent work has been done in this field. This increase in the number of systems available encouraged other authors to organize and list these data in a logical manner. A few partial lists were compiled by Bachman(2) in 1940, Brancker(7) in 1940, Seidell(48) in 1941, and Smith(52) in 1942. Current listings became available with the advent of the yearly Unit Operations Review on Extraction in Industrial and Engineering Chemistry. Here, Elgin(14, 15, 16, 17) and later Treybal(55.....66) presented the systems and associated references studied in the year which was reviewed. The latest and most complete bibliography of available ternary-liquid systems was published in 1959 at the University of Texas(25). In this bulletin, Himmelblau presented the sources of approximately 120 aqueous ternary systems and approximately 40 nonaqueous ternary systems.

Sources of Binary Equilibria Data

There is a wealth of data with which to calculate activity coefficients, and hence activities of binary solutions. Thus, extending the binary data to ternary systems becomes a powerful tool in predicting the usefulness of solvents in liquid extraction processes. A few of the many sources of binary vapor-liquid equilibrium data are: (1) The International Critical Tables(31), (2) The Chemical Engineer's Handbook(41), and (3) Chu(13). Excellent azeotropic data from which activity coefficients may be calculated were compiled in 1952 by Horsley(26).

Binary Solution Constants

Extraction operations depend upon the fact that solutions which form immiscible liquid phases are of necessity extremely nonideal. The extent to which solutions depart from ideality is manifested by deviations of the properties of the solution from certain standard characteristics. If the equilibria relationships are to be predicted for ternary-liquid systems from these deviations in properties of its related binary systems, methods of expressing the binary deviations in a manner than may be extended to the ternary case are necessary. The most useful methods of expressing deviations of binary solutions from ideality are those which depend upon vapor-liquid equilibria, boiling points of solutions, or the formation of azeotropes. This is true because considerable information on these properties has now been accumulated in the literature for many mixtures.

Activity Coefficients. The advantages of extending binary vapor-liquid equilibria data to predict the equilibrium between two phases of a ternary-liquid mixture have been explained many times in the literature(10, 19, 23, 41, 52, 54). It was noted that the major advantage of this technique is the comparative availability of binary vapor-liquid equilibria data to ternary-liquid equilibria data. The customary manner of correlating binary vapor- liquid equilibria data, that is, to plot y, the mole fraction of the more volatile component in the vapor, against x, the mole fraction of the more volatile component in the liquid(7), results in curves which have little apparent order. Consequently, no convenient analytical method of expressing these relationships has been obtained for curves plotted in this manner. On the other hand, these data may be used to calculate the deviation factors from Raoult's Law, termed activity coefficients, to arrive at an orderly array of curves.

Raoult's Law states that the partial pressure of a component from a mixture is equal to the product of the vapor pressure of the pure component at the given temperature and mole fraction of the component in the mixture. When Raoult's Law holds, the mixture is considered ideal. When deviations are observed, the correction factor which is introduced into this relation is called the activity coefficient. The liquid composition, vapor composition, and equilibrium temperature data as reported for most binary vapor-liquid systems may be expressed as activity coefficients. Activity coefficients are defined by Equation 1.

$$g_1 = (P\ y_1)/(x_1\ p_1) \qquad (1)$$

where:

g_1 = activity coefficient, unitless

p_1 = vapor pressure of pure component at given temperature, pressure units

x_1 = composition of component in liquid, mole fraction

y_1 = composition of component in vapor, mole fraction

P = total pressure on system, pressure units

The obvious advantages of this technique is that orderly and consistant curves result from a plot of the logarithm of the activity coefficient against the associated liquid composition. From these plots, binary constants relating the properties of the binary liquid system to the related ternary system may be obtained.

Margules Equation for Binary Systems. Starting from the Gibbs-Duhem Equation(32), Margules(68) assumed that the relationship between activity coefficients and concentration could be expressed by a geometric series expansion in terms of concentration, where the number of terms required would depend upon the degree of non-ideality of the binary system considered. A somewhat similar approach is given by Redlich, Kister, and Turnquist(43). However, the algegraic form of their final equation makes the determination of the constants more difficult. Also, the constants cannot be extended directly to the ternary-liquid case. The original Margules equations were revised by Carlson and Colburn(10) so the constants have the property of being equal to the terminal values of the logarithm of the activity coefficients. So expressed, the Margules equations are:

$$\log g_1 = (2B - A)\, x_2^2 + 2(A - B)\, x_2^3 \qquad (2)$$

$$\log g_2 = (2A - B)\, x_1^2 + 2(B - A)\, x_1^3 \qquad (3)$$

where:

g = activity coefficient, unitless

x = liquid composition, mole fraction

A = constant for binary system, unitless

B = constant for binary system, unitless.

It is observed that at $x_1 \to 0$, $\log g_1 = A$ and $\log g_2 = 0$, also at $x_1 \to 1$, $\log g_1 = 0$ and $\log g_2 = B$. This form satisfies the limiting condition that Raoult's Law holds for a component whose concentration approaches 100 mole per cent.

van Laar Equations for Binary Systems. Equations other than the Margules equations have been worked out on the basis of different assumptions with respect to the size of the molecular groups which affect the excess free energy, and the relative magnitudes of the molar volumes of the constituents of the solution(5, 24, 27, 36). The most important of these for present purposes are the van Laar equations as revised by Carlson and Colburn(10). These equations are:

$$\log g_1 = A/(1 + Ax_1/Bx_2)^2 \tag{4}$$

$$\log g_2 = B/(1 + Bx_2/Ax_1)^2 \tag{5}$$

where:

g = activity coefficient, unitless

x = liquid composition, mole fraction

A = constant for binary system, unitless

B = constant for binary system, unitless.

The van Laar equations may be derived by several methods. Robinson and Gilliland(46) discuss the theoretical approach used by van Laar and the empirical derivation is presented by Cooper(12). Wohl(68) presents a generalized theoretical derivation.

Limitations. Although these equations, the Margules and the van Laar, represent satisfactorily a large share of existing reliable data, some precautions are necessary in their use. These have to be considered chiefly where the physical properties of the vapors depart appreciably from the ideal. In general, the Margules equations are quantitatively most useful for relatively symmetrical systems(53), that is, where the absolute value of A nearly equals the absolute value of B. The van Laar equations can satisfactorily follow data showing high values of A and B and greater dissymmetry than the Margules equations, but large ratios of A to B cannot be handled. The van Laar equations fit the cases where the ratio of A to B is in the neighborhood of two better than the Margules equations(53).

Calculation of Binary Constants from Azeotropic Data. When complete measurements of the equilibrium liquid and vapor compositions are lacking, one may estimate the binary constants for extrapolation to the ternary-liquid case from an azeotropic composition. A wealth of azeotropic data has been tabulated by Horsley(25). Since the azeotropic liquid and vapor compositions are identical, the activity coefficients defined by Equation 1 simplify to:

$$g_1 = P/p_1 \tag{6}$$

$$g_2 = P/p_2 \tag{7}$$

where:

g = activity coefficient, unitless

P = total pressure, pressure units

p_1 = vapor pressure of pure component at given temperature, pressure units.

From these two values of activity coefficients and their associated concentrations, the binary constants A and B, may be calculated from the appropriate integrated Gibbs-Duhem equation. Greatest precision will result if the single datum is known at a liquid composition between 0.25 and 0.75(1).

Calculation of Binary Constants from Vapor-Liquid Data. Vapor-liquid equilibria data are reported as liquid composition, vapor composition, and equilibrium temperature at a constant pressure. From such data and Equation 1, page 6, activity coefficients as a function of liquid composition may be calculated. Since the end value of the log of the activity coefficient is equal to one of the binary constants(10), the values of the binary constants, A and B, may then be determined by extrapolating a curve of log activity coefficient of component one as a function of composition of component one to the point where the composition of component one equals unity. Similarly, at the point where the second composition equals unity, the other constant is found. This procedure, while simple and common, is not usually recommended since the values of the activity coefficients are most often in error in the low concentration ranges where the extrapolation is carried out(44).

A preferable method is to rearrange the appropriate equation to the standard point-slope form for a straight line(33) and extrapolate from the best straight line fit. Reid(44) suggests that the line should be drawn through the points resulting from the high concentrations, as at low concentrations the values often become erratic.

Calculation of Binary Constants from Mutual Solubility Data. Binary liquid systems frequently form two liquid phases over a range of compositions. Since the activity of a component is the same in each liquid phase at constant temperature, it is possible to calculate the binary constants from measurements of liquid-liquid solubility.

For systems which are mutually insoluble, the binary constants may be calculated by the method described in detail by Scatchard(47), Carlson(10), and Treybal(53). The basis for this method involves the principal that "In any two phases at equilibrium, including two liquid phases, the fugacities of each component are the same in the two phases. Provided that the same standard state for a substance is chosen for its conditions in each phase, the activities of the substance in each phase are also equal"(53).

Prediction of Distribution

For the prediction of the distribution of a solute between partially miscible solvents from a minimum of data, the general procedure which could presumably be followed would be to establish values of activity coefficients in the three binary systems from the various types of binary data as described in the previous sections. From these binary activity coefficients, predictions of activity coefficients and activities in the ternary systems can be made by the use of the ternary integrated Gibbs-Duhem equations, or some other method justified by thermodynamics or empirical evidence. Equilibrium ternary-liquid layers then exist where activities of all three components are equal(52).

Unfortunately, the activity coefficient equations cannot be made explicit in terms of the liquid composition, and the location of the constant activity curves on the triangular extraction diagram is possible only by a lengthy series of interpolations. Location of the triple intersection points becomes an even more impractical and difficult trial and error procedure. On these grounds, the use of the ternary activity coefficient equations is limited to cases where the solubility curve of the ternary-liquid system is known. For such a situation, it is merely necessary to use some method to compute the activities of the solute along the known solubility curve and to join equal values on opposite sides of the curve by the tie lines. The problem is, in this case, to chose the most appropriate equation or method of calculating the activities of the solute along the solubility curve.

Previous Methods. Othmer and Tobias(39) described a method of predicting the distribution of a solute between two immiscible solvents based on partial pressure data for the two binary solutions formed with the solute and the two solvents. Carlson and Colburn(10) described a method for predicting the ternary equilibria data which they considered unsatisfactory because it was not in agreement with the Gibbs-Duhem equation in a hypothetical case. Colburn and Schoehborn(71) found that this method of Carlson gave good agreement with the data for a ternary system involving one ideal binary mixture, but observed that it could not be applied where all three binary systems were non-ideal. White(69) applied the 2-suffix van Laar equation to the analysis of ternary equilibria data, and proposed methods for evaluating the necessary constants. The method was applied(69) to three ternary systems which involved one ideal binary mixture and the agreement was good. However, it was not applied to systems where all of the binary systems were non-ideal. Treybal(53) presented several of the simpler methods for predicting ternary-liquid distribution. However, he did not apply them to the same systems. Therefore, very little comparison of their application was possible. Scheibel and Friedland(70) presented an interesting empirical method which gave good results on three systems. It should be pointed out that Treybal(53) is the only one of the above mentioned authors whose chief concern was liquid-liquid systems. The remainder were primarily interested in ternary vapor-liquid equilibrium, and even though the thermodynamic principles are the same, they just briefly mentioned liquid-liquid systems.

The most complete theoretical background on the various integrated forms of the Gibbs-Duehm equation is presented by Wohl(68) who showed that all of the major forms, as the van Laar and Margules equations, were merely modifications and simplifications of a more complicated equation.

Wohl termed this equation the "q" equation. From this equation, which contains eleven binary constants and three ternary constants, other simpler forms may be derived. In a personal communication to Treybal(11), Colburn suggested an additional constant calculated from the binary activity coefficients to the standard 3-suffix van Laar equation. The use of this constant in the prediction of ternary-liquid distribution data, as well as the use of several of Wohl's equations, has not been reported in the literature.

The "q" Equation. The basic equation derived by Wohl(68) by relating the contributions to the excess free energy of interactions of unlike molecules in groups of two, three, four, etc., with the ultimate size of the groups considered characterizing the resulting equation, is termed the "q" equation. If molecular groups of two and three are considered, a "three-suffix" equation results. The most general "q" equation is a four-suffix equation which leads to subsequent simplifications. These simplifications have a smaller number of constants and thus are the more practical. The four-suffix "q" equation is given by Equation 8.

$$\log g_1 = Z_2^{\,2} \left[A_{12} + 2Z_1 \left(A_{12}\frac{q1}{q2} - A_{12}\right) \right] + Z_3^{\,2} A_{13} +$$

$$2Z_1 Z_3^{\,2} \left(A_{31}\frac{q1}{q3} - A_{13}\right) + Z_2 Z_3 \left(A_{21}\frac{q1}{q2} + A_{13}\right) -$$

$$Z_2 Z_3 \left(A_{32}\frac{q1}{q3}\right) + 2Z_1 Z_2 Z_3 \left(A_{31}\frac{q1}{q3} - A_{13}\right) +$$

$$2Z_3^{\,2} Z_2 \left(A_{32}\frac{q1}{q3} - A_{23}\frac{q1}{q2}\right) - Z_2 Z_3\, C\,(1-2Z_1) \qquad (8)$$

$$Z_i = \frac{X_i\left(\frac{qi}{q1}\right)}{X_1 + \frac{q2}{q1}X_2 + \frac{q3}{q1}X_3} \qquad (9)$$

where:

g = activity coefficient, unitless

X = composition, mole fraction

q = arbitrary factor replacing the molal volume

Z = effective volume fraction, unitless

C = constant from ternary equilibrium data

A = binary solution constants

Subscripts:

1 = solute

2 = solvent

3 = carrier

The binary constants, A_{12}, A_{21}, etc. are defined as follows: (10)

$\text{limit} \log g_1 \; (x_1 \rightarrow 0,\ x_2 \rightarrow 1) = A_{12}$

$\text{limit} \log g_1 \; (x_1 \rightarrow 0,\ x_3 \rightarrow 1) = A_{13}$

$\text{limit} \log g_2 \; (x_2 \rightarrow 0,\ x_3 \rightarrow 1) = A_{23}$

$\text{limit} \log g_2 \; (x_2 \rightarrow 0,\ x_1 \rightarrow 1) = A_{21}$

$\text{limit} \log g_3 \; (x_3 \rightarrow 0,\ x_1 \rightarrow 1) = A_{31}$

$\text{limit} \log g_3 \; (x_3 \rightarrow 0,\ x_2 \rightarrow 1) = A_{32}$

The "A" terms occurring in Equation 8 represent the limit of the logarithms of the binary activity coefficients as defined in Equation 10. These terms, known as binary solution constants, present a means of extrapolating binary equilibria data to the ternary-liquid case. The evaluation of the ternary constant, C, requires one known piece of ternary-liquid equilibrium data. However, Colburn(11) suggested that as an approximation, C may be calculated in the following manner:

$$C = \tfrac{1}{2}(A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23}) \qquad (11)$$

The Colburn constant, however, has not been previously applied to ternary-liquid equilibria data. If this constant is valid, it would be feasible to use it with various simplifications of the "q" equation to predict ternary distribution from the binary data and ternary-liquid solubility data. The "q" equation simplifies to various forms of the van Laar and Margules equations.

Ternary van Laar Equation. The "q" equation is simplified to the van Laar equation by the addition of the van Laar conditions(68). These conditions are:

$$(q1/q2) = (A_{12}/A_{21}) \qquad (12)$$

$$(q1/q3) = (A_{13}/A_{31}) \qquad (13)$$

$$(q2/q3) = (A_{23}/A_{32}) \qquad (14)$$

A = binary constant, unitless

q = effective molal volume, volume units

Subscripts 1, 2, 3 correspond to the components of the mixture.

If these restrictions are substituted in the general equation, Equation 8, for the various "q" fractions, and the ternary constant, C, is set at zero, the standard 2-suffix van Laar equation for the ternary case will result. This resulting equation has been applied to the ternary-liquid case with moderate success(54). If these van Laar restrictions are substituted in the general equation and the ternary constant is allowed to remain, the 3-suffix van Laar equation for the ternary case will result. Although the 3-suffix van Laar equation has not been applied to the ternary-liquid case, it is supposed that the additional constant would lead to more accurate results. This introduces the question, would the 3-suffix van Laar equation combined with the ternary constant defined by Equation 11 be superior to the standard 2-suffix van Laar? It should be noted that the van Laar equations are restricted by the conditions defined in Equations 12, 13, and 14. This situation may be checked by the following equation:

$$(A_{13}/A_{31})\ (A_{32}/A_{23}) = (A_{12}/A_{21}) \tag{15}$$

where:

A = binary constant, unitless

1 = solute, unitless

2 = solvent, unitless

3 = carrier, unitless

If this relationship holds for a particular system, it is valid to use a van Laar expression to predict the ternary effects. How great the deviation can be without invalidating the van Laar equations is not known.

Ternary Margules Equations. The ternary Margules equation may be obtained from the general "q" equation, Equation 8, by the substitution of the following relationships for the "q" fractions:

$$q1/q2 = q1/q3 = 1 \tag{16}$$

where:

q = effective molal volume, volume units

1 = solute, unitless

2 = solvent, unitless

3 = carrier, unitless

If the ternary constant, C, is considered, a 3-suffix Margules equation results. On the other hand, if the ternary constant is set at zero, a 2-suffix Margules equation results. In these cases, the binary terms are entirely independent of each other so that the restrictions imposed on them by Equation 15, which limit the applicability of the ternary van Laar equations from the start, do not exist for the Margules equations. As in the case of the van Laar equations, the ternary constant, C, may be calculated from the equation of Colburn, Equation 11, page 15.

Empirical Method. Scheibel and Friedland predicted ternary vapor-liquid equilibria from equilibria data of the three binary systems composing the ternary system. This prediction was done by an empirical-graphical technique(70). This graphical technique, when correlated with the ternary-liquid mutual solubility data for a two-phase liquid system, may be used to predict the equilibria distribution of components between the two phases. The basis of this empirical method, as presented by Scheibel and Friedland, resulted from "a careful analysis of the equilibria data presented in a previous paper."(70) This method is merely a totally empirical method of interpolating binary activity coefficients to the ternary case.

Scheibel and Friedland define three types of ternary mixtures on the basis of the deviation of the related binary systems from Raoult's Law, and a different method of correlation is presented for each type. The deviations from Raoult's Law will result in activity coefficients which are either less than or greater than unity, and for these cases the deviations are defined as negative or positive, respectively.

<u>Type I</u>. Ternary systems that compose this type are made up of the three binary systems which all show the same deviations, either all positive or all negative.

<u>Type II</u>. Ternary systems that compose this type are made up of one ideal binary system and two non-ideal systems, both of which give the same qualitative deviations from Raoult's Law.

<u>Type III</u>. Ternary systems that compose this type are made up of three non-ideal binary systems, but one binary exhibits a different qualitative deviation from Raoult's Law than the other two. That is, all of the binaries are non-ideal, but one of them shows a positive deviation from Raoult's Law while the other two show negative deviations or vice-versa.

Figure 1, page 19, shows a ternary diagram for components 1, 2, and 3. Line 1-2 represents the binary 1 and 2 with pure liquid 1 at point 1, and pure liquid 2 at point 2. Values of the activity coefficients of component 1 have been superimposed on the liquid composition coordinates of line 1-2. Similar reasoning applies to lines 1-3 and 2-3. The method proposed by Scheibel and Friedland lays down empirical rules for drawing the lines of constant activity coefficients for all components. To extend the method to ternary liquid-liquid systems, it is only

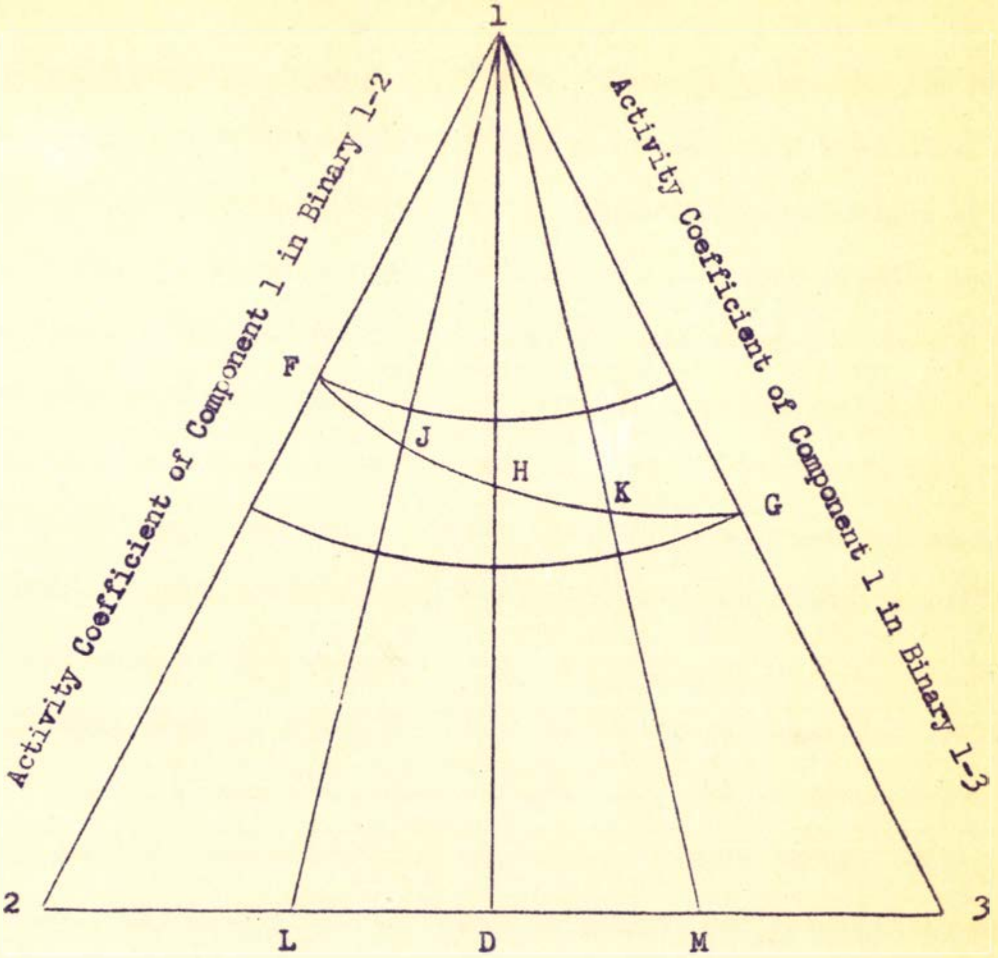


Figure 1. Estimation of Constant Activity Coefficient Curve for Ternary Systems with Three Non-Ideal Binaries Having Similar Deviations From Raoult's Law

necessary to extrapolate the lines for the activity coefficients of the solute. The rules for extrapolating the activity coefficient lines are as follows:

<u>Construction of Type I</u>. Refer to Figure 1, page 19. To draw the constant activity coefficient lines, assume that the radial length from 1 between 1F and 1G is proportional to the angle of the radial line. In other words, if the bisector of angle 2-1-3 is 1D, the distance 1H is the mean of 1F and 1G. Likewise, if lines 1L and LM are bisectors of angles 2-1-D and D-1-3, then distances 1J and 1K are mean values of 1F plus 1H and 1H plus 1G, respectively. The curve FJHKG represents the constant activity coefficient curve for one value. Other curves for different values of activity coefficients are drawn in a similar manner.

<u>Construction of Type II</u>. Refer to Figure 2, page 21. In this case, binary 1-2 exhibits values of activity coefficients always greater than or less than unity, and binary 1-3 is ideal. For the ideal case, the activity coefficient is unity, and independent of concentration. Thus, it is assumed that the activity coefficient of 1 is only a function of the amount of 2 present. So, the lines of constant activity coefficient for 1 will be parallel to side 1-3 and drawn to intersect 1-2 at the appropriate concentration.

<u>Construction of Type III</u>. Refer to Figure 3, page 22. In this case, binary 1-2 shows positive deviations from Raoult's Law, and binary 1-3 shows negative deviations. It is assumed that the bisector of angle 2-1-3 represents the constant activity coefficient line of unity, while lines QP and RS, parallel to 1D, represent

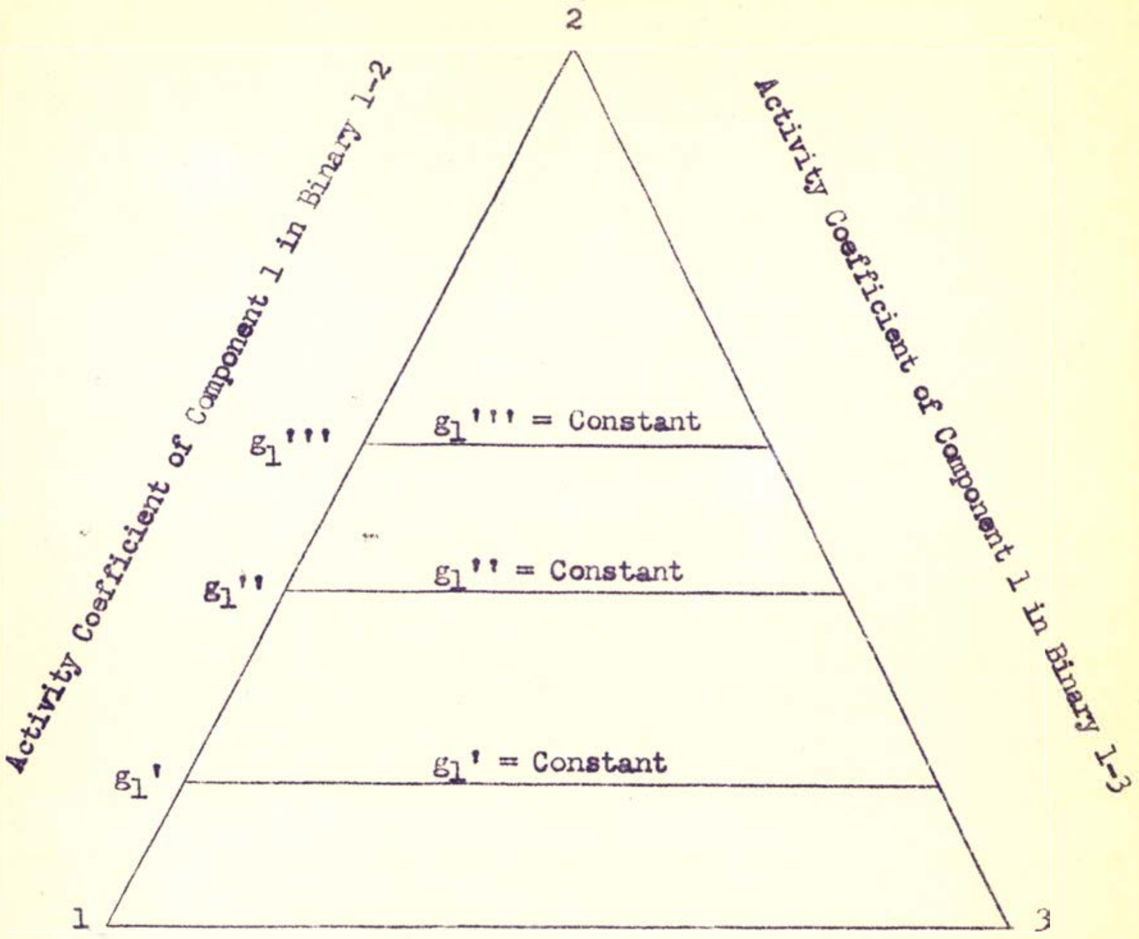


Figure 2. Estimation of Constant Activity Coefficient Curve for Ternary System With One Ideal Binary and Two Non-Ideal Binary Systems

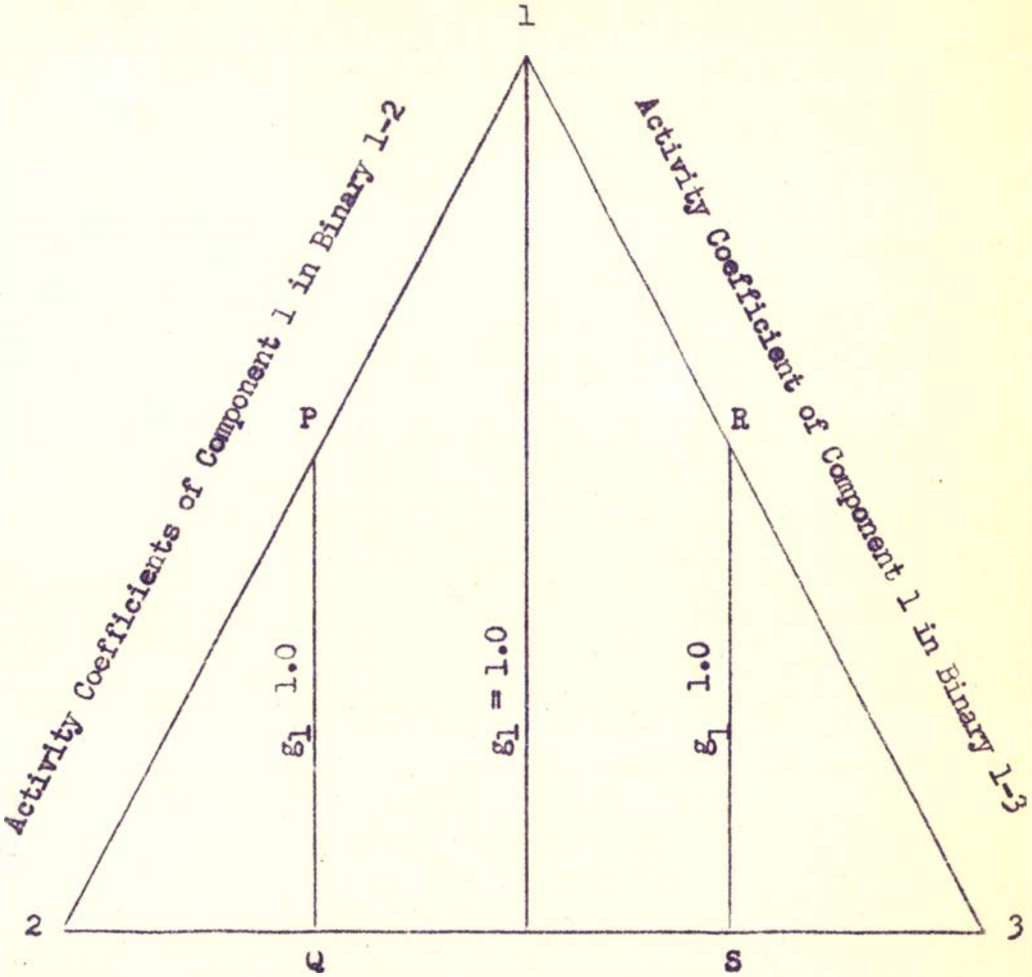


Figure 3. Estimation of Constant Activity Coefficient Curves for Ternary Systems With One Binary System Having Deviations Opposite From Those of the Other Two Binary Systems.

constant activity coefficients of other values, greater than unity and less than unity respectively.

Once the lines of constant activity coefficients for the solute are drawn on the ternary diagram, the known mutual solubility curve is superimposed on the diagram. The problem is then resolved by computing activities around the solubility curve, and connecting the ends of tie lines to values of constant activity.

The value of the method described above for predicting ternary-liquid equilibria data has not been substantiated. It should be applied to several different systems and checked, for it has the obvious advantage of requiring no special techniques for calculation.

III. EXPERIMENTAL

The experimental section of this thesis is composed of the following: (1) purpose of investigation, (2) plan of investigation, (3) materials, (4) apparatus, (5) method of procedure, (6) data and results, and (7) sample calculations. The nomenclature used is presented in Appendix A.

Purpose of Investigation

The purpose of this investigation was to experimentally determine the ternary-liquid solubility and equilibria data for a previously unreported ternary-liquid system, and to compare these data, along with equilibria data obtained from the literature, for other ternary systems with those data approximated by five major prediction methods. The system chosen for experimental study consisted of methanol, water, and 1-nitropropane. Experimental systems reported in the literature and chosen for study were: (1) ethanol, ethyl acetate, water; (2) acetone, chloroform, water; (3) acetone, benzene, water; (4) acetic acid, benzene, water; and (5) cyclohexane, aniline, N-heptane. The results of this study were the formulation of a set of rules postulating the choice and application of methods for predicting ternary-liquid equilibria data.

Plan of Investigation

The sequence of steps established for this investigation was: (1) to review the literature for the purpose of ascertaining the principal methods of predicting ternary-liquid equilibria data, (2) to select five experimental systems which are reported in the literature, (3) to select a previously unreported ternary-liquid system, (4) to determine experimentally its equilibria and solubility data, and (5) to compare five major predictive methods with respect to their ability to describe the equilibria relationships of ternary-liquid systems.

Literature Review. The literature was reviewed for the purpose of (1) listing the major sources of ternary equilibria and solubility data, (2) studying the major methods utilized in predicting ternary-liquid equilibria data, (3) locating published systems for which the binary and ternary data were available so that the prediction methods could be compared with actual experimental results, and (4) studying various standard methods for experimentally determining the solubility and equilibria data for ternary-liquid systems.

Selection of Experimental Systems. Experimental data for five ternary-liquid systems were obtained from the literature. The data obtained on each system were: (1) ternary-liquid equilibria data, (2) ternary-liquid solubility data, and (3) binary vapor-liquid equilibria data or binary mutual solubility data for each of the three binary systems composing a ternary system. The liquid systems used were: (1) ethanol, ethyl acetate, water; (2) acetone, chloroform, water; (3) acetone, benzene, water; (4) acetic acid, benzene, water; and (5) cyclohexane, aniline, N-heptane.

Choice of Ternary-Liquid System. A previously unreported ternary-liquid system was selected and its solubility and equilibria data were experimentally determined. The choice of the system was governed by the relative safety of the system with respect to toxicity and flammability. The system selected consisted of methanol, water, and 1-nitropropane.

Experimental Determination of Ternary-Liquid Relationships. The ternary-liquid solubility and equilibria data were experimentally determined for the system methanol, water, and 1-nitropropane at 25 °C and 30 °C. The solubility data were determined by a modification of the "cloud point" method which is described in detail by Othmer(37) and Hand(22). The synthetic method of Othmer(37) was used to procure the equilibria data.

Comparison of Prediction Methods. Ternary equilibria data for five different liquid systems were predicted from binary vapor-liquid equilibria data by five different methods. These predicted data were compared with the experimental data reported in the literature. From these comparisons, a set of rules concerning the use and applicability of the prediction methods were formulated. The prediction methods studied were: (1) the 2-suffix van Laar method(10, 12, 68), (2) the 3-suffix Margules method(10, 12, 68), (3) the 3-suffix van Laar equations and the 3-suffix Margules equations modified with the Colburn constant(11), (4) the 3-suffix van Laar equations and the 3-suffix Margules equations modified with the Wohl constant(68), and (5) the Scheibel and Friedland method(70).

Materials

The materials used in the experimental work are listed in Appendix B.

Apparatus

The apparatus used in the experimental work are listed in Appendix B.

Method of Procedure

The procedures used in this investigation involved two major techniques: (1) the calibration and use of standard experimental equipment, and (2) the programming and use of a digital computer. The first technique was employed in the determination of solubility and equilibria characteristics for a ternary-liquid system. The second technique was used in the prediction of ternary equilibria data.

Experimental Determination of Solubility Data. For the liquid system studied, methanol was the solute, water was the solvent, and 1-nitropropane was the carrier. To determine the solvent lean portion of the solubility curve, 20 cubic centimeter mixtures of carrier and solute were made at 10 weight per cent increments from pure carrier to pure solute. These mixtures were placed in polyethylene containers, sealed from the atmosphere, and immersed in a constant temperature bath for approximately four hours. Each container in turn was opened and titrated with solvent which had been previously brought to a constant temperature. The end point or "cloud point" of the titration was the formation of turbidity in the mixture. From the knowledge of the quantities of solute and carrier in each mixture and the quantity of solvent necessary to produce turbidity in that mixture, a point of solubility data was calculated. The solvent-rich portion of the solubility curve was obtained by reversing the procedure. That is, prepared samples of solvent and solute were titrated with carrier until the turbidity was observed.

The vessel containing the mixture being titrated was continually agitated in the constant temperature bath during titration. The bath used for this purpose has a glass bottom with a light below the glass, thus allowing the end point of the titration to be observed while keeping the vessel in the constant temperature bath. This procedure was unlike those of Othmer(37) and Hand(22) who removed their samples from the temperature bath to perform the titrations. The solubility curve was determined at 25 °C and 30 °C.

Determination of Experimental Equilibria Data. The equilibria data were determined experimentally by the synthetic method of Othmer(37). This method involved, first, the recording of the refractive index at various points on the solubility curve. This established a curve of refractive index on the solubility curve as a function of solute concentration. The next step was to make solutions consisting of all three components. These solutions were of such composition that they would be in the two-phase region. Six such mixtures were prepared at different compositions. These two-phase mixtures were then sealed in polyethylene containers and placed in the constant temperature bath. The containers were vigorously shaken each day for two weeks to insure that the mixtures would reach equilibrium. At the end of this two week period, each container was removed from the constant temperature bath, the two phases separated, and the refractive index of each phase determined. As the end of each equilibrium tie-line must fall on the mutual solubility curve, a comparison of the refractive indices of the split phases with the curve of refractive index as a function of solute concentration on the solubility curve established the tie-lines. The equilibria data for the system water, methanol, and 1-nitropropane at 25 °C were experimentally determined in this manner.

Calculation of Binary Constants. Experimental binary data were obtained from the literature for each binary system related to the ternary systems studied. The binary data obtained were of two types: (1) vapor-liquid equilibria data reported at constant pressure, and (2) mutual solubility data. From these data, binary solution constants, as defined for use in integrated forms of the Gibbs-Duhem equation, were calculated for each binary system. The binary constants are defined for the integrated forms as follows:

$$A_{12} = \text{limit of } \log g_1 \text{ as } X_1 \rightarrow 0 \text{ and } X_2 \rightarrow 1 \tag{17}$$

$$A_{21} = \text{limit of } \log g_2 \text{ as } X_2 \rightarrow 0 \text{ and } X_1 \rightarrow 1 \tag{18}$$

where:

g = activity coefficient, unitless

X = liquid composition, mole fraction

A = constants for binary system, unitless

Subscripts indicate component in mixture, unitless.

From Vapor-Liquid Data. The first step in calculating binary solution constants from total pressure vapor-liquid equilibria data was to transform the data to activity coefficients. Activity coefficients, as defined by Equation 1, page 6, were calculated from the total pressure data by the use of Program II, Appendix C. The output from this computer program prints activity coefficients and the corresponding liquid compositions for both components of the binary solution. The binary solution constants were then evaluated from these activity coefficient-composition relationships by the method described by Reid(32). This method involved rewriting the integrated forms of the Gibbs-Duehm equation in the standard point-slope form for a straight line(33), then calculating the binary constants by the method of least squares(34). This was accomplished by the use of Program III, Appendix C.

From Mutual Solubility Data. The mutual solubility data reported in the literature includes the composition of one of the components in the two immiscible layers and the accompanying equilibrium temperature. This type of data was used only for systems where no vapor-liquid equilibria data were available. These systems were: (1) benzene, water; (2) ethyl acetate, water; (3) water, 1-nitropropane; (4) aniline, N-heptane; and (5) aniline, cyclohexane. Binary solution constants were calculated for these systems from mutual solubility data by the method of Carlson(10).

Calculation of Ternary Activity Coefficients. Ternary activity coefficients were calculated for each liquid system studied from the binary solution constants and ternary mutual solubility data, by five major prediction methods. These methods were: (1) the 2-suffix van Laar method, (2) the 3-suffix Margules method, (3) the 3-suffix van Laar equations and the 3-suffix Margules equations modified with the Colburn constant, (4) the 3-suffix van Laar equations and the 3-suffix

Margules equations modified with the Wohl constant, and (5) the Scheibel and Friedland method.

2-Suffix van Laar Equations. The general "q" equation, Equation 8, page 14, was transformed to the 2-suffix van Laar equation by equating the ternary constant to zero and inserting the van Laar conditions. The van Laar conditions, as described by Wohl(68), are:

$$(A_{13}/A_{31})(A_{32}/A_{23}) = (A_{12}/A_{21}) \tag{15}$$

where:

A = binary constant, unitless

1 = solute, unitless

2 = solvent, unitless

3 = carrier, unitless

The resulting 2-suffix van Laar equation was programmed for the digital computer. The complete program is Program V, Appendix C. By using this program, ternary activity coefficients for all liquid systems studied were calculated from the binary solution constants and the ternary mutual solubility data.

3-Suffix Margules Equations. The general "q" equation, Equation 8, page 14, was reduced to the 3-suffix Margules equation by the following equations:

$$(q1/q2) = (q1/q3) = 1 \tag{16}$$

$$C = 0 \tag{19}$$

where:

q = effective molal volume, volume units

C = ternary constant, unitless

Subscripts 1, 2, 3, correspond to the separate components of the mixture, unitless.

Ternary activity coefficients for all liquid systems studied were calculated from the 3-suffix Margules equation. The computer program for the solution of this equation is Program VI, Appendix C.

Integrated Forms with the Colburn Constant. Colburn suggested that the accuracy of the van Laar equations and the Margules equations could possibly be improved by the addition of an approximate ternary constant(11). The constant is defined in the following manner:

$$C = \tfrac{1}{2}(A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23}) \qquad (11)$$

where:

C = ternary constant, unitless

A = binary constant, unitless

1 = solute, unitless

2 = carrier, unitless.

The Colburn constant was calculated for each ternary-liquid system studied, then applied to both the van Laar and Margules equations. Program V, Appendix C was used to solve the resulting van Laar equation, and Program VI, Appendix C was used to solve the Margules equation.

Integrated Forms with the Wohl Constant. A technique was derived to calculate the ternary constant found in Wohl's "q" equation, Equation 8, page 14. From one known equilibrium measurement on each ternary system studied, the constant was calculated for the van Laar equations. The following is the derivation used for the van Laar case:

$$a_1 = (g'_1)(X'_1) = (g''_1)(X''_1) \tag{20}$$

Represent the right hand member of the van Laar equation by V. Thus:

$$\log (g'_1) = V' \quad \text{for phase one} \tag{21}$$

$$\log (g''_1) = V'' \quad \text{for phase two}$$

or

$$g'_1 = 10^{V'} \quad \text{and} \quad g''_1 = 10^{V''} \tag{22}$$

Combine Equations 20 and 22 to obtain

$$a_1 = (X'_1)(10^{V'}) = (X''_1)(10^{V''}) \tag{23}$$

Rewrite in the form

$$(X'_1)/(X''_1) = 10^{(V'' - V')} \tag{24}$$

Take the logarithm of both sides to obtain

$$\log (X'_1/X''_1) = V'' - V' \tag{25}$$

From Equation 8, page 14, for the van Laar Equation

$$V'' = Q'' - C(W)'' \tag{26}$$

$$V' = Q' - C(W)'$$

where:

$$Q = (Z_2^{\,2} A_{12} + Z_3^{\,2} A_{13} + Z_2Z_3A_{12} + Z_2Z_3A_{13} - A_2Z_3M)$$

$$W = (Z_2Z_3 - 2Z_1Z_2Z_3)$$

Superscript ' indicates phase one.

Superscript " indicates phase two.

Subtract $V'' - V'$

$$V'' - V' = Q'' - Q' - C(W)'' + C(W)' =$$

$$Q'' - Q' - C(W'' - W') \tag{27}$$

Combine Equations 25 and 27 to obtain

$$\log (X'_1/X''_1) = Q'' - Q' - C(W'' - W') \tag{28}$$

Solve Equation 28 for C

$$C = \frac{(\log X'_1/X''_1) - (Q'' - Q')}{(W' - W'')} \qquad (29)$$

A computer program was written to compute the ternary constant, C, from Equation 29, for each of the liquid systems studied. Refer to Program IV, Appendix C for the complete program. The constant solved for at one point of known equilibrium, was then used to compute activity coefficients for the entire range of points covered by the solubility curve.

Method of Scheibel and Friedland. The graphical-empirical method of Scheibel and Friedland(70) was applied to all systems studied. However, this was successful in only three of the cases. The systems, ethanol, ethyl acetate, water, and acetic acid, benzene, water were correlated by calculations of Type I, page 20. The system acetone, chloroform, water was correlated by calculations of Type II, page 20.

Calculation of Ternary-Liquid Equilibrium. Once the solute activities as a function of solute compositions in each liquid phase were obtained, the method of Hildebrand(20) was applied to obtain the ternary-liquid equilibria data. This method involved plotting the values of solute mole fractions on the abcissa, as a function of solute activities on the ordinate. For a two-phase liquid system, two curves result on the same graph. One curve represented the concentration of the solute in one phase, while the other curve represented the concentration of the solute in the other phase. Values of solute concentration in equilibria in each phase were obtained by drawing lines of constant activity through the two curves and reading the two abcissa values of concentration.

Data and Results

The first portion of this section deals with the data collected and the results obtained from the experimental determination of the ternary characteristics of the system water, methanol, and 1-nitropropane. The second portion of this section deals with the processing of binary data and the consequental prediction of ternary-liquid equilibria data for six different systems.

Experimental Work. The experimental values of the mutual solubility data and the ternary-liquid distribution data for the system water, methanol, and 1-nitropropane, are presented in Tables I, II, and III. These data are plotted on a triangular diagram in Figure 4. The experimental data recorded in the laboratory are found in Appendix D.

Comparison of Prediction Methods. The binary solution constants for each system studied, as calculated from binary data obtained in the literature, are presented in Table IV. Tables V through X present the comparisons of the experimental values of the ternary-liquid distribution data for each system studied, with the values approximated by the prediction methods used. These comparisons are shown graphically in Figures 5 through 15. The sources of data obtained from the literature and the computer output for each system studied are found in Appendix D.

TABLE I

Experimentally Determined Ternary-Liquid Solubility Data for the System Water, Methanol, and 1-Nitropropane at 30 °C

Composition 1-Nitropropane	Composition Water	Composition Methanol
Weight %	Weight %	Weight %
1.810	98.190	0.00
2.441	84.210	13.349
3.298	73.424	23.278
4.121	68.659	27.209
4.518	64.709	30.772
6.449	57.251	36.300
8.649	50.960	40.391
10.873	45.679	43.447
13.549	40.978	45.472
16.045	38.356	45.600
19.143	34.445	46.412
22.858	30.784	46.358
27.359	27.263	45.378
21.719	26.429	51.852
28.399	26.402	45.199
41.069	19.709	39.220
52.363	14.299	33.337
61.355	10.734	27.905
70.089	7.599	22.310
82.964	3.832	13.205
99.798	0.201	0.00

TABLE II

Experimentally Determined Ternary-Liquid Solubility Data for the System Water, Methanol, and 1-Nitropropane at 25 °C

Composition 1-Nitropropane	Composition Water	Composition Methanol
Weight %	Weight %	Weight %
0.985	99.014	0.00
2.187	84.459	13.355
2.794	73.851	23.355
3.139	65.696	31.164
5.259	58.036	36.706
7.318	51.760	40.921
9.229	46.579	44.191
12.090	41.726	46.184
13.827	38.046	48.127
28.837	25.369	45.794
34.256	22.225	43.519
41.899	18.179	39.922
52.958	13.403	33.639
61.614	10.431	27.955
71.739	5.476	22.785
83.405	3.350	13.245

TABLE III

Experimentally Determined Equilibria Distribution for the
System Water, 1-Nitropropane, and
Methanol at 25 °C

Water Phase		
Weight per cent		
A	B	C
3.00	77.10	19.9
3.15	73.95	22.9
3.65	68.05	28.30
4.56	63.13	32.31
6.04	56.05	37.91
8.37	49.32	42.31

1-Nitropropane Phase		
Weight per cent		
A	B	C
93.90	1.45	4.65
86.85	2.99	10.16
75.23	5.63	14.14
65.17	8.71	26.12
54.20	12.90	32.90
48.15	12.16	35.99

A = 1-Nitropropane

B = Water

C = Methanol

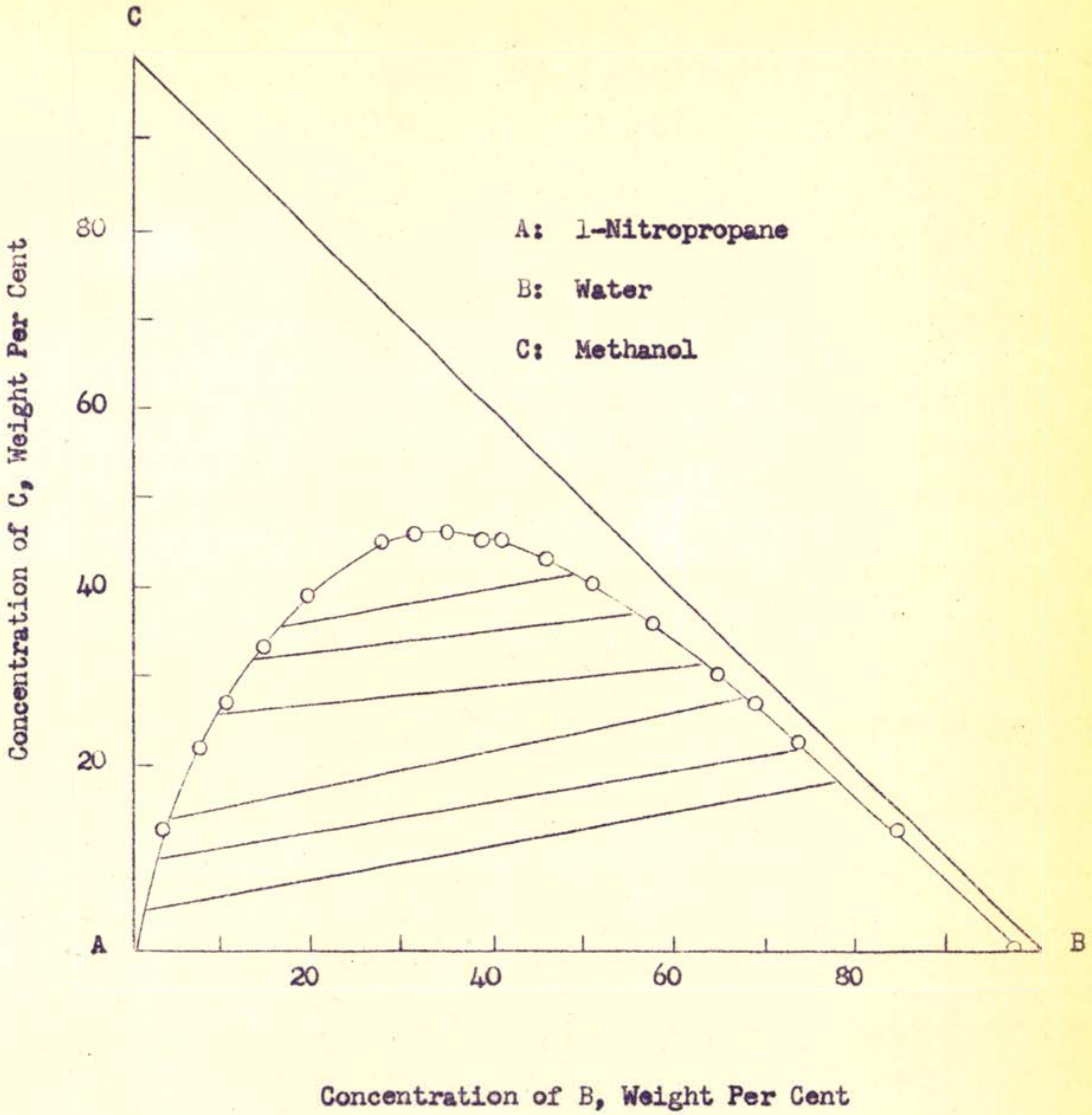


Figure 4. Equilibria Data for the System Water, Methanol, 1-Nitropropane at 25 °C

TABLE IV

Binary Solution Constants Obtained From Binary Data for Use in Ternary Prediction Equations

Ternary System	Binary 3-2		Binary 2-1		Binary 3-1	
	A_{32}	A_{23}	A_{21}	A_{12}	A_{31}	A_{13}
Acetic Acid (1)						
Benzene (2)	3.48	4.55	0.348	0.439	0.666	0.0477
Water (3)						
Source	(31)		(41)		(21)	
Ethanol (1)						
Water (2)	1.79	1.03	0.380	0.633	0.362	0.342
Ethyl Acetate (3)						
Source	(31)		(31)		(46)	
Cyclohexane (1)						
N-Heptane (2)	1.29	1.359	(*)	(*)	1.12	0.867
Aniline (3)						
Source	(30)				(30)	
Acetone (1)						
Water (2)	4.55	3.48	0.655	0.890	0.176	0.176
Benzene (3)						
Source	(31)		(9)		(39)	
Acetone (1)						
Chloroform (2)	(*)	(*)	-0.344	-0.446	0.655	0.890
Water (3)						
Source			(41)		(3)	
Methanol (1)						
1-Nitropropane (2)	0.241	0.356	(*)	(*)	0.203	0.251
Water (3)						
Source	(71)				(41)	

* No data available
All tabular values unitless

TABLE V

Comparison of the Predicted Liquid Distribution With the Actual Distribution for the System Acetone, Benzene, and Water at 30 °C

Acetone in Benzene Phase	Acetone in Water Phase					
Experimental[1]	Experimental[1]	2-suffix van Laar	3-suffix van Laar[2]	Colburn van Laar[3]	3-suffix Margules	Colburn Margules[3]
Mole %	Mole %	Mole %	Mole %	Mole %	Mole %	Mole %
7.59	1.61	1.60	1.92	2.00	1.50	1.60
16.75	3.34	3.02	2.75	3.21	3.52	3.32
36.03	7.23	6.43	5.91	6.54	6.60	6.66
50.27	11.85	7.49	11.1	8.00	8.00	7.90
55.66	17.45	8.53	16.9	9.05	8.52	8.52
53.18	24.88	8.00	30.1	8.25	8.65	8.20

1. Data of Briggs, S. W. and E. W. Comings: Ind. Eng. Chem., 35, 411 (1943)
2. Ternary constant, C = 10.69, Calculated by method of Wohl from Data of Briggs
3. Ternary constant, C = 0.43, Calculated by Colburn approximation

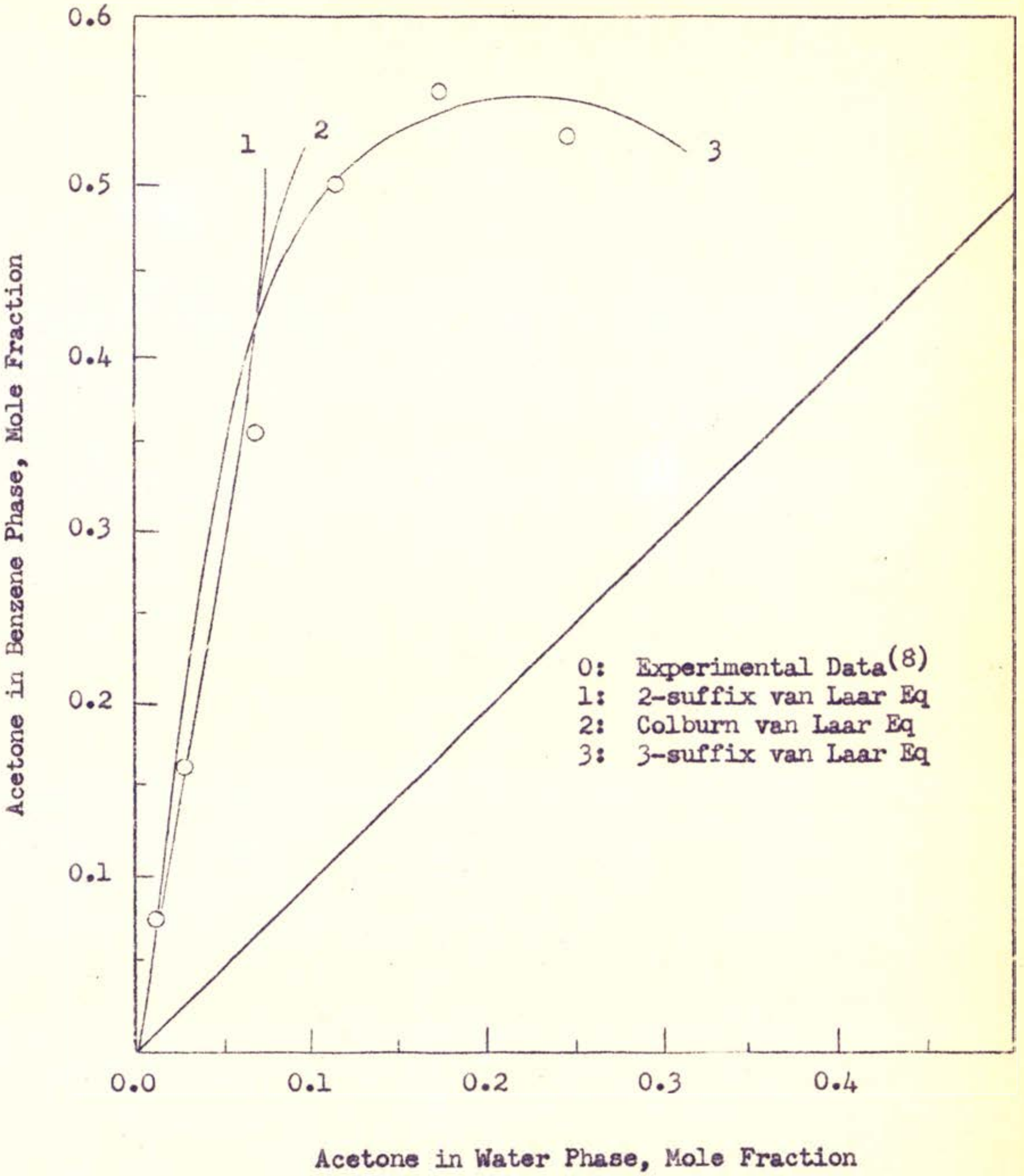


Figure 5. Comparison of the Experimental Ternary Distribution Data for the System Acetone, Benzene, Water, With Those Data Predicted by Three Forms of the van Laar Equation

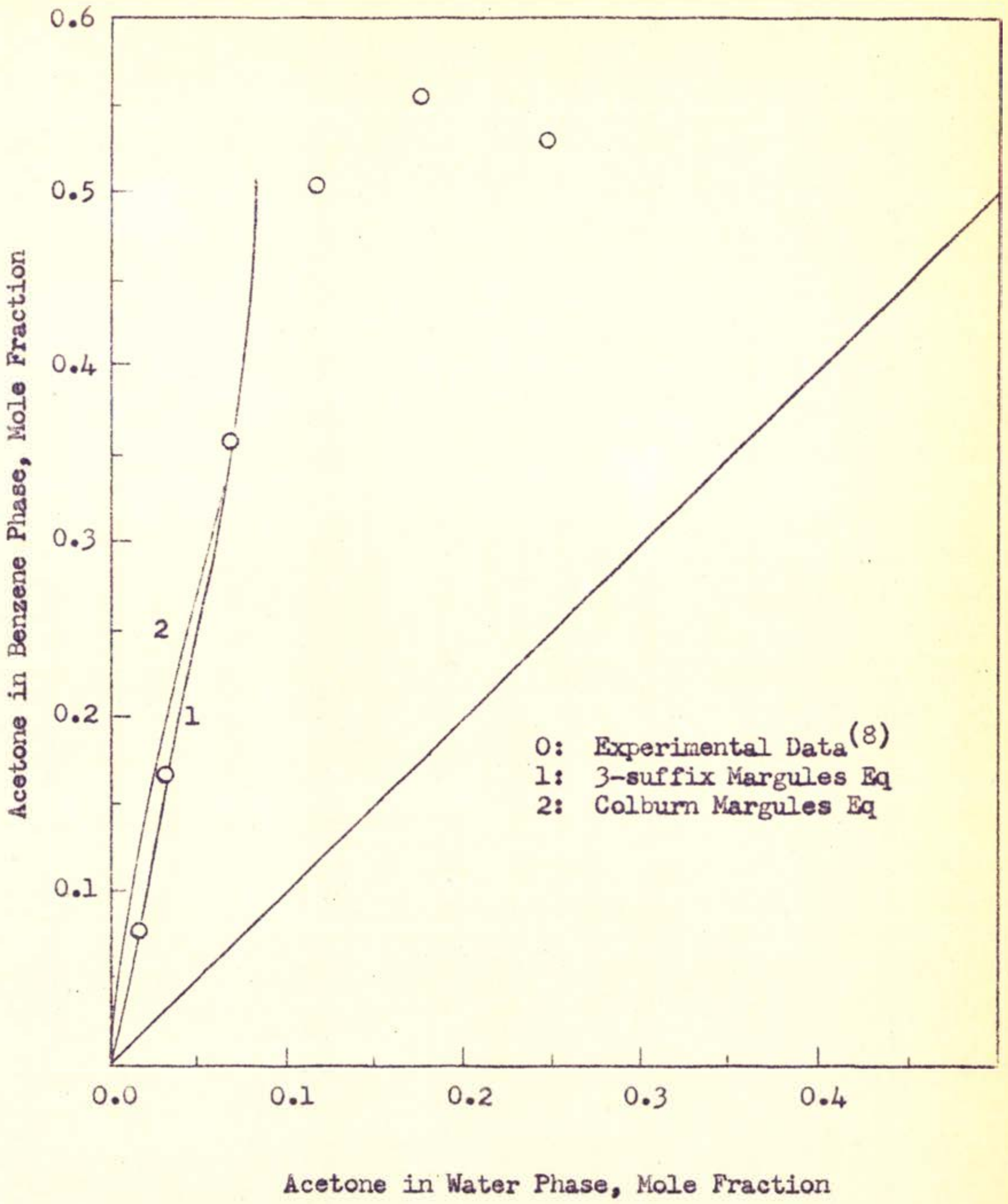


Figure 6. Comparison of the Experimental Ternary Distribution Data for the System Acetone, Benzene, Water, With Those Data Predicted by Two Forms of the Margules Equation

TABLE VI

Comparison of the Predicted Liquid Distribution With the Actual Distribution for the System Ethanol, Ethyl Acetate, and Water at 20 °C

Ethanol in Ethyl Acetate Layer	Ethanol in Water Layer					
Experimental[1]	Experimental[1]	2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar	3-suffix Margules	Colburn[3] Margules
Mole %	Mole %	Mole %	Mole %	Mole %	Mole %	Mole %
3.30	1.72	1.50	1.60	1.70	1.70	1.50
8.35	3.41	3.71	4.60	3.70	3.90	3.52
11.10	4.82	4.80	6.20	4.70	4.91	4.25
13.60	6.50	5.50	7.40	5.40	6.00	5.25
16.70	8.20	7.00	9.50	6.60	7.21	6.25
17.50	10.41	7.40	10.4	7.00	7.50	7.00

[1] Data of Beech, D. G., and S. Glasstone: J. Chem. Soc. (1938) 67

[2] Ternary constant, C = -1.363, Calculated by method of Wohl from data of Beech and Glasstone

[3] Ternary constant, C = 0.2428, Calculated by Colburn approximation

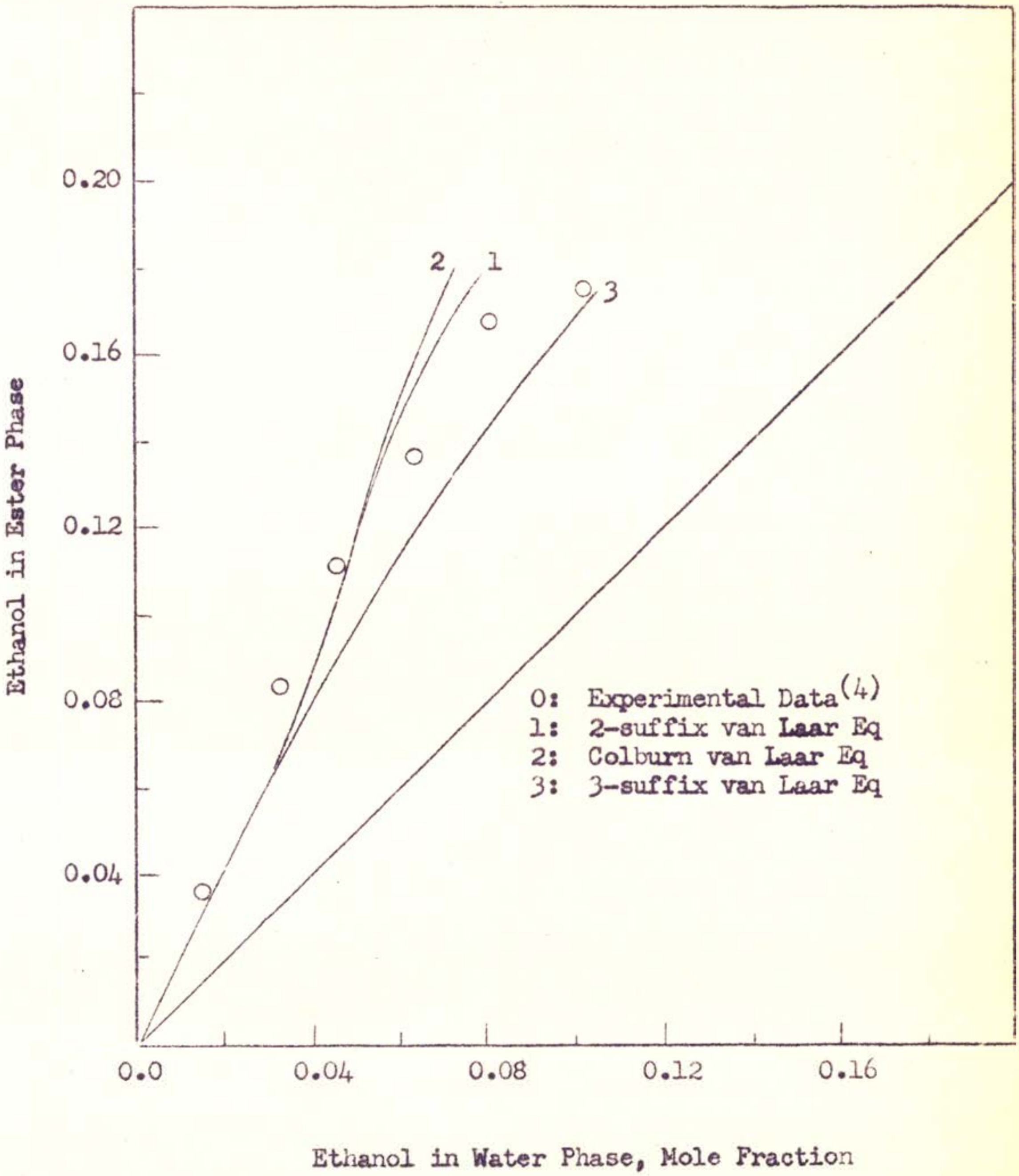


Figure 7. Comparison of the Experimental Ternary Distribution Data for the System Ethanol, Ethyl Acetate, Water With Those Data Predicted by Three Forms of the van Laar Equation

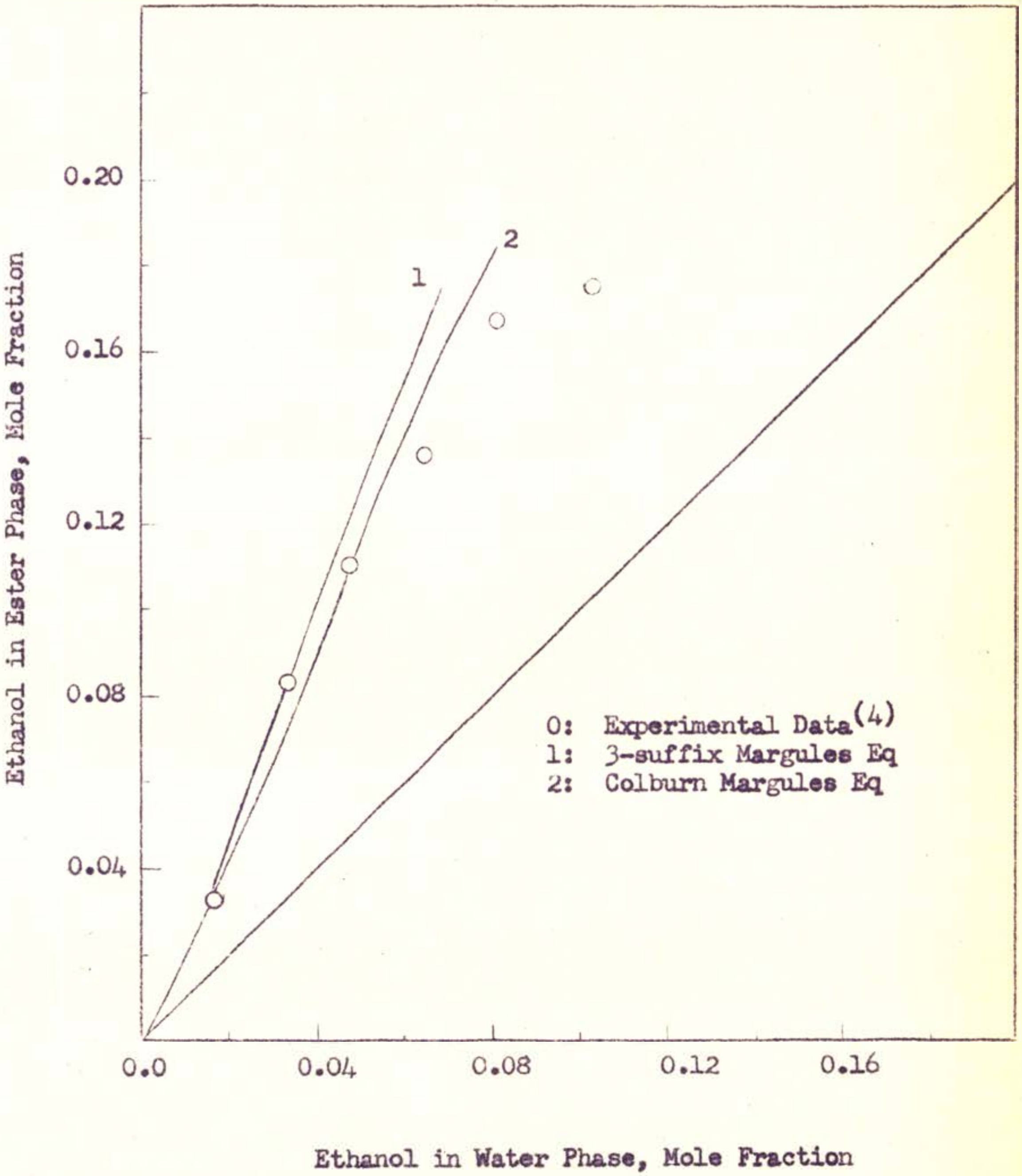


Figure 8. Comparison of the Experimental Ternary Distribution Data for the System Ethanol, Ethyl Acetate, Water, With Those Data Predicted by Two Forms of the Margules Equation

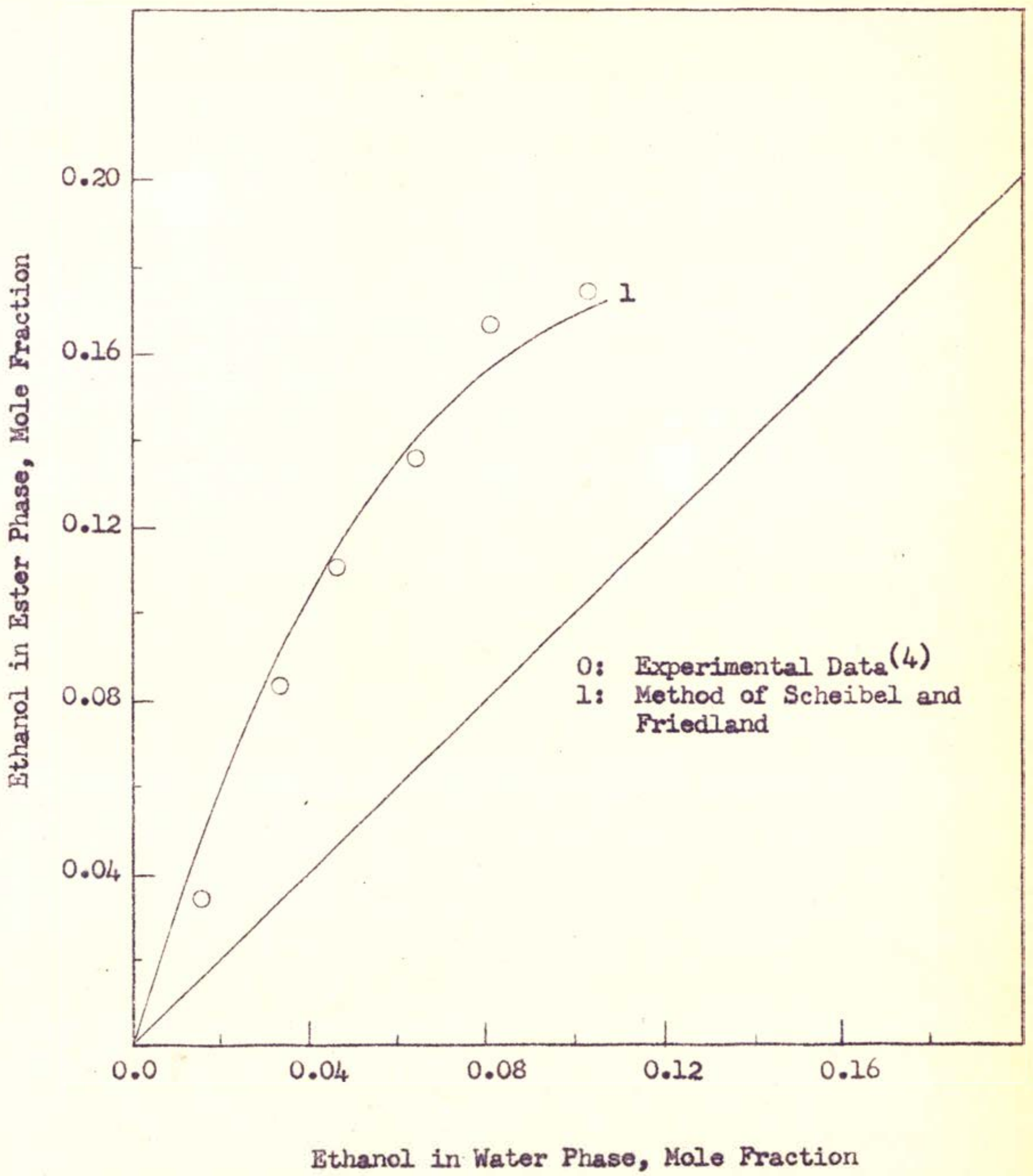


Figure 9. Comparison of the Experimental Ternary Distribution Data for the System Ethanol, Ethyl Acetate, Water, With Those Data Predicted by the Method of Scheibel and Friedland

TABLE VII

Comparison of the Predicted Liquid Distribution With the Actual Distribution for the System Acetic Acid, Benzene, and Water at 30 °C

Acetic Acid in Benzene Layer	Acetic Acid in Water Layer			
Experimental[1]	Experimental[1]	2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar
Mole %	Mole %	Mole %	Mole %	Mole %
16.4	29.61	23.5	30.0	19.0
18.3	32.00	25.2	33.0	21.8
27.0	39.89	32.0	41.0	34.5
34.8	49.33	37.5	43.5	42.7
38.5	50.10	40.1	46.1	45.8
40.5	50.56	41.6	49.9	49.5
48.6	50.24	49.7	*	50.2

1. Data of Hand, D. B.: J. Phys. Chem., 34, 1961 (1930)
2. Ternary constant, C = 1.204, Calculated by method of Wohl from data of Hand
3. Ternary constant, C = -.8864, Calculated by Colburn approximation

* Prediction did not extend to this point.

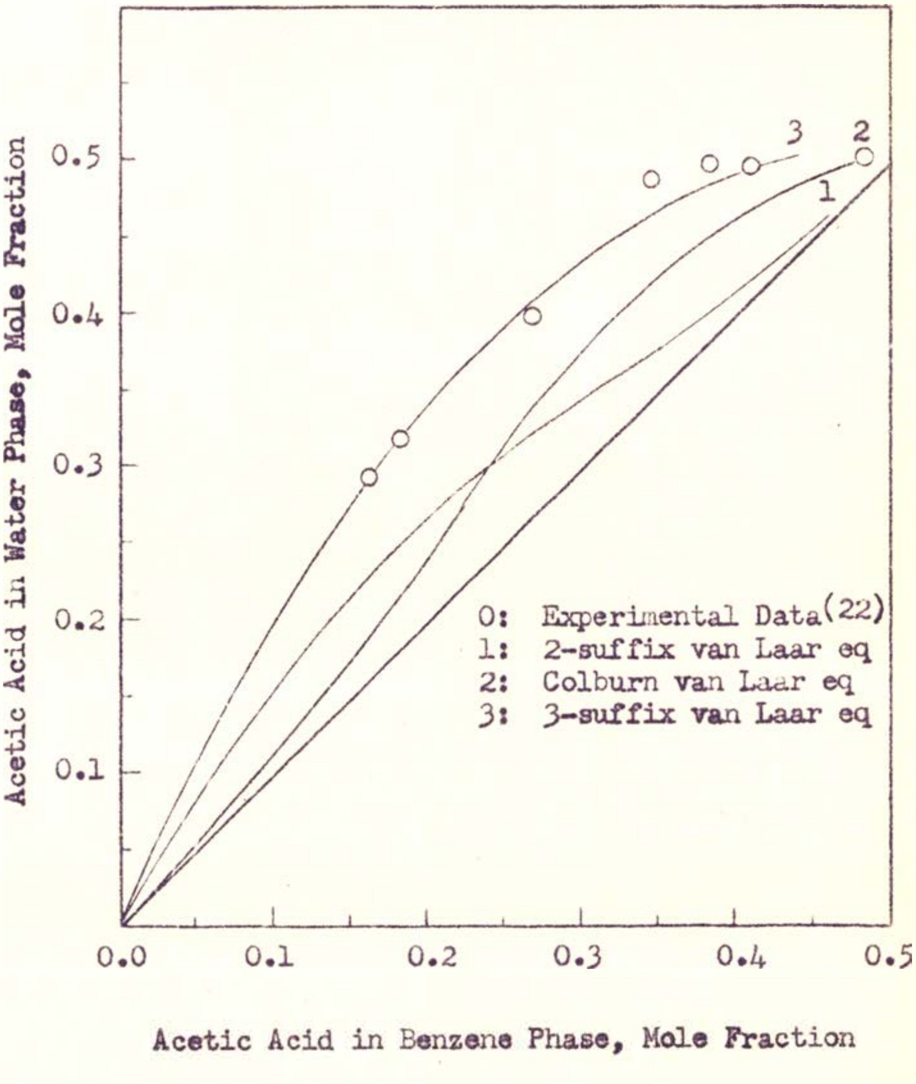


Figure 10. **Comparison of the Experimental Ternary** Distribution Data for the System Acetic Acid, Benzene, Water, With Those Data Predicted by Three Forms of the van Laar Equation

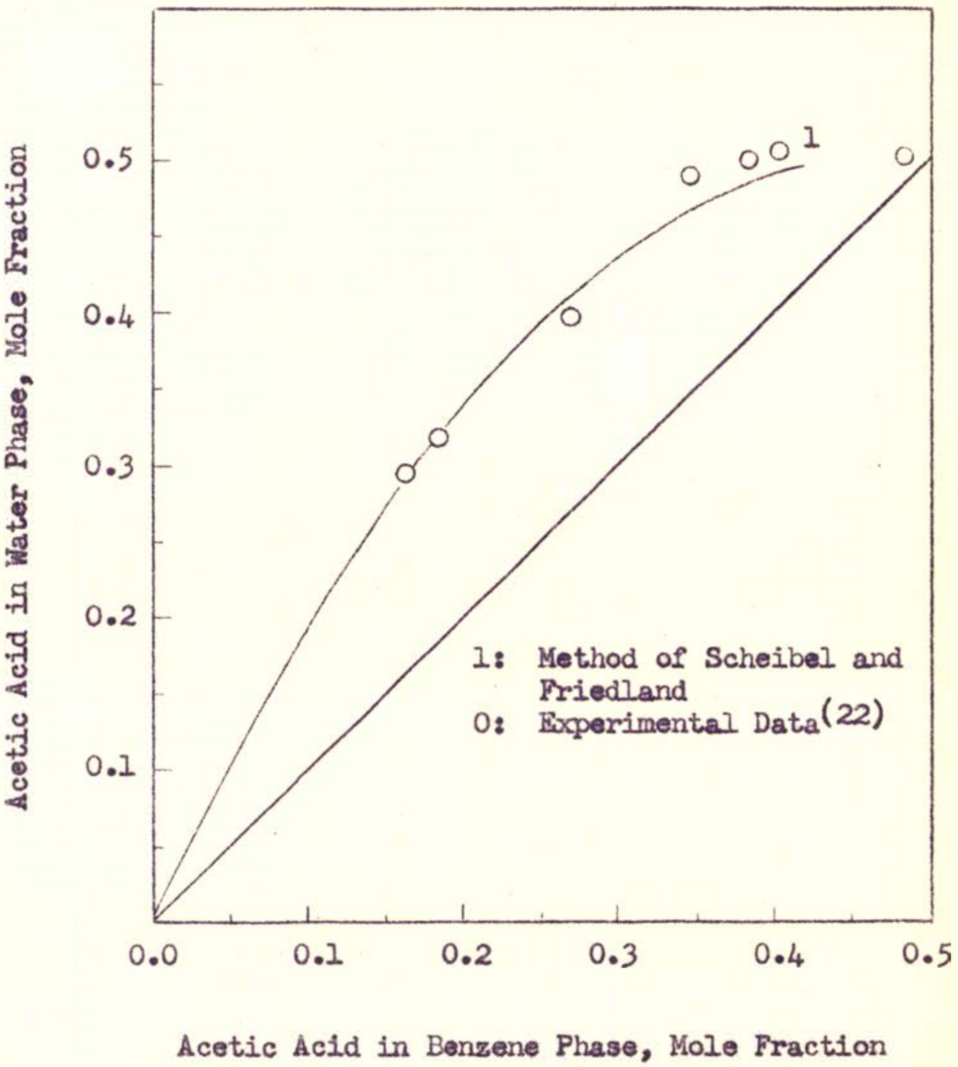


Figure 11. Comparison of the Experimental Ternary Distribution Data for the System Acetic Acid, Benzene, Water With Those Data Predicted by the Method of Scheibel and Friedland

TABLE VIII

Comparison of the Predicted Liquid Distribution With the Actual Distribution for the System Acetone, Chloroform and Water at 25 °C

Acetone in Water Phase	Acetone in Chloroform Phase					
Experimental[1]	Experimental[1]	2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar	3-suffix Margules	Colburn[3] Margules
Mole %	Mole %	Mole %	Mole %	Mole %	Mole %	Mole %
5.56	42.9	38.5	40.0	34.6	39.0	39.2
9.76	55.2	51.0	48.5	42.1	52.3	52.5
15.13	60.0	57.8	56.2	49.6	59.0	61.4
19.51	57.2	59.0	57.2	50.7	59.2	*
24.77	56.6	58.9	56.6	45.4	47.0	*
32.42	46.6	46.5	*	*	*	*

1. Data of Hand, D. B.: J. Phys. Chem., 34, 1961 (1930)
2. Ternary constant C = -1.162, Calculated by method of Wohl from data of Hand
3. Ternary constant C = 0.336, Calculated by Colburn approximation

* Prediction did not extend to this point

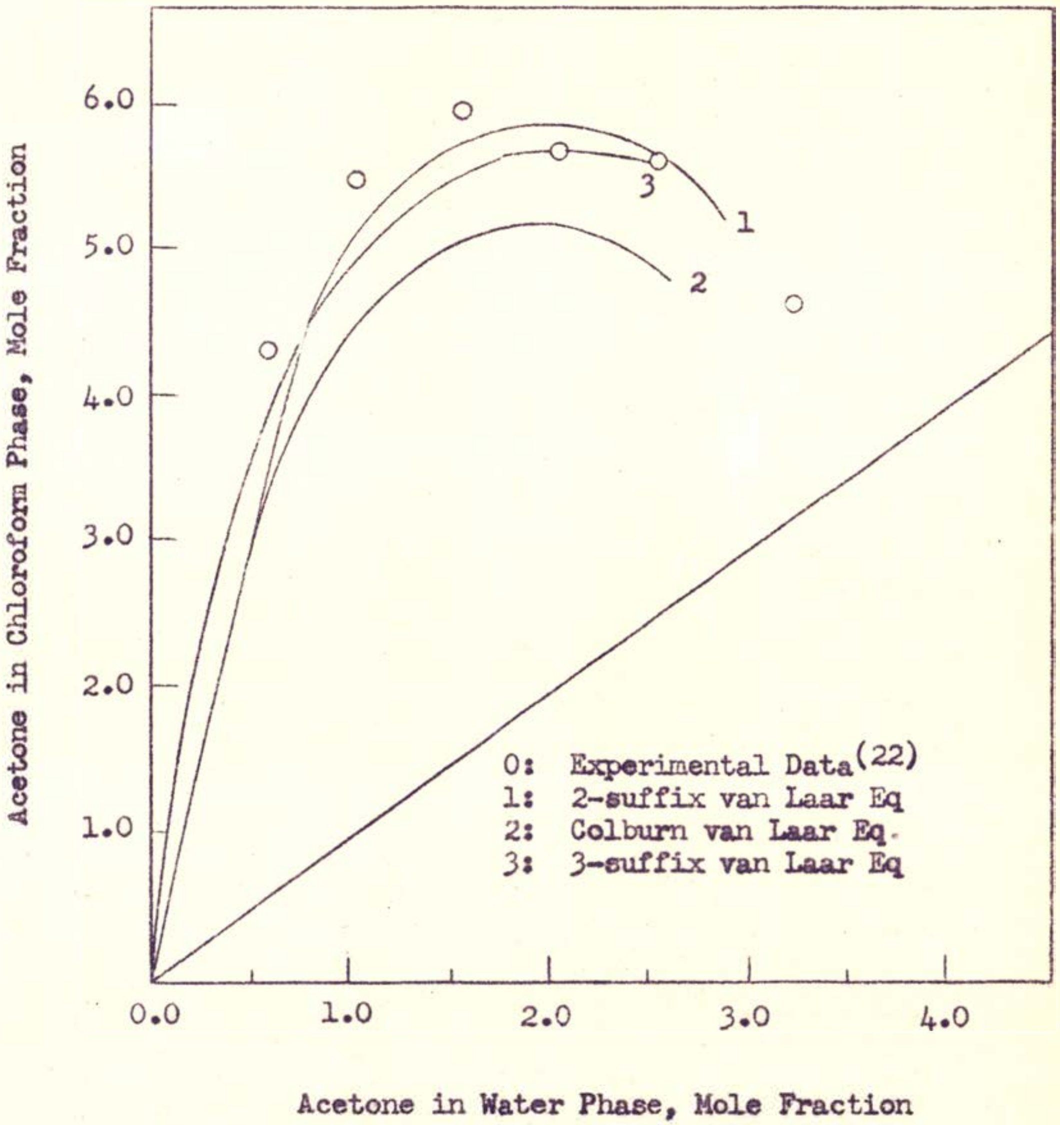


Figure 12. Comparison of the Actual Ternary Distribution Data for the System Acetone, Chloroform, and Water, With That Predicted by Various Forms of the van Laar Equation

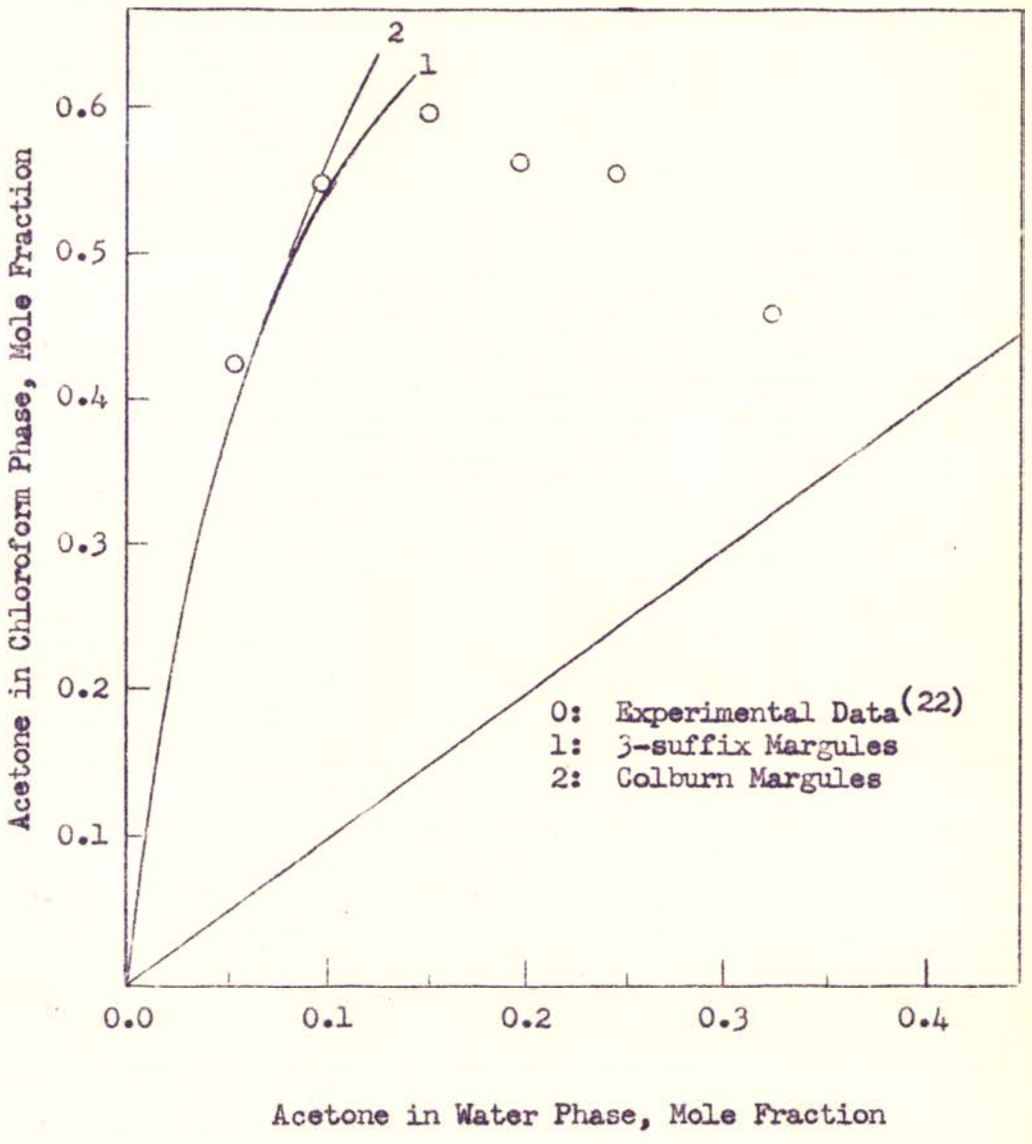


Figure 13. Comparison of the Experimental Ternary Distribution Data for the System Acetone, Chloroform, Water, With Those Data Predicted by Various Forms of the Margules Equation

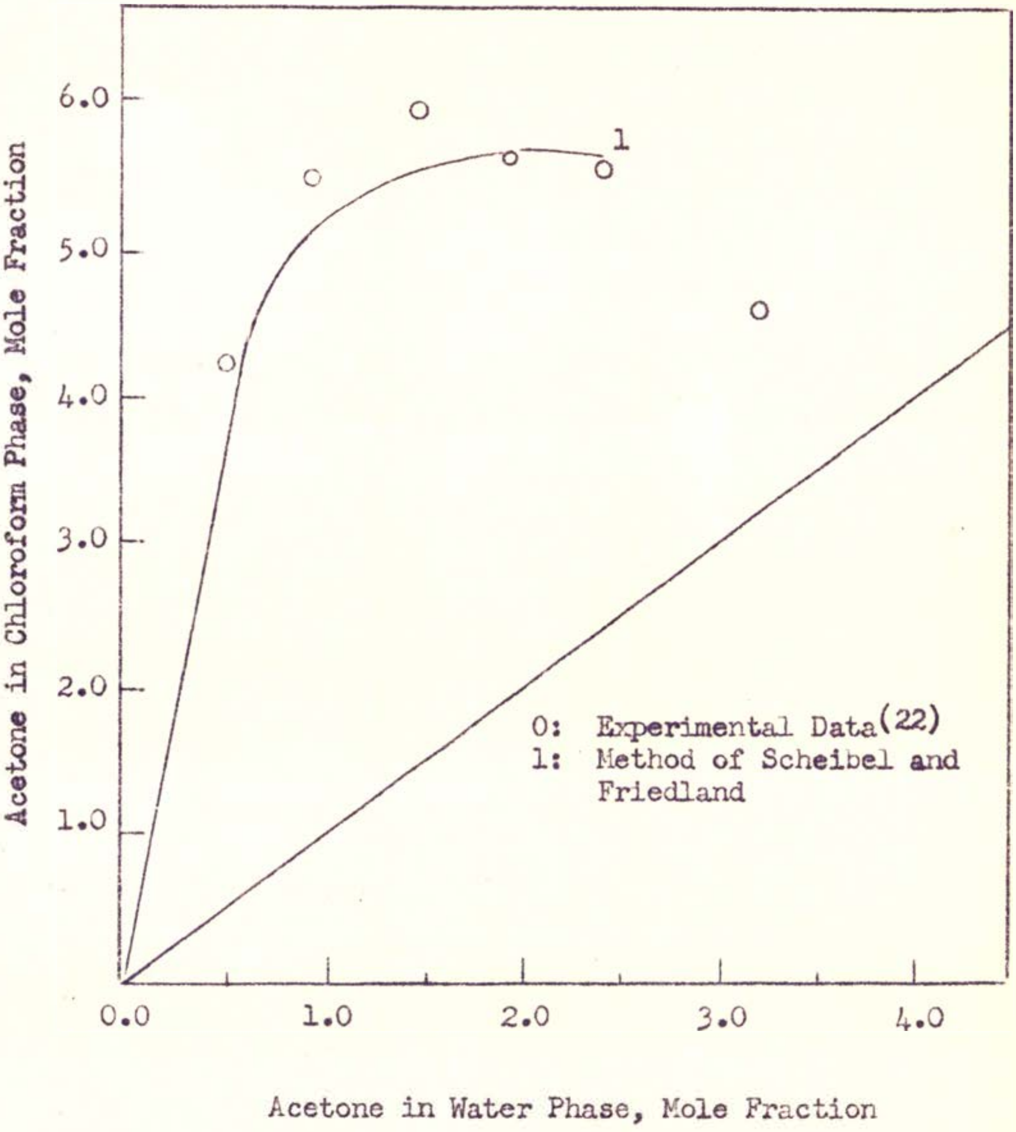


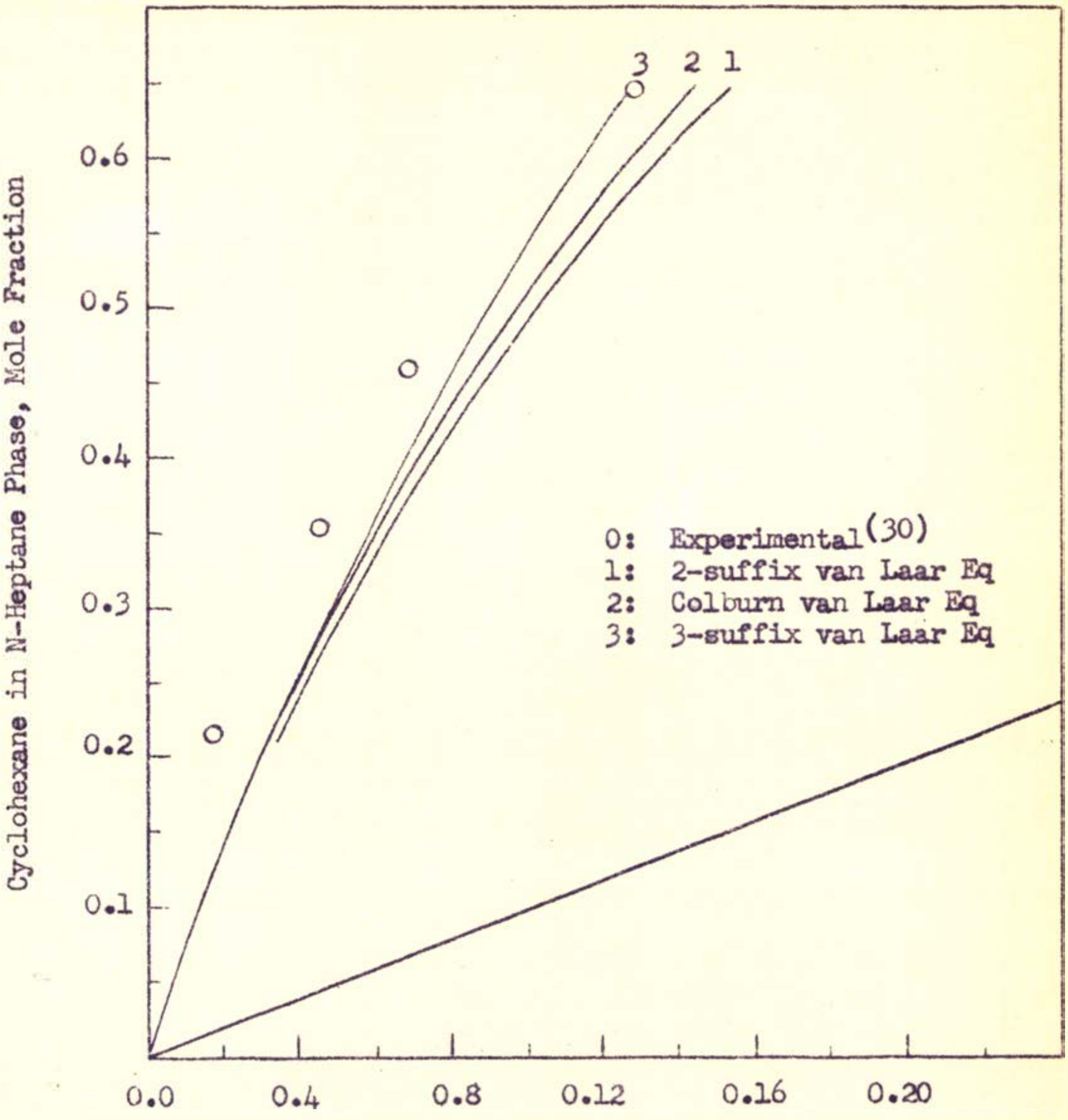
Figure 14. Comparison of the Actual Ternary Distribution Data for the System Acetone, Chloroform, and Water, With That Predicted by the Method of Scheibel and Friedland

TABLE IX

Comparison of the Predicted Liquid Distribution With the Actual Distribution for the System Cyclohexane, N-Heptane, and Aniline at 25 °C

Cyclohexane in N-Heptane Layer	Cyclohexane in the Aniline Layer				
Experimental[1]	Experimental[1]	2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar	3-suffix Margules
Mole %	Mole %	Mole %	Mole %	Mole %	Mole %
21.0	1.66	3.13	3.22	4.02	4.05
45.8	6.84	9.31	8.20	8.76	9.42
35.0	4.53	6.20	5.81	6.05	7.04
64.9	13.9	15.0	13.9	14.2	16.5

1. Data of Hunter, T. G., and T. Brown: Ind. Eng. Chem. 39, 1343 (1947)
2. Ternary constant, C = -1.67, Calculated by method of Wohl from data of Hunter and Brown
3. Ternary constant, C = -0.161, Calculated by Colburn approximation



Cyclohexane in Aniline Phase, Mole Fraction

Figure 15. Comparison of the Experimental Ternary Distribution Data for the System Aniline, Cyclohexane, N-Heptane, With Those Data Predicted by Three Forms of the van Laar Equation

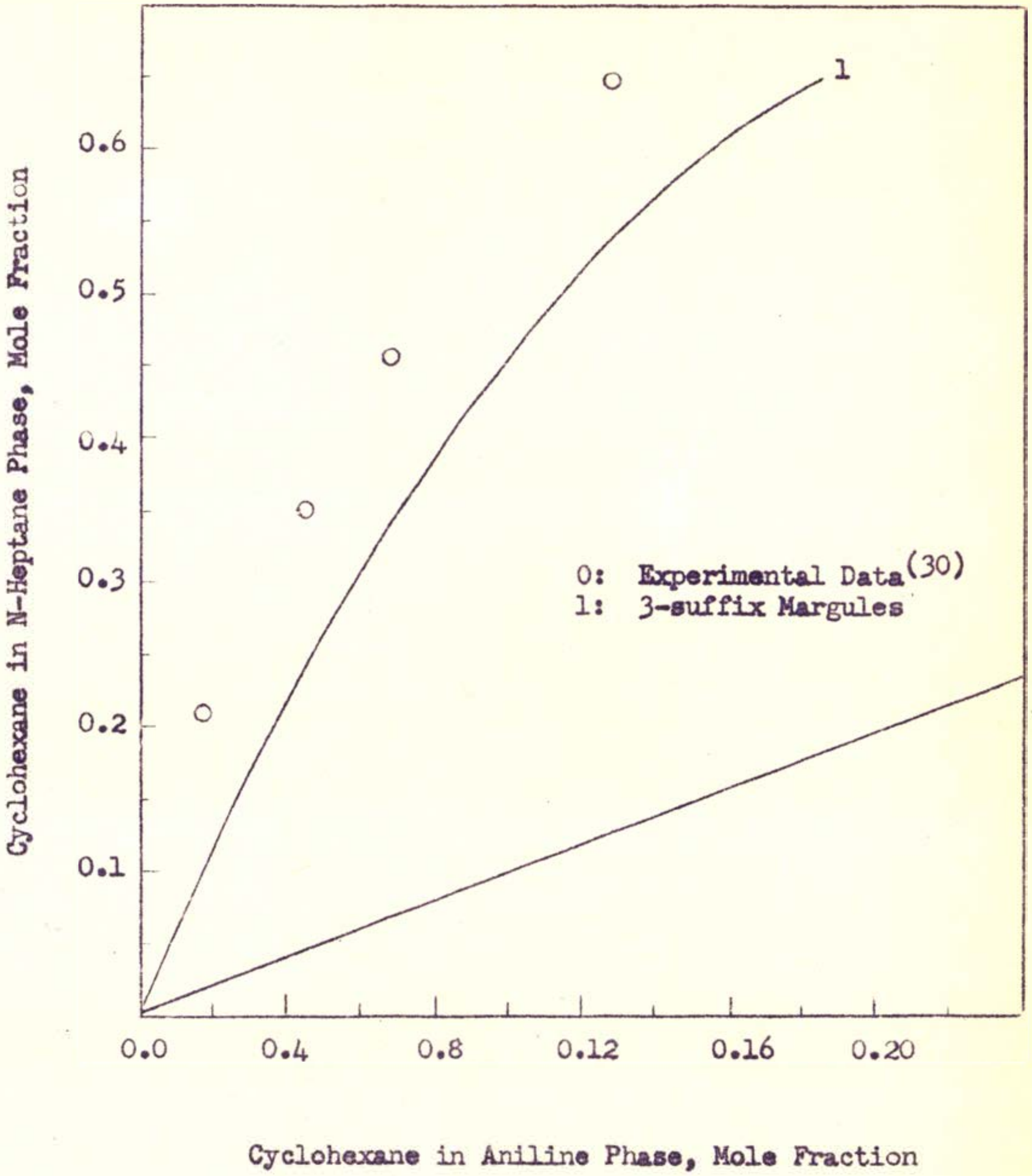


Figure 16. Comparison of the Experimental Ternary Distribution Data for the System Aniline, Cyclohexane, N-Heptane, With Those Data Predicted by the 3-suffix Margules Equation

TABLE X

Comparison of the Predicted Liquid Distribution
With the Actual Distribution for the
System Methanol, Water, and
1-Nitropropane at 25 °C

Methanol in Water Phase	Methanol in 1-Nitropropane Phase			
Experimental	Experimental	2-suffix van Laar	3-suffix[2] van Laar	Colburn[1] van Laar
Mole %	Mole %	Mole %	Mole %	Mole %
14.71	21.74	23.96	29.18	23.07
18.77	27.62	28.43	36.34	27.92
22.08	40.13	36.06	39.92	36.62
27.10	43.64	40.91	40.91	41.03
31.77	48.02	46.27	*	43.11

[1] Ternary constant, $C = -0.163$ by Colburn approximation
[2] Ternary constant, $C = -0.481$ by method of Wohl

* Prediction did not extend to this point

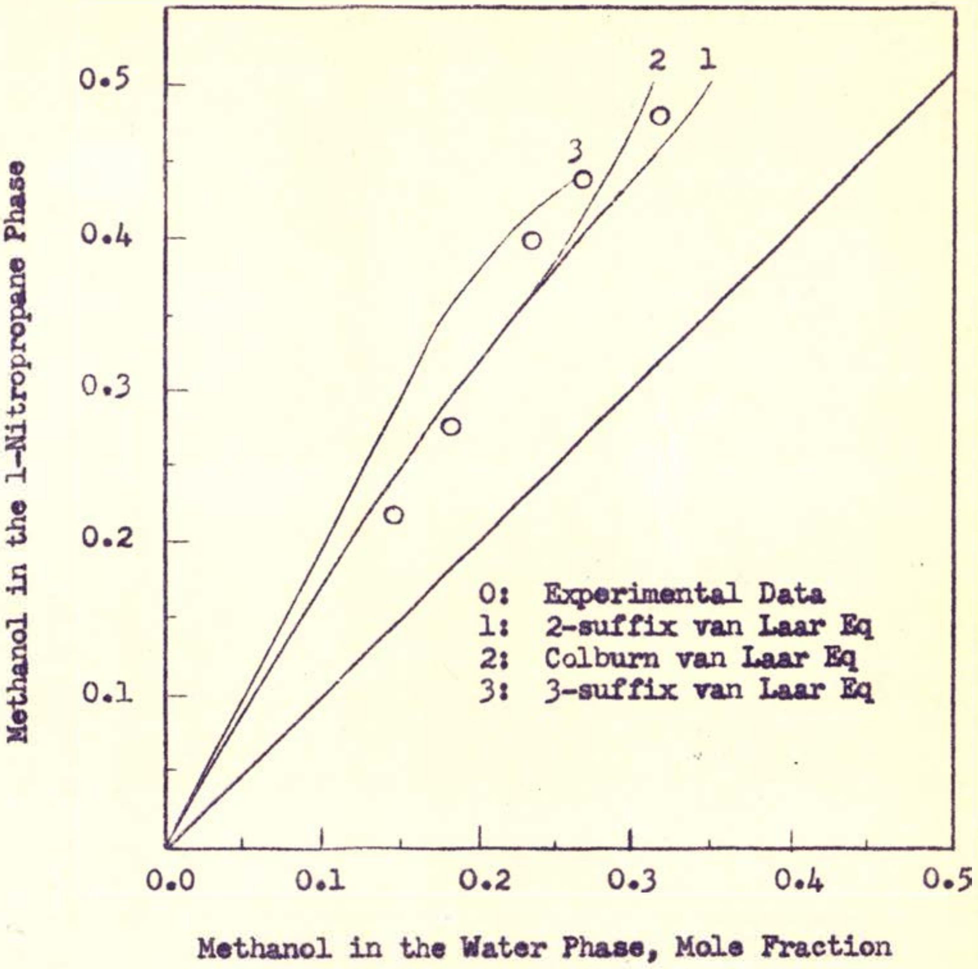


Figure 17. Comparison of the Experimental Ternary Distribution Data for the System Methanol, Water, 1-Nitropropane, With Those Data Predicted by Three Forms of the van Laar Equation

TABLE XI

Comparison of the Experimental Distribution Data of Three Systems With Those Data Predicted by the Method of Scheibel and Friedland

Ethanol in Water* Phase		Acetic Acid in Water* Phase		Acetone in Chloroform* Phase	
Exp.(1)	Predicted	Exp.(2)	Predicted	Exp.(3)	Predicted
1.72	1.69	29.6	29.2	42.9	40.1
3.41	3.37	32.0	32.4	55.2	52.1
4.82	4.76	39.9	38.1	60.0	55.8
6.50	6.64	49.3	45.4	57.2	56.1
8.20	8.99	50.1	48.6	56.6	52.4
10.41	11.20	50.5	49.4		

* All Tabular values in mole per cent

1. Data of Beech, D. G., and S. Glasstone: J. Chem. Soc. 67, (1938)
2. Data of Hand, D. B.: J. Phys. Chem, 34, 1961, (1930)
3. Data of Hand, D. B.: J. Phys. Chem, 34, 1961, (1930)

Sample Calculations

The sample calculations presented cover the following basic phases of the computations: (1) calculation of ternary solubility data, (2) calculation of ternary distribution data, (3) calculation of binary solution constants, (4) calculation of ternary constants, (5) prediction and comparison of the values of ternary-liquid distribution data.

Calculation of Ternary Solubility Data. From experimental test number 16, Table XXII, Appendix D, one ternary solubility datum point was obtained for the system water, methanol, and 1-nitropropane. This calculation involved the pure component density data which are found in Table XX, Appendix D. The calculation was performed as follows:

$$W_n = V_n d_n \tag{30}$$

$$W_t = V_n d_n \tag{31}$$

$$W\% = (W_n/W_t)(100) \tag{32}$$

where:

W_n = weight of component n in solution, gm

W_t = weight of solution, gm

$W\%$ = weight per cent of component n in solution, gm/gm

d_n = density of component n, gm/cc

V_n = volume of component n in solution, cc

thus:

$$W_t = (5.00)(1.002) + (10.00)(0.7906) + (4.38)(0.9928)$$

$$W_t = 17.285 \text{ gm}$$

$$W_1/W_t = (5.010)/(17.285) = 28.837 \text{ wt \% 1-nitropropane}$$

$$W_2/W_t = (7.906)/(17.285) = 45.794 \text{ wt \% methanol}$$

A similar calculation was performed for each point of cloud point datum in Tables XXI, and XXII, Appendix D. By this procedure, the ternary solubility curve for water, methanol, and 1-nitropropane was obtained.

Calculation of Ternary Distribution Data. From experimental test number 6, Table XXV, Appendix D, one ternary-liquid distribution datum point was calculated for the system water, methanol, and 1-nitropropane as follows:

From test number 6, Table XXV, Appendix D

refractive index of light phase = 1.34509

refractive index of heavy phase = 1.37107

The above values were used to obtain the concentration of methanol on the ternary solubility curve from Figure 23, Appendix D. This resulted in:

equilibrium concentration of methanol in the light phase = 42.31 wt %

equilibrium concentration of methanol in the heavy phase = 35.99 wt %

These two points determine the equilibrium line passing through the original one-phase mixture and terminating on the solubility curve. Thus, from the solubility data, Table II, the equilibrium mixtures are obtained as:

Light phase	Heavy phase
8.37 wt % 1-nitropropane	48.15 wt % 1-nitropropane
49.32 wt % water	12.16 wt % water
42.31 wt % methanol	35.99 wt % methanol

Conversion of Data to Mole Fraction Units. As it was logical to work consistantly in one set of units, it was necessary to convert much of the data found in the literature from weight fraction units to mole fraction units. This was performed on the LGP-30 Digital Computer using the data format described for Program I, Appendix C. An example of the data input and computer output is shown in Table XII, page 64. This example uses the ternary distribution data for aniline, N-heptane, and cyclohexane, as reported by Hunter and Brown(30).

Computation of Binary Solution Constants. Binary solution constants were obtained from two sources: (1) vapor-liquid equilibria data, and (2) mutual solubility data. To calculate binary solution constants from vapor-liquid data, activity coefficients had to first be calculated.

Activity Coefficients. The vapor-liquid data, as reported, were converted to mole fraction units if necessary, then converted to activity coefficients by the use of Program II, Appendix C. Program II was written to convert total pressure vapor-liquid equilibria data to activity coefficients using Raoult's Law as defined by Equation 1, page 6. An example of the data input and computer output for the binary vapor-liquid system benzene and acetic acid, as reported in Perry's Handbook(41), is shown in Table XIII, page 65.

Vapor-Liquid Equilibria Data. After the activity coefficients, as a function of liquid mole fractions, were obtained from Program II, all points except those between 0.20 and 0.80 mole fraction were eliminated, as recommended by Reid(45). Program III, Appendix C, was then used to calculate the binary solution constants from the

TABLE XII

Sample Data Input and Output for Program I Using the LGP-30 Digital Computer, the Conversion of Weight Fraction Units to Mole Fraction Units

---

Data Input

```
9320'+04-'7190'+04-'256'+03-'593'+03-'478'+03-'
735'+03-'34'+03-'54'+03-'49'+03-'60'+03-'f'

660'+04-'820'+04-'130'+03-'93'+03-'104'+03-'81'+03-'
839'+03-'905'+03-'889'+03-'925'+03-'f'

0'+00-'1990'+04-'614'+03-'314'+03-'418'+03-'
184'+03-'127'+03-'41'+03-'62'+03-'15'+03-'f'

1002'+01-'9312'+02-'8416'+02-'100'+02-'
10'+00-'100'-02-'100'-02-'f'
```

Computer Output

```
X1                     X2                     X3

.929195                .070804                .000000
.688590                .084502                .226906
.227170                .124131                .648698
.555857                .093794                .350397
   .                      .                      .
   .                      .                      .
   .                      .                      .
```

Conversion from weight fraction to mole fraction of data reported by Hunter and Brown(30) for the system N-heptane (1), aniline (2), and cyclohexane (3).

TABLE XIII

Sample Data Input and Output for Program II Using the LGP-30 Digital Computer, the Calculation of Activity Coefficients from Binary Total Pressure Vapor-Liquid Data

Data Input

```
27316'+02-'760'+00+'152860'-02-'7207'+03-'2111566'-03-'
8278'+03-'100'+00+'1'+00+'1-00+'9'+00+'f'

3149'+02-'3882'+02-'4782'+02-'5776'+02-'
6443'+02-'6859'+02-'7421'+02-'7752'+02-'8504'+02-'f'

647'+02-'891'+02-'1272'+02-'1923'+02-'2497'+02-'
2993'+02-'3804'+02-'4539'+02-'6451'+02-'f'

1095'+01-'1068'+01-'1037'+01-'9944'+02-'9623'+02-'
9399'+02-'9085'+02-'8896'+02-'8472'+02-'f'
```

Computer Output

```
   x1             g1             x2            g2
 6.4699         2.2685         93.5299        .9677
 8.9100         2.1679         91.0899        .9711
12.7200         2.0187         87.2799        .9604
19.2300         1.7946         80.7699        .9736
   .              .               .             .
   .              .               .             .
   .              .               .             .
```

Computation of activity coefficients for the binary system benzene and acetic acid from vapor-liquid data(41).

remaining points of activity coefficient data. The basis of Program III is a least-squares fit for the point-slope form of the proper integrated binary Gibbs-Duehm equation. Program III can be used to calculate binary solution constants for either the van Laar case or the Margules case. An example of the data input and the computer output for the binary system benzene and acetic acid is shown in Table XIV, page 67.

Mutual Solubility Data. Binary solution constants were calculated directly from mutual solubility data using the binary forms of the van Laar equation or the Margules equation as presented by Treybal(53). The following is an example of calculating the binary solution constants for the van Laar case for the system benzene and water.

From the International Critical Tables(31)

(A) Water Phase: 99.9664 mole %; 0.0346 mole %

(B) Benzene Phase: 0.29224 mole %; 99.7023 mole %

TABLE XIV

Sample Data Input and Output for Program III Using the LGP-30 Digital Computer, the Calculation of Binary Solution Constants for Use in the van Laar Equations

---

Data Input

```
1'+00+'5'+00+'''''''''f'

6451'+02-'4539'+02-'3804'+02-'2993'+02-'2497'+02-'f'

1149'+03-'1316'+03-'1423'+03-'1529'+03-'1617'+03-'f'
```

Computer Output

```
 Aba                                         Aab

0.3222                                      0.4386
```

Calculation of the binary solution constants for the system acetic acid (a) and benzene (b), from the vapor-liquid equilibria data presented by Perry(41).

Computation of a Ternary Constant. The calculation of a ternary constant for use in the 3-suffix van Laar or the 3-suffix Margules equation, as defined by Wohl(68), was performed for each system by two methods: (1) from one known ternary-liquid equilibrium datum point, and (2) from the binary solution constants by the Colburn approximation.

One Experimental Point. The ternary constant was calculated from one known point of ternary-liquid distribution data for each system studied by Program IV, Appendix C. An example of the data input and computer output for the system water, ethyl acetate, and ethanol, as reported by Beach and Glasstone, is shown in Table XV, page 70.

Colburn Approximation. A general ternary constant for use in the integrated forms presented by Wohl(68) was calculated for each system by the method suggested by Colburn(11). The following is an example of this calculation for the system ethyl acetate, ethanol, and water.

$$C = \tfrac{1}{2}(A_{21} - A_{12} + A_{13} - A_{31} + A_{32} - A_{23}) \qquad (11)$$

$$C = \tfrac{1}{2}(1.788 - 1.030 + 0.3802 - 0.6334 + 0.3424 - 0.3617) = \qquad (39)$$

$$0.2428$$

Computation of Activities from Integrated Forms. The integrated forms of the Gibbs-Duehm equation studied were the van Laar equations and the Margules equations. These equations yield activity coefficients of the solute in a ternary system as a function of liquid composition of the solute. Each activity coefficient was converted to activity as defined in Equation 20, page 33.

TABLE XV

Sample Data Input and Output for Program IV Using the LGP-30 Digital Computer, the Calculation of a Ternary van Laar Constant from One Experimental Ternary Equilibrium Point

Computer Input

```
.0005300'

6334'+04-'3424'+04-'1788'+03-'3617'+04-'3802'+04-'2''1''f'

1754'+04-'522'+03-'303'+03-'f'

1034'+04-'847'+03-'496'+04-'f'
```

Computer Output

```
29116812.-08-      45233559.+09-      58950969.+08-

13631265.-07- = C
```

Ternary constant for ethanol, ethyl acetate, and water from data reported by Beech and Glasstone(4).

van Laar Equations. A general program to solve the 3-suffix van Laar equation from a knowledge of the ternary mutual solubility data and the binary solution constants is Program V in Appendix C. The program is written so it will also solve the 2-suffix van Laar equation if the ternary constant is equated to zero. For each of the ternary systems studied, Program V was used to compute activities of the solute as a function of the solute liquid composition for each of the following cases: (1) 2-suffix van Laar, (2) 3-suffix van Laar with the ternary constant computed from one experimental point of equilibria data, and (3) 3-suffix van Laar with the ternary constant computed by the Colburn approximation. An example of the data input and computer output format is shown in Table XVI, page 72. The example is for the ternary system ethanol, ethyl acetate, and water, using the solubility data of Beech and Glasstone(4), and a ternary constant evaluated by the Colburn approximation.

Margules Equation. A general program to solve the 3-suffix Margules equation from a knowledge of the ternary mutual solubility data and the binary solution constants is Program VI in Appendix C. The program is written so it will also solve the 2-suffix Margules equation if the ternary constant is equated to zero. For each of the ternary systems studied, Program VI was used to compute activities of the solute as a function of the solute liquid composition for each of the following cases: (1) 2-suffix Margules, and (2) 3-suffix Margules with the ternary constant computed by the Colburn approximation. An example of the data input and computer output is shown

TABLE XVI

Sample Data Input and Output for Program V Using the LGP-30 Digital Computer, the Solution of the 3-Suffix van Laar Equation

---

Data Input

```
0''1718'+05-'355'+04-'473'+04-'645'+04-'812'+04-'1034'+04-'0''
330'+04-'837'+04-'1110'+04-'1368'+04-'1678'+04-'1754'+04-'f'

933'+03-'966'+03-'947'+03-'932'+03-'909'+03-'886'+03-'847'+03-'
1321'+04-'1520'+04-'2055'+04-'2545'+04-'294'+03-'396'+03-'522'+03-'f'

1738'+05-'1772'+05-'1939'+05-'2185'+05-'2635'+05-'335'+04-'496'+04-'
8679'+04-'815'+03-'711'+03-'634'+03-'569'+03-'437'+03-'303'+03-'f'

6334'+04-'3802'+04-'3424'+04-'3617'+04-'1030'+03-'1788'+03-'
2428'-04-'1''f'
```

Computer Output

```
  X              Log                                      a

.00000          .56467          3.67010          .00000
.01718          .53492          3.42712          .05887
.03350          .50061          3.16672          .10608
.04730          .47015          2.95226          .13964
   .               .                .                .
   .               .                .                .
   .               .                .                .
```

Solution of the 3-suffix van Laar equation for the system ethyl acetate, ethanol, and water, from the solubility data of Beech and Glasstone(4). The ternary constant, C = 0.2428, by the Colburn approximation.

in Table XVII, page 74. The example is for the ternary system ethanol, ethyl acetate, and water using the solubility data of Beech and Glasstone in the 2-suffix Margules equation.

Computation of Activities by the Method of Scheibel and Friedland. The empirical method of Scheibel and Friedland was applied successfully to three of the ternary systems studied. It would not apply to the other four. The systems correlated by this method were: (1) ethanol, ethyl acetate, and water; (2) acetic acid, benzene, and water; and (3) acetone, chloroform, and water. An example of this calculation is given for the ternary system acetone, chloroform, and water, as follows:

1. The binary vapor-liquid equilibria data for the system acetone and water(3) were converted to activity coefficients by the use of Program II, Appendix C. These activity coefficients were plotted by their respective liquid concentrations on side 13 of a ternary concentration diagram. This is shown in Figure 18, page 75.
2. The binary vapor-liquid equilibria data for the system acetone and chloroform(44) were converted to activity coefficients by the use of Program II, Appendix C. These activity coefficients were plotted by their respective liquid concentrations on side 12 of a ternary concentration diagram. This is shown in Figure 19, page 76.
3. The ternary solubility data as reported by Hand(22) were plotted on this ternary concentration diagram.
4. Lines perpendicular to the base, 23, of the ternary concentration diagram were drawn through each point of solubility data and extended to the side of the diagram.

TABLE XVII

Sample Data Input and Output for Program VI Using the LGP-30 Digital Computer, the Solution of the 3-Suffix Margules Equation

---

Data Input

```
0''1718'+05-'335'+04-'473'+04-'645'+04-'812'+04-'1034'+04-'0''
330'+04-'837'+04-'1110'+04-'1368'+04-'1678'+04-'1754'+04-'f'

933'+03-'966'+03-'947'+03-'932'+03-'909'+03-'886'+03-'847'+03-'
1321'+04-'1520'+04-'2055'+04-'2545'+04-'294'+03-'396'+03-'522'+03-'f'

1738'+05-'1772'+05-'1939'+05-'2185'+05-'2635'+05-'355'+04-'496'+04-'
8679'+04-'815'+03-'711'+03-'634'+03-'569'+03-'437'+03-'303'+03-'f'

6334'+04-'3802'+04-'3424'+04-'3617'+04-'1030'+03-'1788'+03-'
0'+00+'1''f'
```

Computer Output

```
XI                      ac                    Activity

.00000               3.42469                   .00000
.01718               3.67522                   .06314
.03350               3.41943                   .11455
.04730               3.22522                   .15255
  .                     .                         .
  .                     .                         .
  .                     .                         .
```

Solution of the 3-suffix Margules equation for the system ethyl acetate, ethanol, and water, from the solubility data of Beech and Glasstone(4). The ternary constant, $C = 0$.

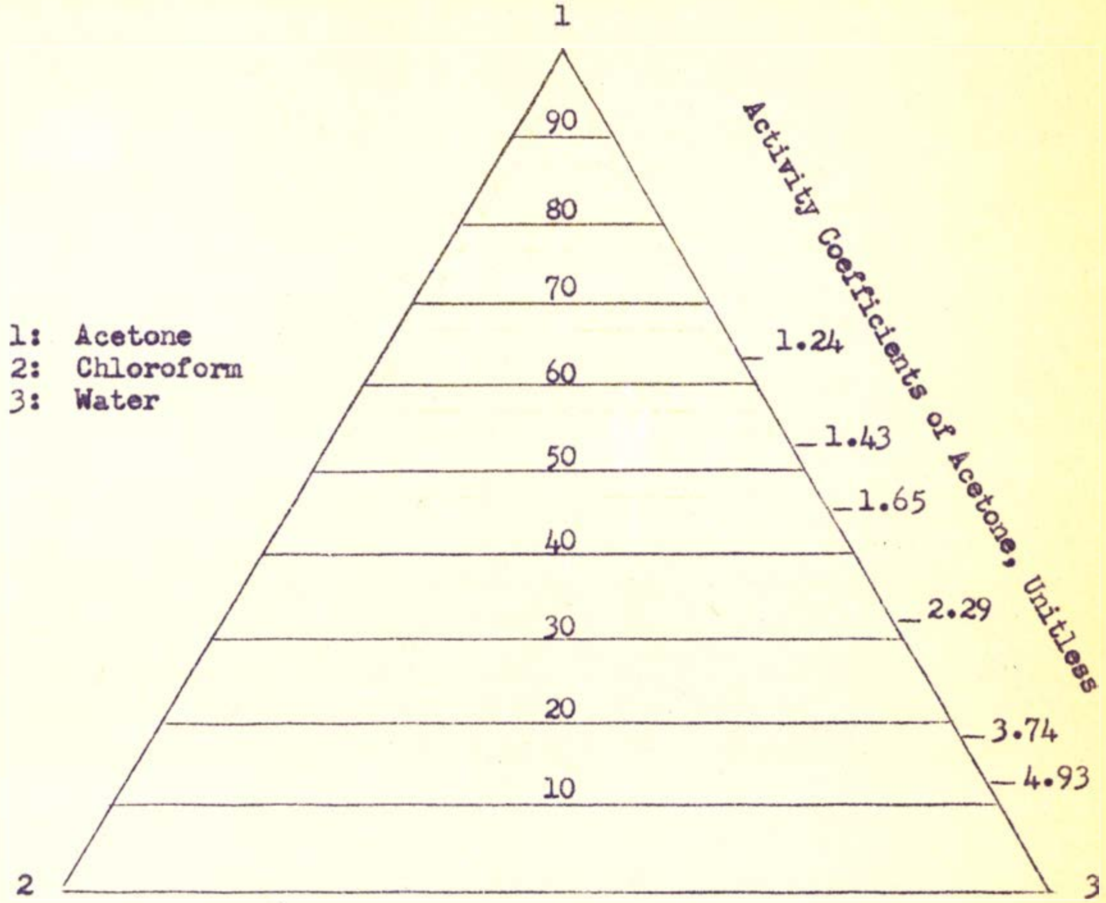


Figure 18. Activity Coefficients of Acetone in the Binary System Acetone, Water Plotted on Ternary Concentration Diagram

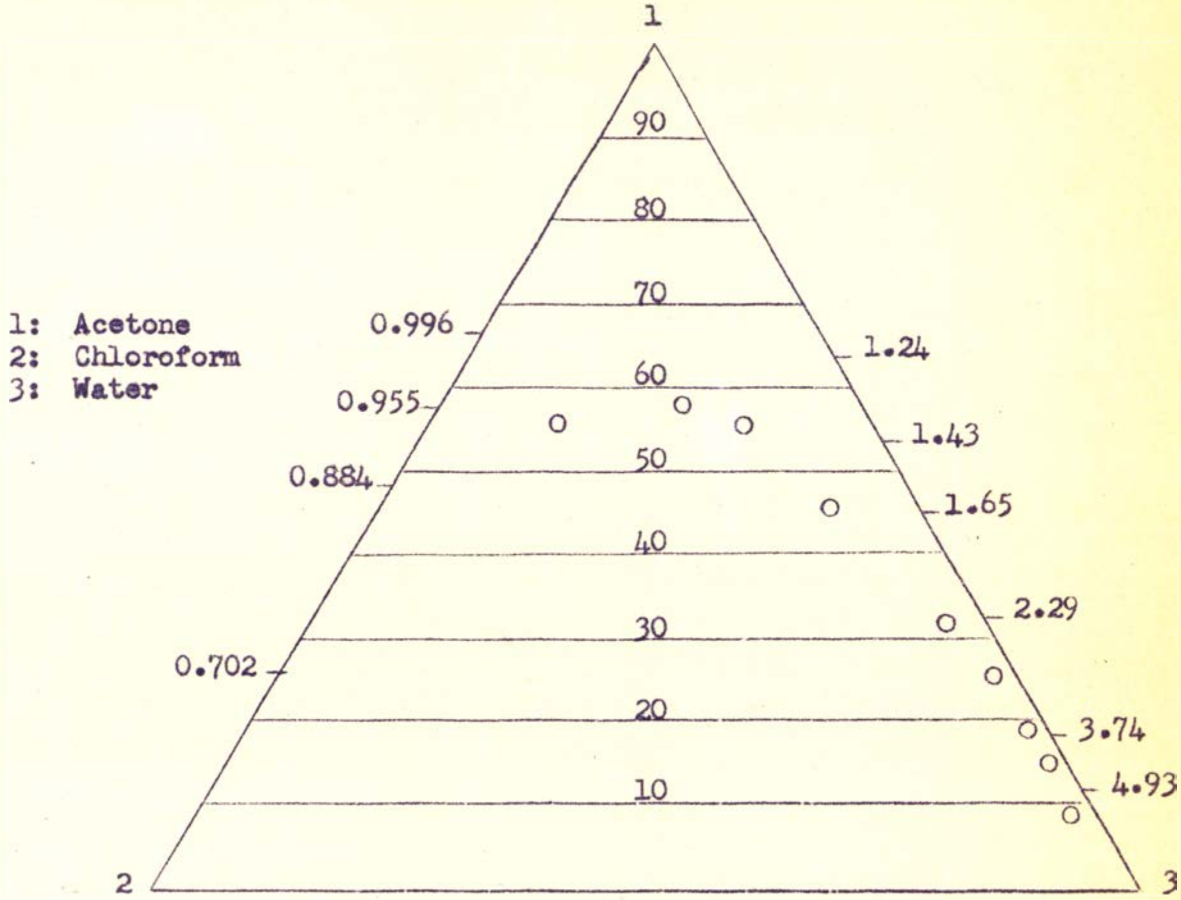


Figure 19. Ternary Solubility Data and Binary Activity Coefficients for System Acetone, Chloroform, Water Plotted for Scheibel and Friedland Interpolation

5. The ternary activity coefficient of the solute, acetone, was then read at the intersection point of the perpendicular line through the solubility point and the side of the triangular diagram. For example, from Figure 20, page 78:

   The perpendicular line through the solubility point

   46.63 mole % acetone
   45.89 mole % water
   7.48 mole % chloroform

   intersects the side 13 at an activity coefficient value of 1.237.

6. A cross plot of binary activity coefficients as a function of binary liquid mole fractions was made to increase the accuracy of obtaining the ternary activity coefficients. Then each point of solubility data were used to obtain a point of ternary-liquid activity coefficient data.

7. Each ternary activity coefficient was multiplied by its respective solute mole fraction to obtain a point of ternary activity. For example, using the example sited in step 5:

   $$(\text{Mole fraction solute})(\text{activity coefficient}) = (\text{Activity}) \qquad (40)$$

   $$(46.63/100) \qquad (1.237) \qquad = (0.5778)$$

Computation of Ternary-Liquid Distribution. After the values of solute activity as a function of solute composition were obtained for each system studied by the van Laar equations, the Margules equations, and the Scheibel and Friedland method, the ternary-liquid distribution was calculated for each case by the method of Hildebrand(24). This method involved plotting values of the solute activity as a function of solute mole fraction in each of the two phases. Equilibrium points were

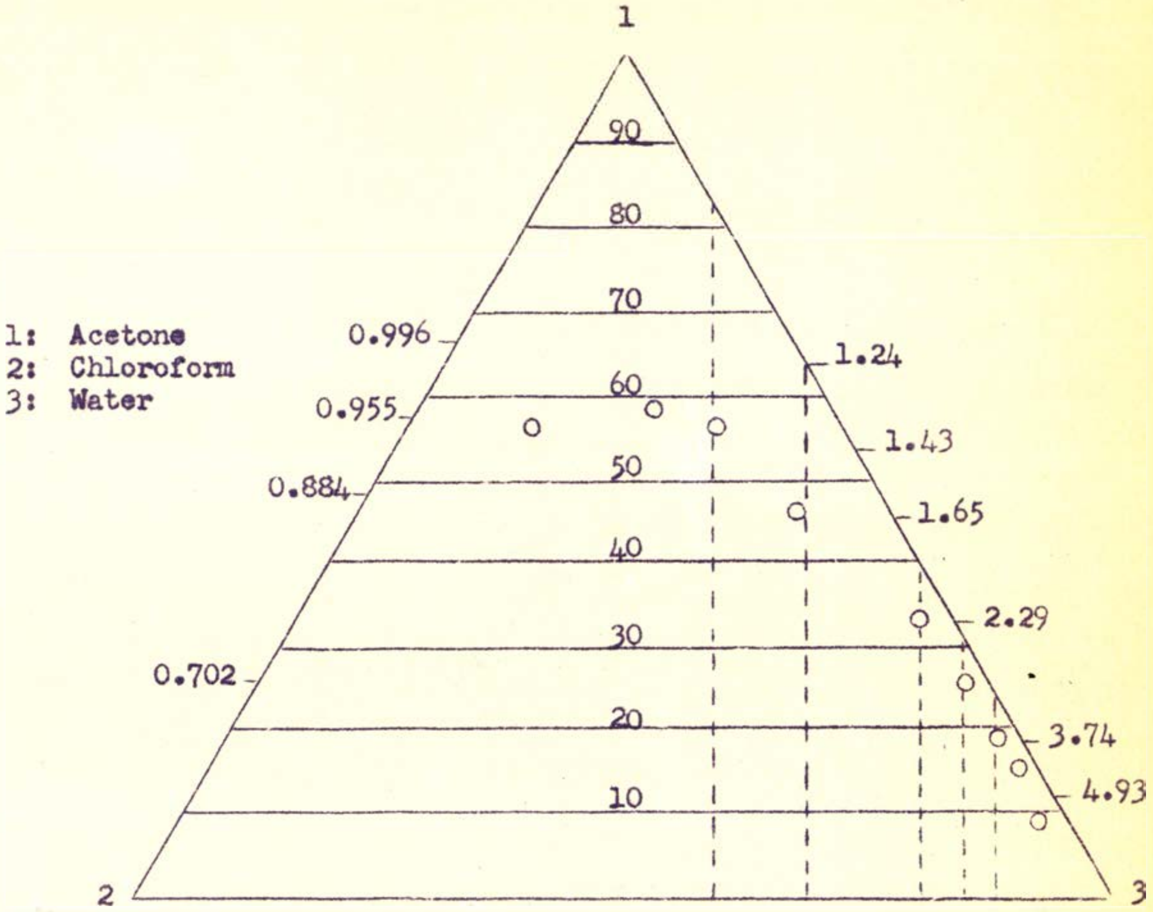


Figure 20. Method of Scheibel and Friedland Applied to System Acetone, Chloroform, Water

then read off this plot at values of constant activity in each phase. For an example of this procedure involving the ternary systems acetic acid, benzene, and water as predicted by the 3-suffix van Laar with an experimental constant, refer to Figure 21, page 80. At a constant value of activity, a:

$$a = 0.4 \tag{41}$$

$x_{12} = 0.215$ mole fraction

$x_{13} = 0.359$ mole fraction

$$a = 0.2 \tag{42}$$

$x_{12} = 0.084$ mole fraction

$x_{13} = 0.180$ mole fraction

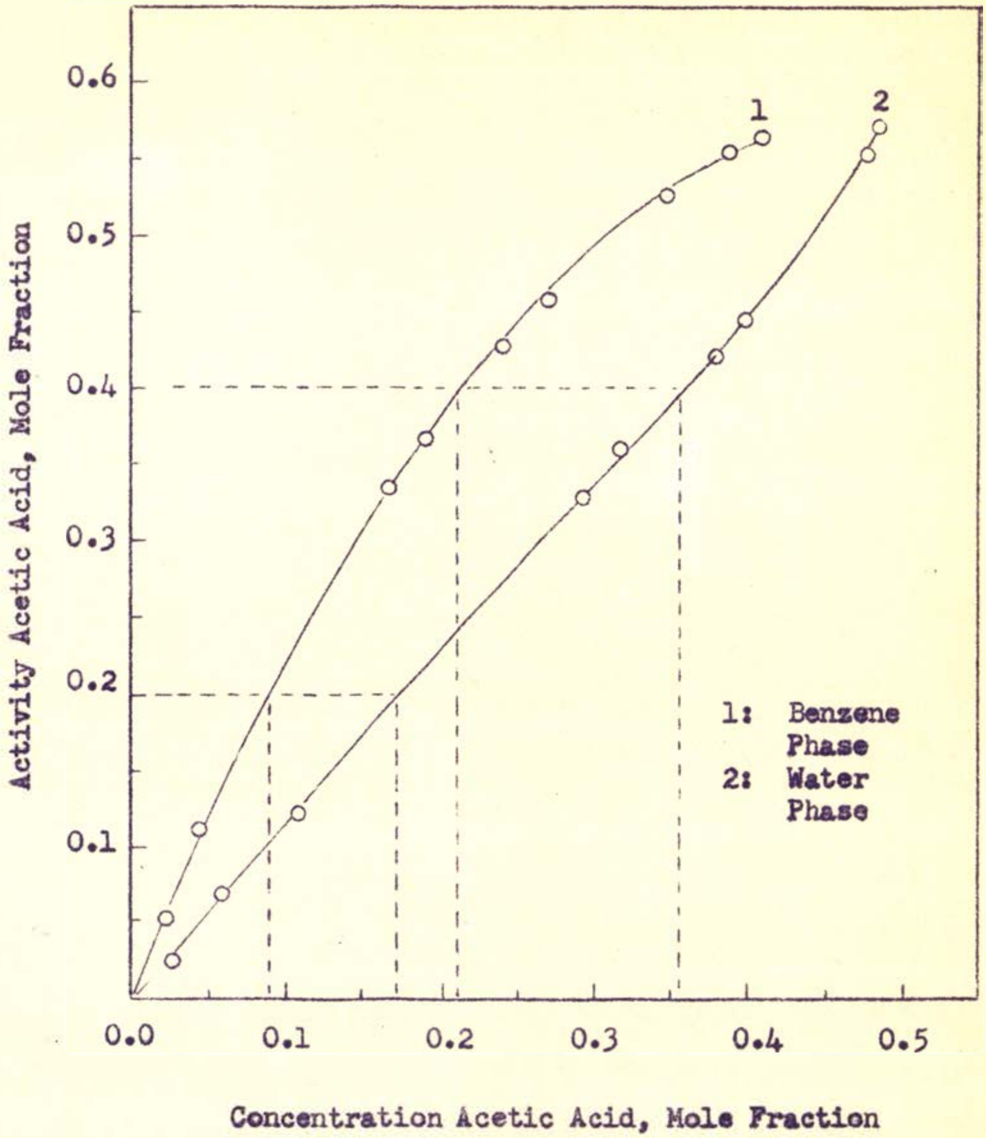


Figure 21. Graphical Computation of Phase Equilibria from Activity-Concentration Data

IV. DISCUSSION

The discussion section of this thesis is concerned with the following: (1) discussion of experimental procedure, (2) discussion of experimental results, (3) a comparison of five methods used to predict ternary distribution data, (4) recommendations, and (5) limitations.

Discussion of Experimental Procedure

The experimental procedures used to determine the solubility and equilibria data for a ternary system were modifications of those procedures described in detail by Hand(22) and Othmer(37). The modifications concerned: (1) titration at a constant temperature, (2) agitation time, and (3) titration near plait point.

Titration at a Constant Temperature. During the "cloud Point" titrations used to determine ternary mutual solubility, Hand(22) and Othmer(37) removed their samples from the constant temperature bath. In doing this, they ignored the effects of the ambient temperature and the heat of mixing on the mutual solubility, thus introducing error. The mutual solubility data reported in this thesis were obtained without removing the sample from the temperature bath during titration. This was accomplished by using a glass bottomed constant temperature bath with a light below the glass, thus allowing the end point of the titration to be observed while keeping the sample in the bath.

Agitation Time. A problem arose concerning the proper agitation time after the titration of the two-phase mixture with the third component. An erroneous cloud point results from this type of titration unless the mixture is agitated in the constant temperature bath for ten to fifteen minutes after each titration. This problem was solved by connecting the capped flask containing the three-component mixture to the shaft of a variable-speed laboratory mixer. The flask was then immersed in the constant temperature bath while the agitation motor was supported by a ring stand.

Titration Near Plait Point. A problem occurred while attempting to obtain a cloud point in the concentration range of 25 to 30 weight per cent water. In this case the cloud point was indistinguishable. It should be observed on Figure 4, page 39, that there are no data points in this region of the curve. This situation occurred because this region is near the plait point. At this point, one phase cannot be distinguished from the other.

Discussion of Experimental Results

The mutual solubility data for the ternary-liquid system water, methanol, and 1-nitropropane, were determined at two temperatures ---- 25 °C and 30 °C. Table I, page 36, lists the solubility data at 30 °C, while Table II, page 37 lists the solubility data at 25 °C. The ternary distribution data for the system were determined at 25 °C. This is given in Table III, page 38.

Mutual Solubility Curve. From a study of Tables I and II, it was observed that the solubility relationships for this system do not change appreciably with temperature. Since this is true, the data at the two temperatures result in the same phase envelope. Figure 4, page 39, shows that this phase envelope resembles the anticipated curve. According to Treybal(52), this curve is in the class termed Type I, which means the solution forms but two immiscible phases over its entire concentration range.

Ternary Distribution Data. The ternary distribution data for the system methanol, water, and 1-nitropropane, was determined at 25 °C. The validity of these data points was checked by the Othmer plot(38). This method, which was derived from an empirical investigation of published ternary-liquid systems, will result in a straight line plot if the data are valid. The Othmer plot, Figure 22, page 84, indicates that one experimental tie line is in error. That particular tie line is in the concentrated methanol range and intersects the solubility curve at 42.31 weight per cent methanol in the water phase, and 35.99 weight per cent methanol in the 1-nitropropane phase.

It was observed that at the higher concentration of methanol, that is, above 30 weight per cent, in the combined phase mixture, the two phases separated very slowly. At lower concentrations of methanol, the phase split was much more rapid. This situation may be accounted for by a study of the tie line slopes. At the lower concentrations of methanol, a larger per cent of the methanol goes to the water phase than to the 1-nitropropane phase, thus increasing the inherent density difference between water and 1-nitropropane. However, as the concentration of methanol in the original mixture increases, the ratio of the quantity going to each phase decreases. Thus, the density difference between the two phases decreases.

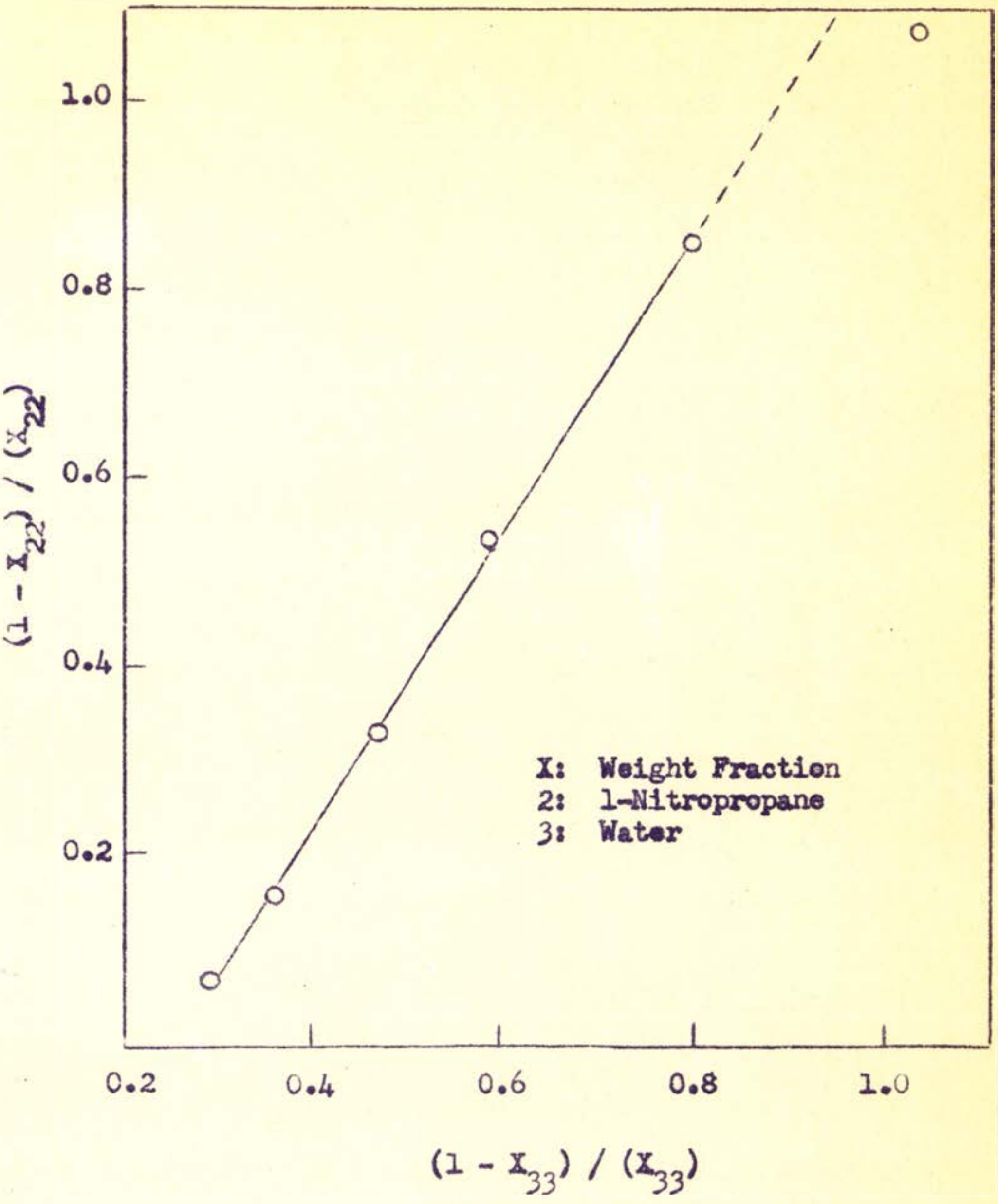


Figure 22. Othmer Plot for System Methanol, Water, 1-Nitropropane at 25 °C

Comparison of Methods Used to Predict Ternary Distribution Data

This section of the thesis is concerned with a discussion of the ability of five major methods to predict the ternary equilibria data for liquids which form two immiscible phases. Each of the five methods were applied to six different liquid mixtures and the results compared with the experimental equilibria data for the respective system. The major prediction methods studied were: (1) the van Laar equations, (2) the Margules equations, (3) the van Laar and the Margules equations modified by the Colburn constant, (4) the van Laar and the Margules equations as modified by Wohl, and (5) the Scheibel and Friedland method. The liquid systems used were: (1) acetone, benzene, water; (2) ethanol, ethyl acetate, water; (3) acetic acid, benzene, water; (4) acetone, chloroform, water; (5) cyclohexane, N-heptane, aniline; and (6) water, methanol, 1-nitropropane.

Predictive Study of the System Acetone, Benzene, and Water. The values presented in Table XVIII, page 86, show the van Laar restrictions are satisfied by the system acetone, benzene, and water. This condition implies that the van Laar equations would result in a more acceptable approximation of the ternary-liquid distribution data for the system than the Margules equations. From Table XVIII, the ratios of the binary constants for each of the three binary systems involved in the ternary system are:

Benzene, Water $\frac{3.480}{4.550} = 0.765$

Acetone, Water $\frac{0.890}{0.655} = 1.35$

Acetone, Benzene $\frac{0.176}{0.176} = 1.00$

TABLE XVIII

Application of the van Laar Conditions to Six Binary Solutions

Ternary System	Binary Solution Constants			van Laar Conditions
	A_{13}/A_{31}	A_{12}/A_{21}	A_{23}/A_{32}	$A_{13}/A_{31} = A_{12}/A_{21}\ A_{23}/A_{32}$
Acetic Acid, Benzene, Water	$\frac{0.0477}{0.6659}$	$\frac{0.4386}{0.3479}$	$\frac{4.547}{3.483}$	$0.0716 \neq 1.65$
Ethyl Acetate, Ethanol, Water				$0.948 \cong 0.960$
Acetone, Benzene, Water	$\frac{0.176}{0.176}$	$\frac{0.890}{0.655}$	$\frac{0.348}{4.55}$	$1.00 \cong 1.04$
Acetone, Chloroform, Water	$\frac{0.890}{0.655}$	$\frac{-0.446}{-0.344}$	(1)*	$1.35 \cong 1.30$
N-Heptane, Aniline, Cyclohexane	$\frac{0.867}{1.120}$	(1)*	$\frac{1.359}{1.290}$	$0.775 \neq 1.05$
Methanol, Water 1-Nitropropane	$\frac{0.251}{0.203}$	(1)*	$\frac{0.356}{0.241}$	$1.24 \neq 1.48$

* No datum available

These ratios indicate that the three associated binary systems are relatively symmetrical and, according to Wohl(69), would be fit quite well by the Margules equations. While according to Perry(41), if the ratio of the binary constants is between 0.75 and 1.3, either the van Laar equations or the Margules equations may be used. It may further be postulated that if the binary systems cannot be fit by a particular equation, whether it be the van Laar or the Margules, then neither could the resulting ternary system. From the above information concerning the three binary systems, one wishing to predict the resulting ternary system, would probably choose the van Laar equations for the prediction.

Acetone, Benzene, and Water by the van Laar Equations. In Table V, page 41, and Figure 5, page 42, the results obtained from predicting the ternary distribution of the acetone, benzene, and water system are compared with the actual experimental values of Briggs and Comings(8). These values are compared on the basis of solute in the carrier phase at constant points of solute in the solvent phase. Figure 5, shows that both the 2-suffix van Laar and the Colburn van Laar equations fit the experimental data in the dilute range, up to 7 mole per cent acetone in the water phase. Above 7 mole per cent acetone, the experimental data curve toward the hypotenuse while the van Laar equations continue their ascent. The 3-suffix van Laar equation containing the experimental constant fits the experimental data at the higher concentration ranges of acetone in the water phase, while it deviates from the experimental values at the lower concentration range of below 7 per cent.

Acetone, Benzene, and Water by the Margules Equations. A comparison of the predicted values of ternary distribution, with the experimental values, is listed in Table V, page 41, and shown in Figure 6, page 43. The 3-suffix Margules equation fits the experimental data in the dilute range, up to 7 mole per cent acetone in the water phase, better than any of the van Laar equations. Yet, like the 2-suffix van Laar and Colburn van Laar equations, the 3-suffix Margules equation will not fit the experimental curve that occures in the higher concentration range. There is no significant difference between the fit of the 3-suffix Margules and the Colburn Margules equations.

Acetone, Benzene, and Water by the Method of Scheibel and Friedland. The method of Scheibel and Friedland did not apply to the system acetone, benzene, and water. This situation arose because the binary activity coefficients of acetone in the benzene solution were of a completely different magnitude than the activity coefficients of acetone in the water solution. Under these conditions, there was no way available to extrapolate to the ternary activity coefficients of acetone.

Predictive Study of the System Ethanol, Ethyl Acetate, and Water. The values presented in Table XVIII, page 86, show that the ternary-liquid system ethanol, ethyl acetate, and water fits the van Laar restrictions quite well. This implies that the ternary distribution data for this system would be approximated by the ternary van Laar equations to an acceptable degree. From Table XVIII, the ratios of the binary constants for the three binary systems which compose the ternary system are:

Ethyl acetate, Ethanol $\frac{0.3424}{0.3617} = 0.946$

Ethanol, Water $\frac{0.6334}{0.3812} = 1.67$

Ethyl acetate, Water $\frac{1.030}{1.780} = 0.578$

The ratio of the binary constants for the system ethyl acetate and ethanol proves the system to be symmetrical, indicating that it could be fit by either the Margules or the van Laar equations. The system ethyl acetate and water is unsymmetrical to the degree that the ratio of its binary constants is in the vicinity of 2. In this case, Treybal(53) states the binary system would best be fit by the van Laar equation. The system ethanol and water indicates a dissymmetry approaching 2, and would be best fit by the van Laar equation. Thus, it is shown that all qualitative examinations of the three binary systems indicate that the ternary system would be best fit by the van Laar equations.

Ethanol, Ethyl Acetate, and Water by the van Laar Equations.

In Table VI, page 44, and Figure 7, page 45, the values of ternary distribution for the system ethanol, ethyl acetate, and water, as predicted by the van Laar equations, are compared with the experimental data of Beech and Glasstone(4). The comparison is based on constant values of solute in the solvent phase. The 2-suffix van Laar fits the experimental data in the dilute concentration range up to 5 mole per cent ethanol in the water phase. Above 5 mole per cent the experimental data curves toward the hypotenuse, while the predicted curve continues upward. The Colburn van Laar fits the experimental data in the dilute range as well as the 2-suffix van Laar. However, the fit in the high concentration range, above 5 per cent ethanol in the water phase, is not as good as that given by the 2-suffix van Laar. For example, at 17.50 mole per cent ethanol in the ethyl acetate phase, the experimental equilibrium concentration of ethanol in the water phase is 10.41 mole per cent. At this same datum point, the 2-suffix van Laar predicts an equilibrium concentration of 7.40 mole per cent, and the Colburn van Laar predicts a concentration of 7.00 mole per cent ethanol in the water phase. The 3-suffix van Laar with the experimental constant fits only the point of data used to determine the constant, while either the 2-suffix van Laar or the Colburn van Laar gives a better approximation of the experimental equilibria data over the remainder of the curve.

Ethanol, Ethyl Acetate, and Water, by the Margules Equations. In Table VI, page 44, and Figure 8, page 46, the results obtained from predicting the ternary distribution of the ethanol, ethyl acetate, and water system are compared with the actual experimental values. The 3-suffix Margules equations do not fit the dilute range, above 5 per cent ethanol in the water phase, as well as the 2-suffix van Laar equations. However, on an average they fit the entire range of concentration more satisfactorily. This was not expected, as an analysis of the binary data indicated that the van Laar equation would be superior to the Margules equations for this system. The Colburn Margules, on the other hand, gives the worst fit for this system of any of the prediction equations.

Ethanol, Ethyl Acetate, and Water by the Method of Scheibel and Friedland. Figure 9, page 47, and Table XI, page 60, give the comparison of the experimental values of the ternary distribution data with those values predicted by the method of Scheibel and Friedland. The predicted curve gives an acceptable approximation of the experimental data over the entire range of concentrations. As an over-all approximation of the actual data, the method of Scheibel and Friedland is superior to either the van Laar or Margules equations for this system.

Study of the System Acetic Acid, Benzene, and Water. From the values presented in Table XVIII, page 86, it is observed that the van Laar restrictions are not satisfied by the system acetic acid, benzene, and water. This condition indicates the van Laar equations would not result in an acceptable approximation of the ternary equilibria data for this system. From Table XVIII, the ratios of the binary constants for each of the three binary systems which compose the ternary system are:

Benzene, Water $\frac{3.480}{4.550} = 0.765$

Acetic acid, Water $\frac{0.0477}{0.6659} = 0.0716$

Acetic acid, Benzene $\frac{0.4386}{0.3479} = 1.26$

These ratios show the systems benzene-water and acetic acid-benzene to be unsymmetrical to the same degree and the value of both ratios to be near unity. This indicates that the Margules equations would fit these two binary systems. The system acetic acid and water exhibits a large dissymmetry and cannot be fit by the Margules equations. Even the van Laar equations will not handle very large ratios of the binary constants with accuracy. For this reason, the binary constants for the system acetic acid and water were obtained by plotting the composition as a function of the logarighm of the activity coefficient. The method of force-fitting the binary data into a point-slope form of the Margules or van Laar equations did not give acceptable results on this system. This examination of the binary data indicates that the ternary system would not be fit by the van Laar equations, but the Margules equations might give an acceptable fit. Also, because the binary system acetic acid and water is not fit by either of the integrated forms, the probability of obtaining an acceptable approximation for the ternary system would be doubtful.

Acetic Acid, Benzene, and Water by the van Laar Equations. A comparison between the experimental ternary-liquid distribution data for the system acetic acid, benzene, and water, and that predicted by the van Laar equations is made in Table VII, page 48, and Figure 10, page 49. Neither the 2-suffix van Laar equation nor the Colburn van Laar equation fit the experimental data in an acceptable manner. Both equations appear to fit at the point 48.6 mole per cent acetic acid in the benzene layer. However, a study of Figure 10 will show that it is by mere chance as the predicted curves tend to cross on the experimental point in that range. The 3-suffix van Laar equation with the experimental constant gives a partially acceptable fit for the entire range of experimental values. This could be explained by considering the fact that all of the known experimental points are in the concentrated range from 29 mole per cent to 50 mole per cent acetic acid in the water phase. Thus, if any equation containing three independent constants which did not fit the experimental data at all, was given a forth constant which forced a fit through one point of experimental data, the over-all fit would be improved. This is, in effect, what the additional ternary constant did.

Acetic Acid, Benzene, and Water by the Margules Equations. It will be remembered that an analysis of the binary data indicated the Margules equations would result in a better fit for the system acetic acid, benzene, and water, than the van Laar equations. This was not the case, for on the plot of concentration of acetic acid versus predicted activity, the lines representing the two phases crossed. This is a physically impossible situation and could only indicate that the Margules equations do not represent this system.

Acetic Acid, Benzene, and Water by the Method of Scheibel and Friedland. Figure 11, page 50, and Table XI, page 60, shows the comparison between the actual ternary distribution data for the system acetic acid, benzene, and water with that data predicted by the method of Scheibel and Friedland. From a study of Figure 11, it is observed that the predicted curve gives an acceptable approximation of the experimental data. As an over-all approximation of the experimental data, the Scheibel and Friedland curve is superior to the curves obtained by either the 2-suffix van Laar or the Colburn van Laar. However, it is not as accurate in the high concentration range as the 3-suffix van Laar with the experimental constant.

Study of the System Acetone, Chloroform, and Water. The system acetone, chloroform, and water satisfies the van Laar restrictions as shown in Table XVIII, page 86. This condition implies that the van Laar equations would result in a more acceptable approximation of the ternary-liquid distribution data for the system than the Margules equations. From Table XVIII, the ratios of the binary constants for each of the three binary systems involved in the ternary system are:

Acetone, Water $\frac{0.890}{0.665} = 1.35$

Chloroform, Water Unity

Acetone, Chloroform $\frac{-0.446}{-0.334} = 1.30$

Thus, the two binary systems, acetone-water and acetone-chloroform, are shown to be relatively symmetrical and, according to Wohl(69), would be fit by the binary Margules equations. The binary system chloroform-water must be assumed as ideal since no binary data is available on this system. This assumption is the same as neglecting the effect of the solubility between these two components and can be justified by the classification system of Ewell(19). Following the preceding analysis of the binary data, it would not be easy to predict which of the equations would best fit the ternary system. The van Laar equations could be justified by the fact that the van Laar restrictions are fulfilled. However, the Margules equation could be justified, as the two binary systems are of the Margules form.

Acetone, Chloroform, and Water by the van Laar Equations. In Table VIII, page 51, and Figure 12, page 52, the results obtained from predicting the ternary distribution of the acetone, chloroform, and water system are compared with the actual experimental values. It is shown in Figure 12, that the 2-suffix van Laar equation fits the experimental points over the entire range of values, and is an excellent approximation of the ternary equilibria data. On the other hand, the Colburn van Laar equation does not result in an acceptable fit of the experimental points. The 3-suffix van Laar equation with an experimental constant fits the region where it was forced by the constant, but does not give an acceptable over-all fit.

Acetone, Chloroform, and Water by the Margules Equations. A comparison of the predicted values of ternary distribution, with the experimental values, is listed in Table VIII, page 51, and shown in Figure 13, page 53. Both the 3-suffix Margules and the Colburn Margules equations fit the experimental points better than any of the van Laar equations in the less concentrated range below 10 mole per cent acetone in the water phase. The Margules equations, however, will not fit the curved portion of the distribution plot.

Acetone, Chloroform, and Water by the Method of Scheibel and Friedland. Figure 14, page 54, and Table XI, page 60, shows the comparison between the actual ternary distribution data for the system acetone, chloroform, and water, and that data predicted by the method of Scheibel and Friedland. Although the predicted curve attempts to follow the curve traced by the experimental data, it does not show the maximum represented by the experimental curve. This method results in a curve very similar to that given by the 3-suffix van Laar equations. However, it better approximates the experimental curve than the Margules equations which will not represent the curved portion of the experimental plot.

Study of the System Cyclohexane, N-Heptane, and Aniline. Working with the system cyclohexane, N-heptane, and aniline, is an example of attempting a prediction from an insufficient quantity of data. No vapor-liquid equilibria data were available for any of the three binaries, and the mutual solubility data could be found for only two of the binary systems. The binary constants for the N-heptane-aniline system and the aniline-cyclohexane system were calculated from the mutual solubility data, while the system N-heptane - cyclohexane was assumed to be ideal. From Table XVIII, page 86, the ratios of the binary constants for this system are:

Aniline, N-heptane $\frac{1.359}{1.290} = 1.05$

Aniline, Cyclohexane $\frac{0.867}{1.120} = 0.775$

As the ratios are between 0.75 and 1.3, it was expected that either the Margules equations or the van Laar equations would fit equally well.

Cyclohexane, Aniline, and N-Heptane by the van Laar and Margules Equations. The predicted values of ternary-liquid equilibria data are compared with the experimental values in Table IX, page 55. The comparison of the experimental distribution data with the values predicted by the van Laar equations is shown in Figure 15, page 56, while the comparison with the values predicted by the Margules equation is shown in Figure 16, page 57. Neither of the standard equations, the 2-suffix van Laar nor the 3-suffix Margules, represent the experimental data accurately. The Colburn van Laar, while not acceptable, does give a closer fit than the two standard equations. The 3-suffix van Laar equation with an experimental constant results in the best over-all fit. This is to be expected as the 3-suffix van Laar was forced through one point of experimental data by the addition of the constant. Thus, its over-all accuracy was increased in the range of the constant.

Cyclohexane, Aniline, and N-Heptane by the Method of Scheibel and Friedland. The method of Scheibel and Friedland was not applied to the system cyclohexane, aniline, and N-heptane. There was not enough ternary solubility data available to sketch the phase envelope, and the binary constants were calculated completely from binary solubility data. Thus, there was not enough information available to apply the Scheibel and Friedland method.

Predictive Study of the System Methanol, Water, and 1-Nitropropane.

The system methanol, water, and 1-nitropropane does not satisfy the van Laar restrictions. This is shown in Table XVIII, page 86. From Table XVIII, the ratios of the binary constants for each of the three binary systems which compare the ternary system are:

Methanol, Water	$\frac{0.251}{0.203} = 1.23$
Methanol, 1-Nitropropane	Unity
Water, 1-Nitropropane	$\frac{0.356}{0.241} = 1.48$

The ratio of the binary constants for the system methanol and water is less than 1.3. Thus, according to Wohl(69), the system would be fit quite well by the Margules equations. In contrast, the ratio of the binary constants for water and 1-nitropropane indicate the system would be best fit by the van Laar equations. The binary system methanol and 1-nitropropane must be assumed as ideal since no binary data is available on the system. Following the preceding analysis of the binary data, it would be very difficult to predict which of the equations would best fit the ternary system. The analysis of the individual binary systems results in no concrete justifications for picking either a van Laar or a Margules form. However, as the data on one system is unknown, one would assume that the accuracy of any prediction would be limited.

Methanol, Water, and 1-Nitropropane by the van Laar Equations. In Table X, page 58, and Figure 17, page 52, the results obtained from predicting the ternary distribution of the methanol, water, and 1-nitropropane system are compared with the experimental values. It is shown that the 2-suffix van Laar equation gives an approximate fit of the experimental points over the entire range of values. The 3-suffix van Laar equation with an experimental constant fits the region where it was forced by the constant, but does not give an acceptable over-all fit. The Colburn van Laar equation follows the 2-suffix equation up to 25 mole per cent methanol in the water phase, then continues to ascend at a steep slope.

Methanol, Water, and 1-Nitropropane by the Margules Equations. The Margules equations, when applied to the system water, methanol, and 1-nitropropane, resulted in an eratic set of values for the ternary activities. This situation indicated that the Margules equations will not represent the system.

Methanol, Water, and 1-Nitropropane by the Method of Scheibel and Friedland. Since the binary activity coefficients for the methanol and 1-nitropropane system were not known, the method of Scheibel and Friedland did not apply to the system.

Discussion of Predictive Study. The material concerning the prediction methods covered in the previous portion of the discussion has been summerized in Tabular form, Table XIX, page 99. From a study of this Table and the previously discussed conditions under which the predictions were made, the author has postulated:

TABLE XIX

Summary of Results Obtained from Comparison of Prediction Methods

System	Binary Coefficients Best Fit By	Fits van Laar Restrictions	Ternary Data Best Fit By	
			Dilute Range	Over-All Range
Acetic Acid, Benzene, Water	None	No	2-suffix van Laar	Scheibel
Ethyl Acetate, Ethanol, Water	van Laar	Yes	2-suffix van Laar	Scheibel
Acetone, Benzene, Water	Margules	Yes	3-suffix Margules	3-suffix van Laar
Acetone, Water, Chloroform	Margules	Yes	3-suffix Margules	Scheibel
N-Heptane, Aniline, Cyclohexane	Margules	No	None	None
Methanol, Water, 1-Nitropropane	van Laar	No	2-suffix van Laar	None

1. The ratio of the binary constants are more indicative of which prediction method will best fit a ternary system than the van Laar restrictions.
2. If the integrated forms will not fit the binary data, they will not fit the ternary data.
3. Accurate predictions of ternary data will not generally result when mutual solubility data are used to obtain the binary constants.
4. The integrated equation which best fits the binary data will result in an acceptable approximation of the ternary system in the dilute range.
5. The Colburn constant when applied to the integrated forms does not aid the accuracy of the prediction.
6. The Wohl constant when applied to the integrated forms will increase the accuracy of the prediction only in the range of the experimental point used.
7. The method of Scheibel and Friedland is limited in application as it can not be used on all ternary systems. If the activity coefficients of the solute in one binary system are of a different order of magnitude than the activity coefficients in the other binary systems, the method will not apply.
8. When the method of Scheibel and Friedland does apply, it will give an acceptable approximation of the ternary distribution data over the entire range of concentrations.

Recommendations

The recommendations presented have evolved in the process of conducting this investigation and evaluating its results. They are concerned both with methods of improving the predictive comparisons mentioned in this thesis, and the possible extensions of the work through the use of more fundamental methods.

Method of Calculating Equilibrium Points from Activities. The present method of plotting solute activities as a function of solute concentrations, drawing lines of constant activity, and reading equilibrium points, is not completely satisfactory. To begin with, this method is mathematically unsound. As pointed out by Mickley(35), a plot on which the ordinate and abscissa are functions of the same variable is not reliable, for large discrepancies in the curve are minimized. Also, this method is the bottleneck in the predictive process in respect to both accuracy and time. The graph is slow to construct and read. Then too, the resulting accuracy to the prediction is limited by the size of graph paper used. It is recommended that a method be perfected whereby the entire operation could be performed on the digital computer. Possibly a series of simultaneous equations could be developed and programmed which would satisfy this condition.

Method of Obtaining Experimental Data. It is recommended that any future investigators attempting to obtain a working prediction method use only data from one source in their correlations. That is, all of the binary-vapor liquid data used to obtain the solution constants for a particular ternary system should come from one source, should be reliable, and should have been obtained by the same experimental methods. Even with the infallible prediction equation, the ternary distribution data approximated by it will be no more accurate than the binary data from which it was obtained. The author feels very strongly that using binary data obtained from 40 years of chemical literature, most of which has been obtained by different experimental techniques, is expecting too much of any predictive method. True, this would be necessary upon occasion when the method was actually being used, but it is no way to test originally the validity of the method.

New Approach to Prediction. It is possible that working for methods to improve the approximate equations resulting from the Gibbs-Duhem equation is a stagnate approach to this problem of predicting ternary-liquid equilibria data. A more satisfactory solution to the problem could, and probably does, lie in a new approach----that of numerical analysis. The recent publication of Boberg and White(72) could possibly be the starting point for such a solution and should be investigated.

Limitations

The experimental work presented in this thesis was limited to the measurement of the mutual solubility data and the ternary distribution data for the liquid system water, methanol, and 1-nitropropane. The portion involving the comparison of the validity of prediction methods was limited to the study of six different ternary-liquid systems. These were: (1) ethanol, ethyl acetate, water; (2) acetone, benzene, water; (3) acetic acid, benzene, water; (4) acetone, chloroform, water; (5) cyclohexane, aniline, N-heptane; and (6) water, methanol, 1-nitropropane.

Temperature Limits. Mutual solubility data for the ternary system, water, methanol, and 1-nitropropane were determined at 25 °C and 30 °C only. As no noticable difference in the solubility data was observed at the two temperatures, the ternary-liquid equilibria data were determined at 25 °C only.

Density Limitations. At high concentrations of methanol, that is, above 30 weight per cent methanol in a one-phase mixture of water and 1-nitropropane, the two phases separated very slowly. This condition would make the system unsuitable for use in a countercurrent continuous liquid extraction unit.

Data Obtained from Literature. The binary solution constants were, in every case, calculated from data obtained in the literature and were assumed to be correct. Wherever possible, the data of the author was checked with that of other authors to see if it was consistent. The data on the system acetone-benzene were checked in three different sources, and three unrelated sets of data were found at one atmosphere pressure. In this case the author chose the most recent work --- that of Othmer(39).

Temperature Limitations on Binary Constants. The binary solution constants obtained from vapor-liquid data were obtained from constant pressure data. That indicates the resulting binary constants were assumed independent of temperature. This is not strictly true. However, in most cases it is a good approximation.

V. CONCLUSIONS

The conclusions of this thesis pertain to: (1) the experimental determination of the ternary-liquid data for the system water, methanol, and 1-nitropropane; and (2) the comparison of six methods to predict ternary-liquid equilibria data. The conclusions are as follows:

1. The liquid system water, methanol, and 1-nitropropane forms but one pair of partially miscible liquids over the entire concentration range. The mutual solubility data for this system were experimentally determined at two temperatures --- 25 °C and 30 °C.
2. The liquid equilibria data for the ternary system water, methanol, and 1-nitropropane were experimentally determined at 25 °C.
3. The equilibria data for six ternary-liquid systems were predicted by six different methods. The predicted data were compared with the experimental data for each system. On the basis of the mole per cent solute in the solvent phase, the prediction methods which resulted in the most accurate fit of the experimental data for each system are:
    a. The equilibria data for the liquid system acetone, benzene, and water at 30 °C were best predicted by the 3-suffix Margules equation up to 7.23 mole per cent acetone and the 3-suffix van Laar equation from 7.23 to 17.5 mole per cent acetone. The Colburn Margules and the 2-suffix van Laar equations fit the data up to 3.34 mole per cent acetone. The method of Scheibel and Friedland did not apply to this system.
    b. The equilibria data for the liquid system ethanol, ethyl acetate, and water at 20 °C were best predicted by the 2-suffix van Laar equation up to 4.82 mole per cent ethanol and the

Scheibel and Friedland method from 4.70 to 10.5 mole per cent ethanol. The Colburn van Laar, the 3-suffix Margules, and the Colburn Margules equations fit the data up to 3.70, 1.70, and 3.41 mole per cent ethanol respectively.

c. The equilibria data for the liquid system acetic acid, benzene, and water at 30 °C were best predicted by the 3-suffix van Laar equation up to 49.3 mole per cent acetic acid and the Scheibel and Friedland method from 49.3 to 50.24 mole per cent acetic acid. The Colburn van Laar, the 3-suffix Margules, and the Colburn Margules equations did not fit the experimental data.

d. The equilibria data for the liquid system acetone, water, and chloroform at 25 °C were best predicted by the 3-suffix Margules equation up to 19.51 mole per cent acetone and the method of Scheibel and Friedland from 19.51 to 32.42 mole per cent acetone. The Colburn van Laar, the 3-suffix van Laar, and the Colburn Margules equations fit the data up to 1.5, 5.56, and 15.13 mole per cent acetone.

e. The equilibria data for the liquid system aniline, cyclohexane, and N-heptane were not approximated to an acceptable degree by any of the six methods used.

f. The equilibria data for the liquid system methanol, water, and 1-nitropropane at 25 °C were best predicted by the 2-suffix van Laar equation up to 48.02 mole per cent methanol. The Colburn van Laar equation fit the data up to 41.03 mole per cent methanol. The remainder of the prediction methods used did not result in an accurate approximation of the data.

VI. APPENDICES

This section is divided into four parts: (1) Appendix A, nomenclature used in the thesis; (2) Appendix B, list of materials and apparatus used in the experimental work; (3) Appendix C, programs for the Royal-McBee LGP-30 Digital Computer used to perform the calculations for the thesis; and (4) Appendix D, the data taken during the experimental work and the output results of the computer.

APPENDIX A

Nomenclature

The nomenclature used in this thesis is as follows:

A = binary solution constant, unitless

a = activity, mole fraction

B = binary solution constant, unitless

C = ternary solution constant, unitless

°C = temperature, degrees Centigrade

d = density, grams per cubic centimeter

g = activity coefficient, unitless

$M = A_{12} - A_{13} - A_{32}(A_{13}/A_{31})$, unitless

P = total pressure, pressure units

p = vapor pressure, pressure units

$Q = Z_2Z_3(A_{12} + A_{13}) - Z_3(Z_3A_{13} - A_{12}M) + Z_2^2 A_{12}$, unitless

q = arbitrary factor replacing molal volume, volume units

V = right hand member of 3-suffix van Laar equation, unitless

V_N = volume of component N in a mixture, volume units

$W = Z_2Z_3 - 2Z_1Z_2Z_3$, unitless

W_t = total weight, grams

W_N = weight of component N in solution, grams

X = liquid composition, mole fraction

Y = vapor composition, mole fraction

Z = effective volume fraction, unitless

Subscripts.

1 = solute

2 = carrier

3 = solvent

N = component N in mixture

Superscripts.

$'$ = phase one of two phases

$''$ = phase two of two phases

$^\circ$ = degrees

APPENDIX B

Materials

This section contains a list of materials used in the performance of the experimental work for this thesis.

Alcohol, Methyl. C. P., over 90 % pure, Catalog No. NA-611. Obtained from Fisher Scientific Company, New York, 14, N. Y. Used as solute in ternary-liquid system.

1-Nitropropane. Purity by weight 99% minimum. Specifications: specific gravity, 1.003; acidity as acetic acid, % by weight, 0.2; water, % by weight, 0.2; color, APHA, max, 20. Obtained from Commercial Solvents Corporation, New York 16, N. Y. Used as carrier in ternary-liquid system.

Water, Distilled. Purified by distillation unit in the Chemical Engineering Department of the University of Missouri School of Mines and Metallurgy. Used as solvent in ternary-liquid system.

Apparatus

The following apparatus was used in the experimental work for this thesis:

Balance, Analytical. Ainsworth Analytical Balance, Model BB with chainweight attachment, sensitivity of 0.05 milligram. Catalog No. V7074. Obtained from Aloe Scientific Company, St. Louis 3, Missouri. Used to calibrate glassware.

Balance, Specific Gravity. Westphal type with Riemann Plummet, displaces 5 grams of distilled water at 20 °C, sensitivity 0.005 gram. Catalog No. V7320. Obtained from Aloe Scientific Company, St. Louis 3, Missouri. Used to obtain specific gravity of ternary system.

Bottles, Polyethylene. Narrow mouth Boston round, no known solvent at room temperature. Catalog No. 2-923. Obtained from Kimble Laboratory Glassware Division of Owens-Illinois, Toledo 1, Ohio. Used to store mixtures of ternary system.

Bottles, Specific Gravity. Weld type, 80 mm high, capacity approximately 25 ml. Obtained from Kimble Laboratory Glassware Division of Owens-Illinois, Toledo 1, Ohio. Used to determine dinsity of pure components.

Buret. Straight glass, stopcock, Micro (Class A), meet requirements of Federal Specification DD-V581A, 10 ml. capacity, subdivision 2/100 ml., tolerance ± 0.02. Obtained from Kimble Laboratory Glassware Division of Owens-Illinois, Toledo 1, Ohio. Used to titrate known quantities of material.

Computer, Digital. LGP-30, desk size, stored program, medium scale capacity. Maximum memory of 4096 words, drum rotates at 4000 revolutions per minute, maximum access time 15 milliseconds. Manufactured by the Royal McBee Corporation, Port Chester, N. Y. Used to process experimental data and predict ternary-liquid equilibria data.

Constant Temperature Control. For Refractometer. Precision, temperature control 15 to 100 °C ± 0.01 °C, pumping capacity 5 gal. per min., both capacity 2.25 gal. Heating capacity is 450 watts at

115 volts, 60 cycle alternating current, single phase. Capacity is two and one-half gallons. Catalog No. VP 66600. Obtained from Aloe Scientific Company, St. Louis 3, Missouri. Used for dipping refractometer constant temperature control.

Cylinder, Hydrometer. Heavy glass, diameter 25 mm., height 150 mm., Capacity 50 ml. Obtained from Kimble Laboratory Glassware Division of Owens-Illinois, Toledo 1, Ohio. Used with Westphal Balance for specific gravity determinations.

Funnel, Separatory. Globe type, length of stem 175 mm., capacity 60 ml. Obtained from Kimble Laboratory Glassware Division of Owens-Illinois, Toledo 1, Ohio. Used to separate two phase mixtures.

Heating Tank. Glass bottom, illuminating mirror. Catalog No. V71410. Obtained from Aloe Scientific Company, St. Louis 3, Missouri. Used when performing cloud point titrations.

Jar, Cylindrical. Plain Pyrex, height 12 inches, diameter 12 inches, capacity 4.5 gallons. Obtained from Aloe Scientific Company, St. Louis 3, Missouri. Used for constant temperature bath for bulk material.

Refractometer, Dipping. Bausch and Lomb. Range between refractive indices of 1.32 and 1.54, accuracy is 3.5 units in 5th decimal place. Catalog No. V71400. Obtained from Aloe Scientific Company, St. Louis 3, Missouri. Used to obtain refractive index of ternary mixture.

Thermoregulator. Constant temperature circulation, 750 watt heater, controls between 0 °C and 100 °C, accuracy ± 0.01 °C. Obtained from Aloe Scientific Company, St. Louis 3, Missouri. Used for constant temperature control of bulk material.

APPENDIX C

Computer Programs

This appendix contains all programs for the Royal-McBee LGP-30 Digital Computer used during the course of this investigation. Complete data input, data output, and coding sheet information are included with each program.

Program I

This program was used to compute mole fractions from weight fractions of a three component system. The maximum capacity for this program is 32 mixtures of different compositions for any three component system.

Input. Via Data Input 24.2. Occupies portion of four consecutive tracks beginning with track 5000. Tracks 5000, 5100, 5200; N words per track arranged in tracks in order of Component A, Component B, Component C. Track 5300, seven words which are constants for system. These words are arranged in sector order of mole weight A, mole weight B, mole weight C, one, number, N, of data words, minus one, and minus one. Maximum N is 32 data words.

Output. Via Data Output 24.2. Printout N times three words in the following order and form:

Mole fraction A	Mole fraction B	Mole fraction C
.XXXXX	.XXXXX	.XXXXX

Storage. Program occupies 67 locations of instructions beginning at track 5400 and 200 maximum location of data and temporary storage beginning at track 5000.

Time. 26 minutes for 18 mixtures

Program I Coding Sheet

```
;0005400'/0000000'

r6300'u0400'i5000'i5100'i5200'i5300'u5448'2c0032'
2i0002'2e0000'b5306'a5310'h5310's5308't5416'u5447'
2b5000'd5300'2h5000'2b5100'd5302'2h5100'2b5200'd5304'
2h5200'2a5000'2a5100'r5306'h5320'2m5000'2h5000'b5320'
2m5100'2h5100'b5320'2m5200'2h5200'2b5000'z0006'd0000'
2b5100'z0006'd0000'2b5200'z0006'm0000'2z5410'z0000'
b5312'h5310'e0000'b5500'y5407'b5501'y5409'r6300'
u0400'u0000',0000005'404020xj'10186020'xj102860'20xj1038'40400000'
u5407'z0032'z0000'.0005400'
```

Program II

This program was used to compute activity coefficients as a function of liquid composition for a binary system from binary total pressure vapor-liquid equilibria data. The maximum capacity for this program is 32 points of vapor-liquid equilibria data. A knowledge of the vapor pressure as a function of temperature relationships as defined by the Antoine equations(50) are necessary for the use of this program.

Input. Via Data Input 24.2. Occupies portion of four consecutive tracks beginning with track 5000. Track 5000, ten words which are constants for the system. These words are arranged in sector order of, 273.16, total pressure in mm Hg, A_a, B_a, A_b, B_b, 100, one, minus one, N. Tracks 5100, 5200, 5300; N words per track arranged in tracks in order of, Ya in mole per cent, Xa in mole per cent, T in °C. Maximum N is 32 data words.

Output. Via Data Output 24.2. Printout N times four words in the following order and form:

Mole fraction A	Activity coefficient A	Mole fraction B	Activity coefficient B
.XXXX	.XXXX	.XXXX	.XXXX

Storage. Program occupies 66 locations of instructions and constants beginning at track 4900. Maximum of three tracks of data beginning at track 5100.

Time. 31 minutes for 32 points of vapor-liquid equilibria data.

Program II Coding Sheet

```
;0004900'/0000000'

r6300'u0400'i5000'i5100'i5200'i5300'2c0032'2i0002'
2e0000'b5016'a5014'h5016'b5018's5016't4956'2b5100'
2d5200'2h5500'2b5300'a5000 '2h5400'b5004'2d5400'a5006'
h0010'2r5500'm5002'2h5500'b5012'2s5200'2h5700'b5012'
255100'2d5700'm5002'2h5800'b5008'2d5400'a5010'h0010'
2r5800'2h5800'm0000'2b5200'z0004'd0000'2b5500'z0004'
d0000'2b5700'z0004'd0000'2b5800'z0004'm0000'2z4909'
z0000'.0004900'
```

Program III

This program was used to compute binary solution constants for the van Laar equations from activity coefficients obtained from binary total pressure vapor-liquid equilibria data. The maximum capacity for this program is 15 points of activity coefficient data. Use only data between 0.25 and 0.75 mole fraction.

Input. Via Data Input 24.2. Occupies portion of three consecutive tracks beginning with track 4700. Track 4700, 6 words which are constants for the system. These words are arranged in sector order of one, number of data points, zero, zero, zero, zero. Track 4800, N data words, mole fractions of component A. 4900, N data words, activity coefficients of component A. Maximum N is 15.

Output. Via Data Output 24.2. Print out binary solution constants in the following order and form:

```
        Aba          Aab
      0.XXXX       0.XXXX
```

Storage. Program occupies 69 locations of instructions beginning at track 5000 and 40 maximum locations of data and temporary storage beginning at track 4700.

Time. 20 minutes

Program III Coding Sheet

```
;0005000'/0000000'

r6300'u0400'u5100'2c0015'2i0002'2e0000'b4700'2s4800'
2r4800'h4712'a4704'b4712'm4712'a4706'2b4900'n0010'
b0000'r0000'r4700'h4714'a4708'b4714'm4712'a4710'
2z5006'b4704'm4708'd4702'h4714'b4710's4714'h4712'
b4704'm4704'd4702'h4714'b4706's4714'h4714'b4712'
d4714'h4712'm4704'h4714'b4708's4714'd4702'h4714'
b4700'd4714'm4714'h4716'b4714'r0000'd4712'h4718'
m0000'm0000'b4716'z0003'd0000'b4718'z0003'z0000'
u0000',0000004'404020a4'10b4a460'20a410a4'b4000000'u5003'
```

Program IV

This program was used to evaluate the ternary constant as defined by Wohl$^{(68)}$ for the 3-suffix van Laar equations. The data necessary to use this program are: (1) the binary solution constants and (2) one point of ternary-liquid equilibria data for the system under consideration.

Input. Via Data Input 24.2. Occupies portions of three consecutive tracks beginning with track 5000. Track 5000; seven words arranged by sectors as, A_{12}, A_{13}, A_{32}, A_{31}, A_{21}, two, one. Track 5100; three words, equilibria mole fractions in the solvent phase arranged by sectors as X_1, X_2, X_3. Track 5200; three words, equilibria mole fractions in the carrier phase arranged by sectors as X_1, X_2, X_3. Subscripts indicate as follows: 1, solute; 2, carrier; and 3, solvent.

Output. Via Data Output 24.2. Four words in the following order and form:

Factor K (XXXXXXXX. - 0X -)
Factor P (XXXXXXXX. - 0X -)
Ratio of mole fractions (XXXXXXXX. - 0X -)
Ternary constant (XXXXXXXX. - 0X -)

Storage. Program occupies 100 locations of instructions and constants beginning at track 5300.

Time. 4 minutes

Program IV Coding Sheet

```
;0005300'/0000000'

r6300'u0400'i5000'i5100'i5200'u5428'2c0000'2i0100'
2e0000'b5008'd5000'h5014'b5006'd5002'h5016'b5004'
d5006'm5002'h5018'b5000'a5002's5018'h5018'b5014'
2m5102'2a5100'2h5106'b5016'2m5104'2a5106'2h5106'2b5100'
2d5106'2h5108'2b5102'm5014'2d5106'2h5110'2b5104'm5016'
2d5106'2h5112'2b5110'2m5110'm5000'2h5114'2b5112'2m5112'
m5002'2a5114'2h5114'2b5110'2m5112'm5018'2a5114'2h5114'
2b5110'2m5112'2h5118'2m5108'm5010'2h5120'2b5118'2s5120'

2h5116'2z5323'b5114's5214'h5020'b5116's5216'h5022'
b5200'd5100'h5024'b5024'n0010'h5026's5020'd5022'
y0000'h5028'm0000'p5020'd0000'p5022'd0000'p5024'
m0000'm0000'p5028'z0000'e0000'b5436'y5306'b5437'
y5308'r6300'u0400'u5306'z0002'z0000'
```

Program V

The function of this program is to compute the activity coefficients and activities of the solute in a three component liquid mixture at various points around the ternary solubility curve. The relationship between activity coefficients and liquid compositions used in this program is the 3-suffix van Laar equations as developed by Wohl(68). The data necessary to use this program are: (1) the binary solution constants, (2) the ternary solubility curve, and (3) one ternary constant, C. The program is written so the 2-suffix van Laar results when the ternary constant, C, is assumed to be zero.

Input. Via Data Input 24.2. Occupies portion of four consecutive tracks beginning with track 5700. Track 5700, 5800, 5900; N words per track arranged in tracks as N points of solubility data in mole fraction units in order of solute, carrier, solvent. Track 6000, eight words arranged in sectors as A_{12}, A_{21}, A_{13}, A_{31}, A_{23}, A_{32}, C, one. Subscripts indicate as follows: 1, solute; 2, carrier; and 3, solvent. Maximum N is 32 data words.

Output. Via Data Output 24.2 with Alpha-numeric table headings. Printout, N times four words in the following order and form:

Mole fraction solvent	Log activity coefficient	Activity coefficient	Activity
.XXXXX	.XXXXX	.XXXXX	.XXXXX

Storage. Program occupies 93 locations of instructions and constants beginning at track 5100. Ten locations of temporary storage (track 6000, sectors 16 to 34). N, the number of points of solubility data, must be typed into location 6100 in the form ZXXXN, maximum N is 32 data words.

Time. 12 minutes

Program V Coding Sheet

```
;0005100'/0000000'

r6300'u0400'i5700'i5800'i5900'i6000'u5223'e0000'
b6100'y5112'r6300'u0400'2c0000'2i0002'2e0000'b6010'
m6004'd6006'h6016'b6000'a6004's6016'h6016'b6000'
d6002'h6018'b6004'd6006'h6020'2b5800'd6018'2a5700'
h6022'2b5900'd6020'a6022'h6022'2b5700'd6022'h6024'
2b5800'd6018'd6022'h6026'2b5900'd6020'd6022'h6028'
b6026'm6026'm6000'h6030'b6028'm6028'm6004'a6030'
h6030'b6026'm6028'm6016'a6030'h6030'b6024'a6024'

s6014'm6026'm6028'm6012'a6030'h6030'h0010'h6030'
2b5700'z0005'd0000'b6030'z0005'd0000'b6032'z0005'
d0000'2b5700'm6032'z0005'm0000'2z5129'z0000'u0000'
,0000005'404020xj'6020L810'0jg8zj20'⊿860⊿860'10a44000'u5107'
```

Program VI

The function of this program is to compute the activity coefficients and the activities of the solute in a three component liquid mixture at various points around the ternary solubility curve. The relationship between activity coefficients and liquid compositions used in this program is the 3-suffix Margules equation as developed by Wohl(68). The data necessary to use this program are: (1) the binary solution constants, (2) the ternary solubility curve, and (3) one ternary constant, C. The program is written so the 2-suffix Margules results when the ternary constant, C, is assumed to be zero.

Input. Via Data Input 24.2. Occupies portion of four consecutive tracks beginning with track 5600. Tracks 5600, 5700, 5800; N words per track arranged in tracks as N points of solubility data in mole fraction units in order of solute, carrier, solvent. Track 5900, eight words arranged in sectors as A_{12}, A_{21}, A_{13}, A_{31}, A_{23}, A_{32}, C, one. Subscripts indicate as follows: 1, solute; 2, carrier; and 3, solvent. Maximum N is 32 data words.

Output. Via Data Output 24.2 with Alpha-numeric table headings. Printout, N times three words in the following order and form:

Mole fraction solvent	Activity coefficient	Activity
.XXXXX	.XXXXX	.XXXXX

Storage. Program occupies 86 locations of instructions and constants beginning at track 4900. N, the number of points of solubility data, must be typed into 6100 in the form ZXXXN. Maximum N is 32 data words.

Time. 13 minutes

Program VI Coding Sheet

```
;0004900'/0000000'

r6300'u0400'i5600'i5700'i5800'i5900'u5016'e0000'
b6100'y4912'r6300'u0400'2c0000'2i0002'2e0000'b5914'
a5914'h6000'b5902's5900'h6002'b5906's5904'h6004'
b5902'a5904's5910'h6006'b5910's5908'h6008'b6002'
2m5600'm6000'a5900'2m5700'2m5700'h6010'b6004'2m5600'
m6000'a5904'2m5800'2m5800'a6010'h6010'b6004'2m5600'
m6000'a6006'h6012'b6008'm6000'2m5800'a6012'h6012'
2b5600'm6000's5914'm5912'a6012'2m5700'2m5800'a6010'

h0010'h6010'2m5600'h6012'm0000'm0000'2b5600'z0005'
d0000'b6010'z0005'd0000'b6012'z0005'2z4931'z0000'
u0000',0000005'404020xj'10186010'a4c460a4'c4t4i4vj'i4t4y400'u4907'.0004900'
```

APPENDIX D

Experimental Data

This section of the thesis contains both the experimental data obtained in the literature, and the data processed by the LGP-30 Digital Computer. Tables XX through XXV and Figure 23 are concerned with the experimental work, while Tables XXVI through XXX are concerned with the prediction studies.

TABLE XX

Density of Pure Components Methanol and 1-Nitropropane Determined by a Weld Pyemometer at 25 °C

Substance	Density
	grams per cc
Methanol	0.7906
1-Nitropropane	1.002

TABLE XXI

Experimental Cloud Point Data Used to Determine
the Ternary Solubility Data for the
System Water, Methanol, and
1-Nitropropane at 30 °C

Test No.	Volume of 1-Nitropropane	Volume of Methanol	Volume of Water at Cloud Point
	cc	cc	cc
1	0.00	10.00	0.185
2	2.00	10.00	0.291
3	4.00	10.00	0.451
4	0.00	10.00	0.179
5	5.00	10.00	0.604
6	6.00	10.00	0.701
7	8.00	10.00	1.131
8	10.00	10.00	1.704
9	12.00	10.00	2.390
10	14.00	10.00	3.320
11	15.00	10.00	4.200
12	17.00	10.00	5.580
13	19.00	10.00	7.455
14	21.00	10.00	10.076
15	2.00	0.54	5.00
16	4.00	1.36	5.00
17	6.00	2.39	5.00
18	10.00	4.63	5.00
19	15.00	6.06	5.00
20	0.00	0.01	5.00
21	4.00	1.22	7.00
22	2.00	0.46	10.00

TABLE XXII

Experimental Cloud Point Data Used to Determine
the Ternary Solubility Data for the
System Water, Methanol, and
1-Nitropropane at 25 °C

Test No.	Volume of 1-Nitropropane	Volume of Methanol	Volume of Water at Cloud Point
	cc	cc	cc
1	0.10	0.00	10.00
2	0.26	2.00	10.00
3	0.38	4.00	10.00
4	0.48	6.00	10.00
5	0.91	8.00	10.00
6	1.42	10.00	10.00
7	1.99	12.00	10.00
8	2.91	14.00	10.00
9	3.65	16.00	10.00
10	5.00	2.00	0.38
11	5.00	4.00	1.26
12	5.00	6.00	2.16
13	5.00	8.00	3.23
14	7.00	4.00	1.18
15	10.00	2.00	0.40
16	5.00	10.00	4.38

TABLE XXIII

Refractive Index Around the Ternary Solubility Curve of Methanol, Water, and 1-Nitropropane at 25 °C

	Test	Composition Methanol	Refractive Index
		Weight %	Unitless
Water Phase	1	0.00	1.33335
	2	13.355	1.33717
	3	23.355	1.33901
	4	31.164	1.34184
	5	36.706	1.34343
	6	40.921	1.34478
	7	44.191	1.34539
	8	46.184	1.34707
	9	48.127	1.34780
1-Nitropropane Phase	10	22.785	1.38396
	11	33.639	1.37258
	12	39.922	1.36584
	13	43.519	1.35604
	14	27.955	1.37962
	15	13.245	1.39211
	16	45.793	1.35395

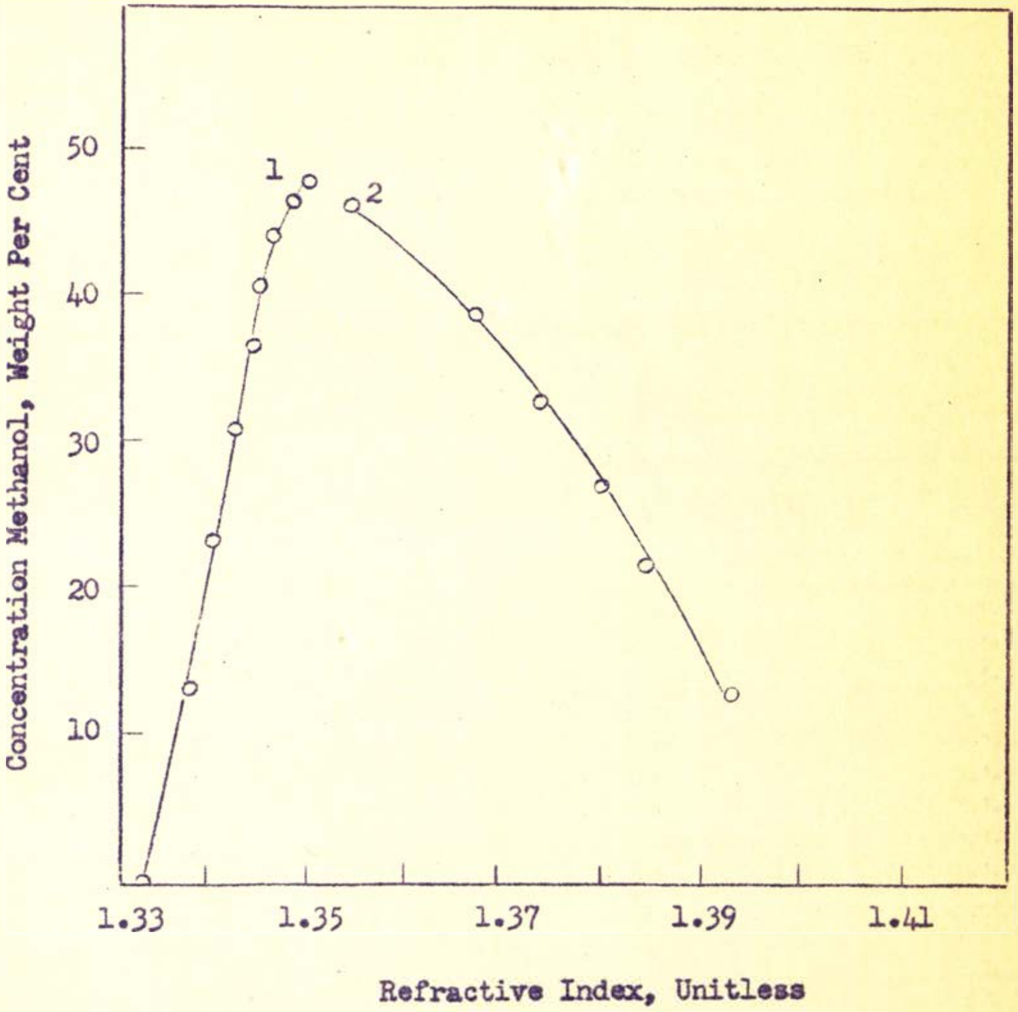


Figure 23. Refractive Index as a Function of Methanol Composition Around the Solubility Curve for the System Methanol, 1-Nitropropane, and Water at 25 °C

TABLE XXIV

Experimental Data for the Determination of Liquid Equilibria in the Two-Phase System, Water, Methanol, 1-Nitropropane, at 25 °C

Test	Composition Water	Composition 1-Nitropropane	Composition Methanol	Weight of Sample
	Weight %	Weight %	Weight %	Grams
1	40.913	51.021	8.0657	97.482
2	50.744	44.254	5.0015	78.596
3	48.327	42.146	9.5272	82.528
4	44.123	38.480	17.397	90.390
5	40.592	35.401	24.007	98.253
6	46.129	40.229	13.641	86.459
7	37.584	32.778	29.638	106.12

TABLE XXV

Experimental Data for the Determination of Equilibria Distribution in the System 1-Nitropropane, Methanol, and Water at 25 °C

	Composition of Original Mixture			Refractive Index of Light Phase	Heavy Phase
Test	Water	1-Nitropropane	Methanol	R. I.	R. I.
	Wt. %	Wt. %	Wt. %	Unitless	Unitless
1	46.129	40.229	13.641	1.33821	1.39721
2	44.123	38.480	17.397	1.33931	1.39362
3	40.592	35.401	24.007	1.34063	1.38662
4	37.584	32.778	29.638	1.34198	1.38052
5	34.215	30.823	34.962	1.34386	1.35501
6	34.796	25.553	39.651	1.34509	1.37107

TABLE XVI

Equilibrium Data Obtained from the Literature Used in Comparison of Prediction Methods

Ternary System			Ternary Distribution Data		Binary Equilibria at Atmospheric Pressure		
Solute 1	Solvent 2	Solvent 3	Reference	Temp. °C	Binary 3-1 Reference	Binary 2-1 Reference	Binary 3-2 Reference
Acetone	Water	Benzene	(37)	45	(38)[1]	(39)[1]	(40)[2]
Acetic Acid	Benzene	Water	(41)	25	(43)[1]	(42)[1]	(40)[2]
Acetone	Chloroform	Water	(41)	25	(44)[1]	(42)[1]	--
Ethanol	Water	Ethyl Acetate	(45)	20	(46)[1]	(40)[1]	(40)
Cyclohexane	N-Heptane	Aniline	(47)	25	(47)[2]	(47)[2]	--

1. Binary vapor-liquid equilibria data at 1 atmo
2. Mutual solubility data at 25 °C

TABLE XXVII

Solute Activity as a Function of Liquid Composition, Predicted by Various Methods, for the System Ethyl Acetate, Ethanol, and Water at 20 °C

	Composition[1]* Ethanol	Activity of Ethanol*				
		2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar	3-suffix Margules	Colburn[3] Margules
Water Phase	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	0.01718	0.05977	0.06506	0.05887	0.06314	0.06255
	0.03350	0.10768	0.11714	0.10608	0.11455	0.11345
	0.04730	0.14181	0.15408	0.13964	0.15255	0.15098
	0.06450	0.17651	0.19380	0.17360	0.19128	0.18906
	0.08120	0.20164	0.22403	0.19789	0.22123	0.21818
	0.10340	0.22104	0.25186	0.21596	0.24591	0.24137
Ethyl Acetate Phase	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	0.03300	0.05338	0.06766	0.05117	0.06057	0.05677
	0.08370	0.11783	0.15304	0.11247	0.13326	0.12449
	0.11100	0.14268	0.18894	0.13572	0.16066	0.14977
	0.13680	0.16470	0.21772	0.15671	0.18381	0.17173
	0.16780	0.18400	0.24364	0.17502	0.20361	0.19094
	0.17540	0.19178	0.25186	0.18270	0.21364	0.20172

* All tabular values in mole fraction units

1. Solubility data of Beech, D. G., and S. Glasstone: J. Chem. Soc. (1938) 67
2. Ternary constant, C = 1.363, Calculated by method of Wohl from data of Beech and Glasstone
3. Ternary constant, C = 0.2428, Calculated by Colburn approximation

TABLE XXVIII

Solute Activity as a Function of Liquid Composition, Predicted by Various Methods, for the System Acetone, Benzene, and Water at 30 °C

	Composition[1]* Acetone	Activity of Acetone*				
		2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar	3-suffix Margules	Colburn[3] Margules
Water Phase	0.03338	0.21466	0.21210	0.21455	0.21755	0.21745
	0.07225	0.37933	0.37127	0.37900	0.38875	0.38843
	0.11842	0.49380	0.47377	0.49298	0.51111	0.51021
	0.17477	0.55970	0.52417	0.55823	0.58347	0.58167
	0.24881	0.56544	0.51202	0.56319	0.59204	0.58877
	0.37237	0.48304	0.45035	0.48168	0.50139	0.49763
	0.53068	0.42947	0.51139	0.43250	0.42997	0.43120
Benzene Phase	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	0.12916	0.17159	0.15483	0.17088	0.17691	0.17598
	0.24699	0.27233	0.23463	0.27021	0.28739	0.28490
	0.35594	0.35566	0.32834	0.35452	0.37213	0.36991
	0.44656	0.38201	0.37964	0.38191	0.39972	0.39826
	0.51893	0.40249	0.45160	0.40435	0.41331	0.41400
	0.55767	0.42115	0.51908	0.42471	0.42234	0.42470

* All tabular values in mole fraction units

1. Solubility data of Briggs, S. W. and E. W. Comings: Ind. Eng. Chem, 35, 411 (1943)
2. Ternary constant, C = 10.69, Calculated by method of Wohl
3. Ternary constant, C = 0.43, Calculated by Colburn approximation

TABLE XXIX

Solute Activity as a Function of Liquid Composition, Predicted by Various Methods, for the System Cyclohexane, Aniline, and N-Heptane at 25 °C

	Composition[1]* Cyclohexane	Activity of Cyclohexane*			
		2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar	3-suffix Margules
Aniline Phase	0.00000	0.00000	0.00000	0.00000	0.00000
	0.22700	0.22726	0.26528	0.23066	0.22102
	0.24900	0.24933	0.28570	0.25261	0.24318
	0.47200	0.47900	0.48812	0.48068	0.47513
	0.62999	0.65218	0.63257	0.65027	0.65023
	0.73100	0.77335	0.74802	0.77089	0.77239
	0.84880	0.91021	0.91021	0.91021	0.90875
N-Heptane Phase	0.00000	0.00000	0.00000	0.00000	0.00000
	0.10980	0.51585	0.56038	0.51997	0.49731
	0.19380	0.74981	0.77950	0.75261	0.74920
	0.28200	0.91221	0.91227	0.91221	0.93490

* All tabular values in mole fraction units

1. Solubility data of Hunter, T. G., and Brown: Ind. Eng. Chem., 39 1343 (1947)
2. Ternary constant, C = 1.67, Calculated by method of Wohl from data of Hunter
3. Ternary constant, C = -0.161, Calculated by Colburn approximation

TABLE XXX

Solute Activity as a Function of Liquid Composition, Predicted by Various Methods, for the System Acetic Acid, Benzene, and Water at 30 °C

	Composition[1]* Acetic Acid	Activity of Acetic Acid*				
		2-suffix van Laar	3-suffix[2] van Laar	Colburn[3] van Laar	3-suffix Margules	Colburn[3] Margules
Benzene Phase	0.00195	0.00532	0.00533	0.00532	0.00532	0.00532
	0.01811	0.04562	0.04911	0.05305	0.04687	0.04702
	0.04196	0.09441	0.11152	0.04834	0.10021	0.10105
	0.16408	0.26297	0.34120	0.21528	0.28202	0.28728
	0.18375	0.27994	0.36837	0.24567	0.29772	0.30403
	0.23896	0.33189	0.43048	0.31849	0.34070	0.34824
	0.27023	0.35892	0.46099	0.35872	0.35885	0.36681
	0.34862	0.41567	0.52806	0.46415	0.35896	0.36825
	0.38598	0.44788	0.55459	0.50338	0.36145	0.36956
	0.40507	0.46414	0.56579	0.52167	0.35771	0.36503
	0.45144	0.50621	0.58885	0.55933	0.35489	0.35920
	0.48677	0.53950	0.59676	0.57897	0.36095	0.36221
Water Phase	0.01413	0.01576	0.01576	0.01576	0.01633	0.01633
	0.06070	0.06768	0.06769	0.06768	0.07747	0.07750
	0.10955	0.12205	0.12207	0.12207	0.15118	0.15143
	0.29613	0.32852	0.32940	0.32917	0.42732	0.43058
	0.32004	0.35481	0.35603	------	0.45203	0.45571
	0.38128	0.42191	0.42471	0.39091	0.49394	0.49816
	0.39898	0.44125	0.44492	0.43755	0.49634	0.50057
	0.49326	0.54361	0.55920	0.55494	0.46070	0.46124
	0.50103	0.55209	0.57199	0.56650	0.44148	0.44139
	0.50557	0.55708	0.58068	0.57410	0.42877	0.42828
	0.50237	0.55425	0.58885	0.57890	0.39063	0.39041

* All tabular values in mole fraction

1. Data of Hand, D. B.: J. Phys. Chem., 34, 1961 (1930)
2. Ternary constant, C = 1.204, Calculated by method of Wohl from data of Hand
3. Ternary constant, C = -0.8864, Calculated by Colburn approximation

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IX. VITA

The author of this thesis, Risdon William Hankinson, was born at St. Joseph, Missouri on December 11, 1938. He was graduated from Lafayette High School of St. Joseph, Missouri, in May 1956. In the following fall he entered the Missouri School of Mines and Metallurgy, Rolla, Missouri, from which he received his degree of Bachelor of Science in Chemical Engineering in June, 1960.

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On August 14, 1962, he will leave Procter & Gamble on a two year military leave of absence and report to Fort McClellan, Alabama, for active duty in the United States Army.

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