

VAPOR-LIQUID PHASE EQUILIBRIA FOR SYSTEM
n-HEXANE-METHYLCYCLOHEXANE-TOLUENE,
EXPERIMENTAL AND CORRELATION INVESTIGATION

By

I-DER HUANG

Bachelor of Science
National Taiwan University
Taipei, Taiwan, China
1957

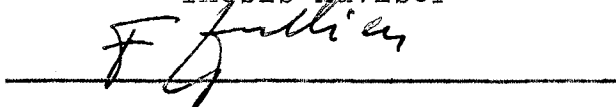
Submitted to the faculty of the Graduate School of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1961

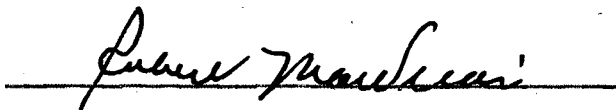
VAPOR-LIQUID PHASE EQUILIBRIA FOR SYSTEM
n-HEXANE-METHYLCYCLOHEXANE-TOLUENE,
EXPERIMENTAL AND CORRELATION INVESTIGATION

Thesis Approved:



Thesis Advisor





Dean of the Graduate School

JAN 2 1962

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Wayne C. Edmister without whose guidance and advice this work would not have been possible. Also the author is indebted to Phillips Petroleum Company for their generous contribution of research grade chemicals. Special appreciation is due to Mr. Richard E. Thompson for his correction in writing this thesis; to Mr. Richard S. Joyner for programming the various calculations involved on an IBM 650 computer.

A special note of thanks goes Miss Lucia Chien, Mr. Anushiravan Amir-Yeganeh for their help in correcting and preparing the manuscript.

The author, finally, would like to pay tribute to the encouragement of his wife, Marian M. Chen, their son, Kung-hwa, who gave inspiration from a far distant land, without whose patience and understanding this work could not have been undertaken.

481151

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. EXPERIMENTAL PROCEDURE	4
Hydrocarbons	4
Apparatus	5
Procedure	10
Experimental Data	13
III. TREATMENT OF DATA	16
Application of van Laar Equation	17
Applicability of the van Laar Equation	24
Thermodynamic Consistency of the Experimental Data	25
IV. DISCUSSION OF THE RESULTS	34
V. SUMMARY AND CONCLUSIONS	43
A SELECTED BIBLIOGRAPHY	45
APPENDIX A - DERIVATION OF THE VAN LAAR EQUATION	47
APPENDIX B - EXPERIMENTAL DATA AND FIGURES	57

LIST OF TABLES

Table	Page
I. Materials Used	4
II. Antoine Constants	15
III. Van Laar Constants For Binary Systems	18
IV. Constants For Scatchard-Hildebrand Equation	23
V. Check on the Consistency of the Measured Data By The Herington Method	28
VI. Correlation of Van Laar Constants	40
VII. Vapor-Liquid Equilibrium Data for n-Hexane-Methylcyclohexane-Toluene System Group 1: Volume ratio n-Hexane: MCH = 90:10.	62
VIII. Vapor-Liquid Equilibrium Data for n-Hexane-Methylcyclohexane-Toluene System Group 2: Volume ratio n-Hexane: MCH = 80:20.	63
IX. Vapor-Liquid Equilibrium Data for n-Hexane-Methylcyclohexane-Toluene System Group 3: Volume ratio n-Hexane: MCH = 60:40.	64
X. Vapor-Liquid Equilibrium Data for n-Hexane-Methylcyclohexane-Toluene System Group 4: Volume ratio n-Hexane: MCH = 40:60.	65
XI. Vapor-Liquid Equilibrium Data for n-Hexane-Methylcyclohexane-Toluene System Group 5: Volume ratio n-Hexane: MCH = 20:80.	66
XII. Vapor-Liquid Equilibrium Data for n-Hexane-Methylcyclohexane-Toluene System Group 6: Volume ratio n-Hexane: MCH = 10:90.	67
XIII. Liquid Activity Coefficients (Group 1)	76
XIV. Liquid Activity Coefficients (Group 2)	77
XV. Liquid Activity Coefficients (Group 3)	78

Table	Page
XVI. Liquid Activity Coefficients (Group 4)	79
XVII. Liquid Activity Coefficients (Group 5)	80
XVIII. Liquid Activity Coefficients (Group 6)	81

LIST OF FIGURES

Figure		Page
1.	The Modified Gillespie Still	7
2.	Calibration Curves	12
3.	Typical Chromatograph Curve	14
4.	Determination of Van Laar Constants by Method of Lu and Lavergne	19
5.	Dependence of $\log \delta_3 / \delta_{12}$ on the liquid Composition of Solute (x_3). System: n-Hexane-Methylcyclohexane-Toluene	30
6.	Correlation Plot of Van Laar Equations (Edmister) at Constant Solvent Composition For Determining the Activity Coefficient of Solvent	33
7.	Correlation Plot of van Laar Equations at Constant Solvent Composition For Determining the A, B Constants	38
8.	Toluene Activity Coefficients System: n-Hexane-Methylcyclohexane-Toluene	41
9.	Typical Vapor-Pressure Temperature Curves	58
10.	Dependence of $\log \delta_1 / \delta_2$ on the liquid Composition (x_1). System: n-Hexane- Methylcyclohexane (Myers)	59
11.	Dependence of $\log \delta_2 / \delta_3$ on the liquid Composition (x_2). System: Methylcyclohexane- Toluene (Quiggle & Fenske)	60
12.	Dependence of $\log \delta_1 / \delta_3$ on the liquid Composition (x_1). System: n-Hexane-Toluene (Sieg)	61
13.	Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene (Group 1)	68
14.	Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene (Group 2)	69

Figure	Page
15. Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene (Group 3)	70
16. Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene (Group 4)	71
17. Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene (Group 5)	72
18. Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene (Group 6)	73
19. Temperature-Liquid Composition Diagram for Ternary System n-Hexane-MCH-Toluene.	74
20. Temperature-Vapor Composition Diagram for Ternary System n-Hexane-MCH-Toluene.	75
21. Experimental n-Hexane Activity Coefficients. System: n-Hexane-MCH-Toluene	82
22. Comparisons of n-Hexane Activity Coefficients System: n-Hexane-MCH-Toluene	83
23. Experimental Methylcyclohexane Activity Coef- ficients. System: n-Hexane-MCH-Toluene	84
24. Comparisons of MCH Activity Coefficients System: n-Hexane-MCH-Toluene	85
25. Comparisons of Toluene Activity Coef- ficients. System: n-Hexane-MCH-Toluene (R=6%).	86
26. Comparisons of Toluene Activity Coef- ficients. System: n-Hexane-MCH-Toluene (R=11.4%)	87
27. Comparisons of Toluene Activity Coef- ficients. System: n-Hexane-MCH-Toluene (R=29.1%)	88
Plate 1. The Modified Gillespie Still	6

CHAPTER I

INTRODUCTION

Vapor-liquid equilibrium phase-distribution ratios are of great importance in the separation operations of the chemical industries. These vapor-liquid distribution ratios are used in the design of distillation columns and in the analysis of performance data on existing columns. Vapor-liquid equilibrium data are also required for the solution of design problems in extractive distillation and absorption.

Chu, et al(1) have compiled experimental vapor-liquid equilibrium data for a large number of mixtures. Numerous methods have been published for making these experimental determinations. Experimental errors due to the apparatus and the nature of the mixture frequently occur. This is particularly true for ternary and multicomponent systems.

Methods have been proposed for testing the experimental data, but most of them are limited to binary systems(2,3). There has been no convenient way, however, for testing the thermodynamic consistency of the ternary or multicomponent data. The application of the Gibbs-Duhem relation(4) and the method suggested by Herington(5) may be used to check on thermodynamic consistency for ternary systems, but these procedures are very lengthy, requiring trial and error calcu-

lations and a large amount of experimental data for the ternary system.

In the present work, experimental vapor-liquid equilibrium data for the ternary system n-hexane-methylcyclohexane-toluene were determined. This system is of industrial importance in the separation of toluene from other hydrocarbons. It is of interest because the compounds are different types of hydrocarbons (i.e., a paraffin, a naphthene and an aromatic). Deviations from ideality of mixtures of these three compounds were found in this work.

The activity coefficient, γ , is defined in this work as follows:

$$\gamma_i = \frac{P y_i}{P_i^0 x_i} \quad (1-1)$$

where

- y_i = mol fraction of component i in vapor
- x_i = mol fraction of component i in liquid
- P_i^0 = vapor pressure of component i at the temperature of system
- P = total pressure or the system pressure, between 739 and 745 mm Hg for this study.

In equation (1-1) it is assumed that the vapor phase is ideal, in which case the activity coefficient, γ , represents the deviation from ideality for the components in the liquid phase.

The most common method used in correlating and predicting the activity coefficient is the well-known van Laar equation, which was originally derived by van Laar(6) from a consi-

deration of the thermodynamic changes occurring on the mixing of pure van der Waals fluids. Similar expressions based on different assumptions have also been obtained by Wohl(7) using excess free energy expansion, any by Scatchard(8) and Hildebrand(9) using the solubility parameter and molar volume relationship. The original van Laar equation was applied to binaries, but through the relations of Wohl and Scatchard-Hildebrand, it can be applied to ternary and multicomponent systems.

It is interesting, therefore, to test the application of those semi-theoretical equations with the δ values derived directly from experimental work. Experimental data are available for the binary systems n-hexane-methylcyclohexane(10), methylcyclohexane-toluene(11), and n-hexane-toluene(12). The coefficients of the ternary van Laar equation can be predicted from these data, using Wohl's expansion. The coefficients of the van Laar equation can also be estimated from physical properties, using the solubility parameters and molar volumes recently published(20). The use of the van Laar equation for ternary mixture is described in Chapter III.

The objectives of this study were: (1) to determine the vapor-liquid phase equilibrium data for ternary mixtures of a paraffin, a naphthene and an aromatic, (2) to evaluate a convenient method for testing experimental vapor-liquid equilibrium data for ternary systems for thermodynamic consistency, and (3) to test the application of the van Laar equation to ternary systems, evaluating the coefficients from the limiting binaries and from physical properties.

CHAPTER II

EXPERIMENTAL PROCEDURE

Research grade chemicals were used in this investigation. The main apparatus was a modified Gillespie still for vapor-liquid equilibrium determination and a gas chromatograph for sample analysis. The equilibrium still had been developed and used by Drehman(15). The Gas Chromatograph had been calibrated by Webster(16). In order to cover the entire range of intermediate ternary compositions, constant ratio mixtures (n-hexane-methylcyclohexane) were prepared, then each of these mixtures was treated in the still with varying amounts of toluene. Details are given as following sections.

Hydrocarbons

Research grade hydrocarbons were used in all experiments. No attempt was made for further purification. The following analyses were reported by the supplier(13).

TABLE I
MATERIALS USED

Hydrocarbon	Source	Mol%	Probable Impurities
n-Hexane	Phillips Petroleum Company, Research grade	99.96	Methylcyclopentane
Methylcyclohexane	"	99.72	Toluene
Toluene	"	99.96	2,4,4,-trimethylpentene-2

Apparatus

The following items of apparatus are described below: Equilibrium still, gas chromatograph, thermometer, pressure controller, reboiler heat supply, and syringes.

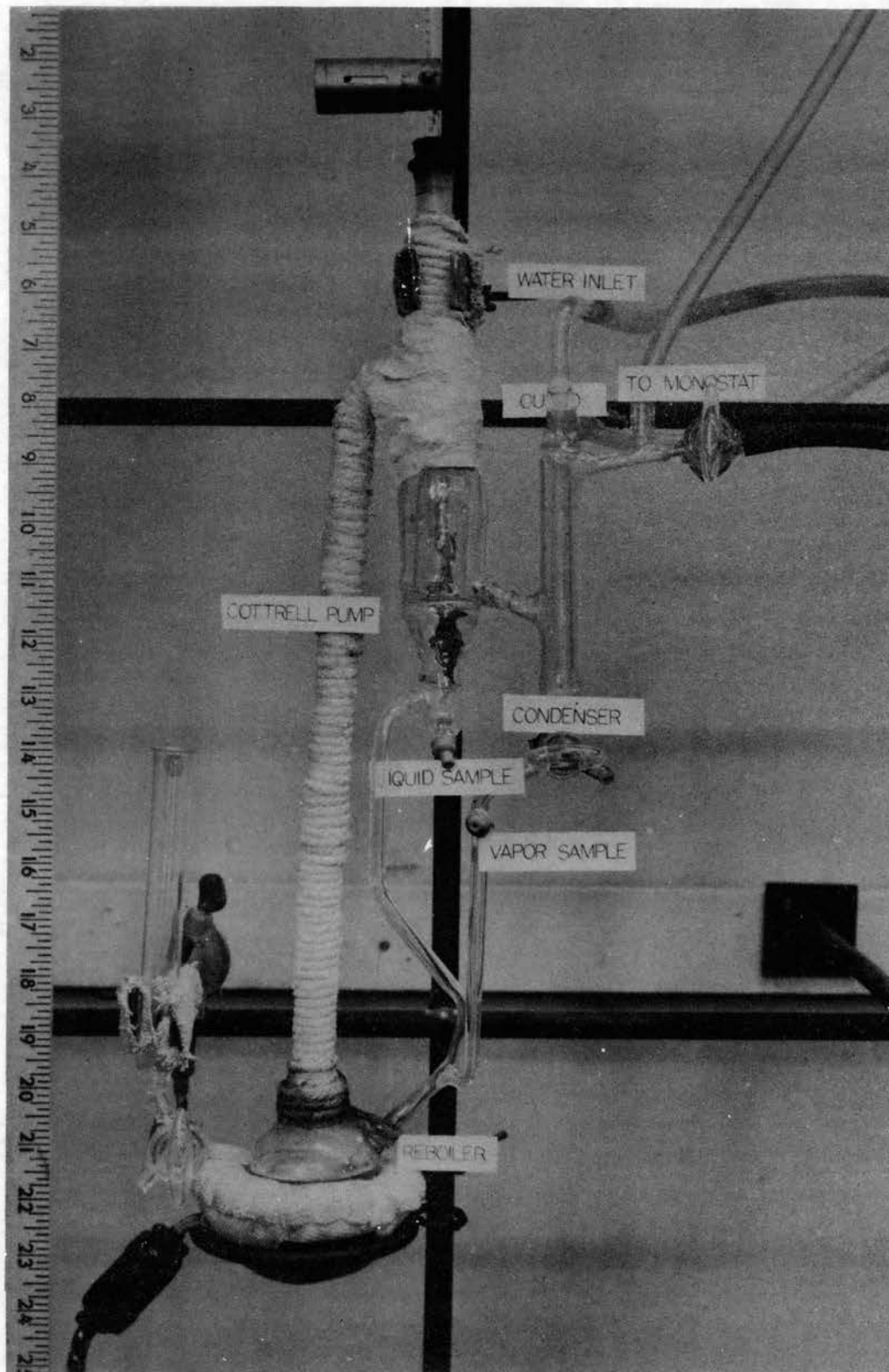
Equilibrium Still

A modified Gillespie type equilibrium still(14) was used in this study. This still was chosen because of its suitability to operation on small samples and also because of its satisfactory operation in a previous study(15).

The Gillespie still(Fig. 1) consists essentially of a reboiler(an electrically heated still) fitted with a Cottrell pump, a vapor-liquid disengagement chamber and a condensate trap. The position of the vapor condenser trap was altered to provide a more compact unit. Vapor and liquid sample points were changed from their original locations and were altered to allow samples to be drawn off by hypodermic syringe.

The Cottrell pump and disengagement chamber were insulated for this study, because heat losses could lead to partial

PLATE I



The Modified Gillespie Still

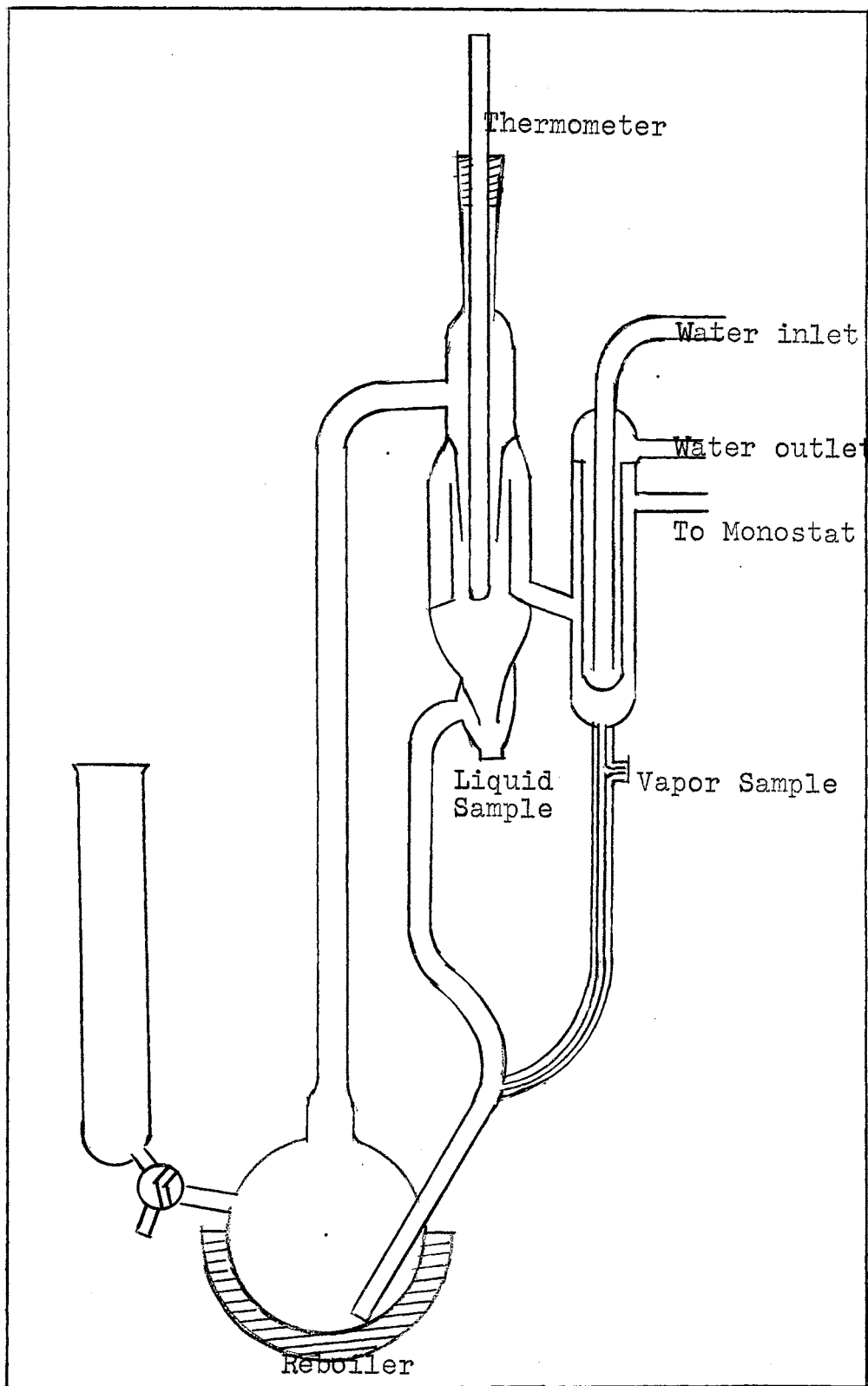


Fig. 1 The Modified Gillespie Still

condensation of the vapor with the rather high boiling systems investigated. The Cottrell pump makes use of evolved vapors in intimate contact with the liquid to lift the mixture. This mixture spurts into the equilibrium chamber and is separated. The liquid phase returns directly to the reboiler. The equilibrium vapor leaving the separator is totally condensed in the external condenser and the condensate is mixed with the returning equilibrium liquid ahead of the reboiler. At equilibrium conditions the liquid mixture returned to reboiler has the same composition as the system originally charged to the still.

The apparatus is made of pyrex glass, except for the teflon sampling valves and a cork stopper for the thermometer connection.

Gas Chromatograph

All the samples were analyzed in a gas chromatograph. The basic unit was a model 119 gas chromatograph, made by the F. & M. Scientific Corporation, Wilmington, Delaware. A one millivolt Bristol Recorder, model 560, with a one-second scale sweep was used to record the output from the sensing element. The important operating variables are:

(1) Temperature. Water was used as coolant in the reflux vapor bath. The temperature of the chromatographic column was observed to be $209^{\circ} \pm 0.2^{\circ}\text{F}$ through all analyses.

(2) Carrier gas. Helium was used as the inert carrier gas. The operating pressure was kept at 10 psig by means of a reducing valve. The outlet pressure was maintained at 760

mm Hg by the control system provided. The gas flow rate was kept at 50 cc/min. as measured by means of a soap-bubble flow-meter.

(3) Chromatographic column. The column was a 4-ft section of $\frac{1}{4}$ -in. copper tubing containing crushed fire brick coated with 20% by weight tricresyl phosphate.

The gas chromatograph used in this study has been reported to have an over-all accuracy of $\pm 0.2\%$ and high reproducibility under the operating conditions used (16).

Thermometer

An A.S.T.M. Petrolatum melting point thermometer, having 79 mm immersion, and a range of 32°C to 127°C in 0.2°C divisions, was used. Temperature readings were made with a precision of $\pm 0.05^\circ\text{C}$ by means of a thermometer magnifying glass. The thermometer was calibrated by determination of the melting point of ice and the boiling point of water (using a hypsometer).

Pressure Controller

An Emil Greiner Cartesian manostat was used to hold the still pressure at normal atmospheric pressure.

Reboiler Heat Supply

A Glas-Col heating mantle was controlled by means of a Variac to supply suitable heat for the reboiler.

Syringes

Two 0.25 cc tuberculin syringes were used to transfer the vapor and liquid samples to sample vials. A Hamilton syringe with 0.05 cc maximum volume was used to inject the

samples into the chromatograph. The 0.05 cc syringe has 0.001 cc divisions.

Procedure

In order to cover the entire range of intermediate ternary compositions, mixtures were prepared containing six different ratios of n-hexane to methylcyclohexane, namely 10, 20, 40, 60, 80, and 90 volume percent of n-hexane in methylcyclohexane. Each of these mixtures was then treated in the still with varying amounts of toluene.

The mixing was done by charging 35 cc of one of the above mixtures to the still; then adding a measured volume of toluene to the still. Then heat was applied to the reboiler and adjusted to give the desired reflux in the vapor condenser. The still was allowed to operate at least one hour and half to allow it to reach equilibrium. The temperature was then recorded. The samples of the vapor and liquid phases were drawn off with 0.25 cc hypodermic syringes and stored in small vials for later analysis.

After the samples were removed a second measured volume of toluene was added and the next run carried out. The procedure was repeated until an approximately 35 cc of toluene had been added. At this point, the still was drained and evacuated and 35 cc of toluene was added. Runs were then made adding consecutive increments of n-hexane-methylcyclohexane mixture. In this manner the entire concentration range was covered.

For each of the constant volume-ratio groups of n-hexane-methylcyclohexane, the experiments were carried out continuously. Slight changes in the normal atmospheric pressure were also recorded.

Before the samples were injected into the chromatograph, all variables such as pressure, temperature, flow rate, bridge system voltage, attenuator setting, etc., were adjusted (if necessary) to the constant values listed above. The helium outlet pressure was controlled by closing a valve on the control panel until the manometer pressure plus the atmospheric pressure equalled 760 mm Hg. The outlet helium stream was controlled at 50 cc per minute. A one cc per minute change in flow at 50 cc per minute will cause 2.1% error of peak area(16). Therefore, control by trial and error was necessary to keep both variables at the required values. The settings were rechecked before running each sample.

Sample size was also maintained at a constant value. For this work 0.02 cc was used for all the vapor and liquid samples. A suitable attenuator setting was 800 for this sample size in order to obtain the largest possible peak without exceeding the range of the recorder.

The injection syringe was washed with the sample two or three times, then evacuated to dry. The dried syringe was rewashed two or three times before using.

A calibration curve of the gas chromatograph for each pure component was prepared. This was done two or three times to make sure of the reproducibility the peak height. Values of volume vs. voltage(peak height) for the three components

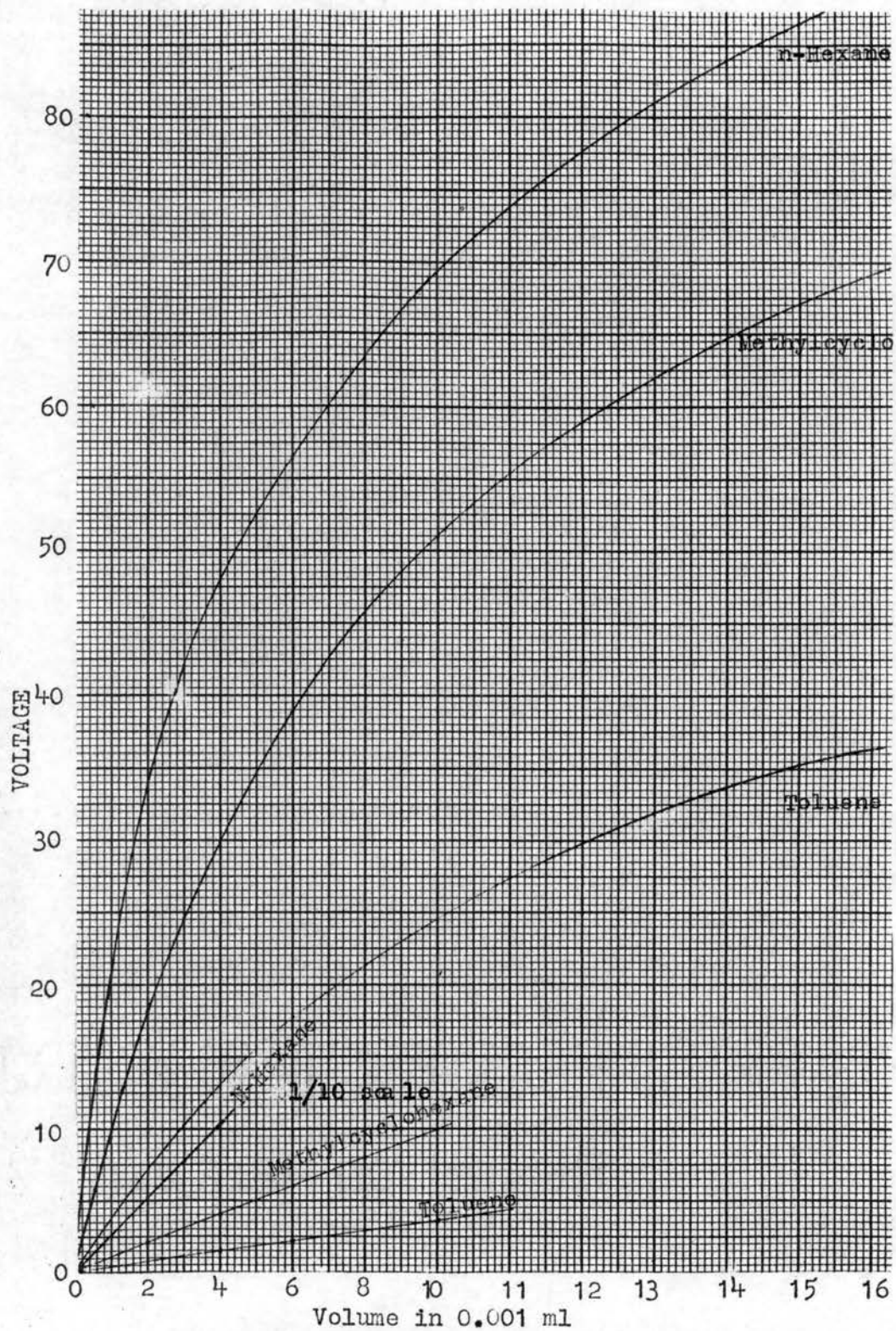


Fig. 2 Calibration Curves

are shown in Fig. 2.

The separation of n-hexane, methylcyclohexane, and toluene in the gas chromatograph was satisfactory. The time required for appearance of each component after sample injection was 48 seconds for n-hexane, 2 minutes and 28 seconds for methylcyclohexane, and 7 minutes and 11 seconds for toluene. Typical peaks for the components are shown in Fig. 3.

Experimental Data

The experimental equilibrium data obtained by gas chromatography are volume ratios which were changed to moles by multiplying by the factor d_i/M_i , where d_i is the density of component "i" and M is its molecular weight. Mole-fraction data for the ternary system n-hexane-methylcyclohexane-toluene are listed in Table VII to XII in the Appendix B. Temperature-composition diagrams for each series of runs were constructed (Fig. 13 to 18). Temperature-liquid composition and temperature-vapor composition diagrams are shown in Fig. 19 and 20. These were obtained by cross-plotting the experimental data.

The Antoine equation was used to calculate the vapor pressure of the hydrocarbons.

$$\log P^{\circ} = A - B/(C + t) \quad 2-1$$

where P° = vapor pressure in mm Hg
 t = temperature in $^{\circ}\text{C}$

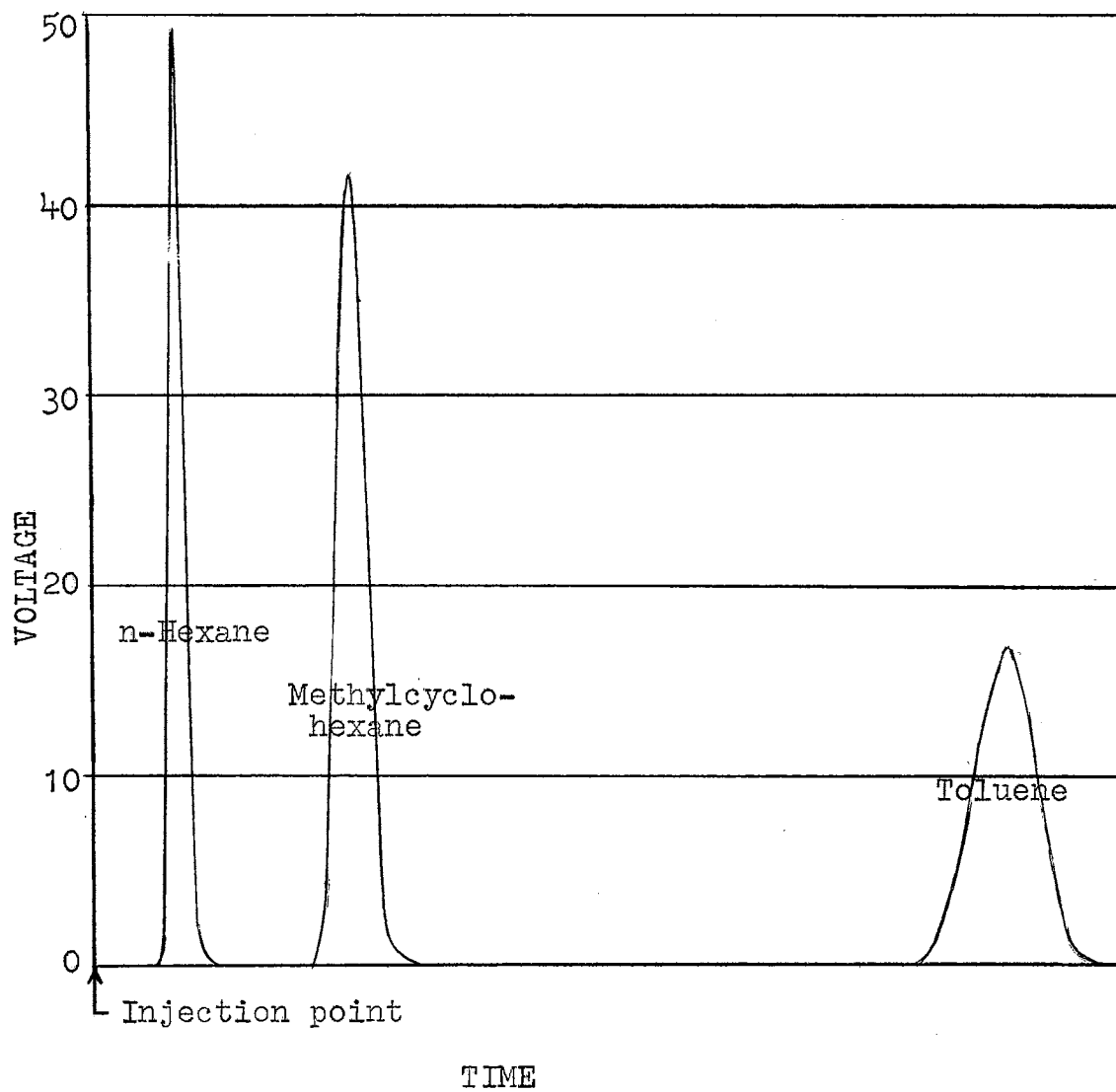


Fig. 3 Typical Chromatograph Curve

A, B, C, are empirical constants, different for each compound.

Values of A, B, and C for each of the three hydrocarbons were obtained from the data published by A.P.I. Project 44(17):

TABLE II
ANTOINE CONSTANTS

Hydrocarbon	A	B	C
n-Hexane	6.87776	1171.530	224.366
Methylcyclohexane	6.82689	1272.864	221.630
Toluene	6.95464	1344.800	219.482

Large scale vapor pressure vs. temperature curves were prepared. The curves are believed to be accurate to ± 0.5 mm Hg. A sample curve is shown in Fig. 9.

The experimental activity coefficient was calculated from the vapor and liquid phase compositions and the vapor pressures of the individual pure components at the observed temperature by Eq. (1-1). Values of activity coefficients are listed in Table VII to XII in the Appendix B.

CHAPTER III

TREATMENT OF DATA

The experimental data were analysed by comparing the activity coefficients with those calculated from the van Laar equation. For the ternary system studied, this was done by two methods: that of Wohl and that of Scatchard-Hildebrand. The applicability of these equations are discussed and the deviations of the prediction methods from the experimental data were examined. There are two possible explanations for these deviations. These and tests follow:

(1) The binary data (from the literature) used for the determination of the constants for the Wohl's ternary van Laar equation could be incorrect. This was checked by applying thermodynamic consistency tests to the two methods. All of the binary data were found to be inconsistent.

(2) The new experimental data for the ternary mixture might not be at equilibrium. Thermodynamic consistency tests showed this was not the case. A method for testing the thermodynamic consistency of the ternary experimental data is proposed. The results are discussed in the next chapter.

Application of the van Laar Equation

Two different expressions of van Laar equations were used to evaluate the activity coefficients in this study:

- (1) from the coefficients of the van Laar equations of the limiting binaries using Wohl's excess free energy expansion,
- (2) from the Hildebrand-Scatchard solubility parameters and volumes.

Ternary van Laar Equation from Limiting Binaries

Wohl(7) expressed a dependence of molar excess free energy on the liquid composition, which can be used to derive activity coefficients for a mixture of three components. The derivation is given in Appendix A. Equations for the three liquid activity coefficients are as follows:

$$\log \gamma_1 = \frac{\left[x_2^2 A_{12} \left(\frac{A_{21}}{A_{12}} \right)^2 + x_3^2 A_{13} \left(\frac{A_{31}}{A_{13}} \right)^2 + x_2 x_3 \left(A_{12} + A_{13} - A_{32} \frac{A_{13}}{A_{31}} \right) \frac{A_{21} A_{31}}{A_{12} A_{13}} \right]}{\left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2} \quad (3-1)$$

$$\log \gamma_2 = \frac{\left(\frac{A_{21}}{A_{12}} \right)^2 \left[x_3^2 A_{23} \left(\frac{A_{32}}{A_{23}} \right)^2 + x_1^2 A_{21} \left(\frac{A_{12}}{A_{21}} \right)^2 + x_1 x_3 \left(A_{23} + A_{21} - A_{13} \frac{A_{21}}{A_{12}} \right) \frac{A_{32} A_{12}}{A_{23} A_{21}} \right]}{\left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2} \quad (3-2)$$

$$\log \gamma_3 = \frac{\left(\frac{A_{31}}{A_{13}} \right)^2 \left[x_2^2 A_{31} \left(\frac{A_{13}}{A_{31}} \right)^2 + x_2^2 A_{32} \left(\frac{A_{23}}{A_{32}} \right)^2 + x_1 x_2 \left(A_{31} + A_{32} - A_{21} \frac{A_{32}}{A_{23}} \right) \frac{A_{13} A_{23}}{A_{31} A_{32}} \right]}{\left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2} \quad (3-3)$$

The constants A_{ij} , A_{ji} are determined from the binary system of components i and j . The subscripts 1, 2 and 3 as used here denote n-hexane, methylcyclohexane, and toluene, respectively.

Vapor-liquid equilibrium data for each of the three binary mixtures of these three components have been published by: Myers(10), Quiggle and Fenske(11) and Sieg(12). These data were used to determine the binary van Laar constants in equations (3-1), (3-2) and (3-3).

Lu and Lavergne(18) have proposed a graphical method for determining the van Laar constants for a binary system. The values of the binary activity coefficients were calculated from the binary data by Eq. (1-1) and plotted on the special graph paper(18) as shown in Fig. 4. Straight lines are drawn through each set of points (γ_1 , γ_2). Values of the constants obtained are given in Table III.

TABLE III
VAN LAAR CONSTANTS FOR BINARY SYSTEMS

System	Symbol	A_{ij} Constant	Symbol	A_{ji} Constant
n-hexane-methylcyclohexane	A_{12}	.0182	A_{21}	.0172
methylcyclohexane-toluene	A_{23}	.104	A_{32}	.099
n-hexane-toluene	A_{13}	.137	A_{31}	.219

Ternary system coefficients were next found from these binary coefficients by substituting the values of A_{ij} into equations (3-1), (3-2) and (3-3), giving

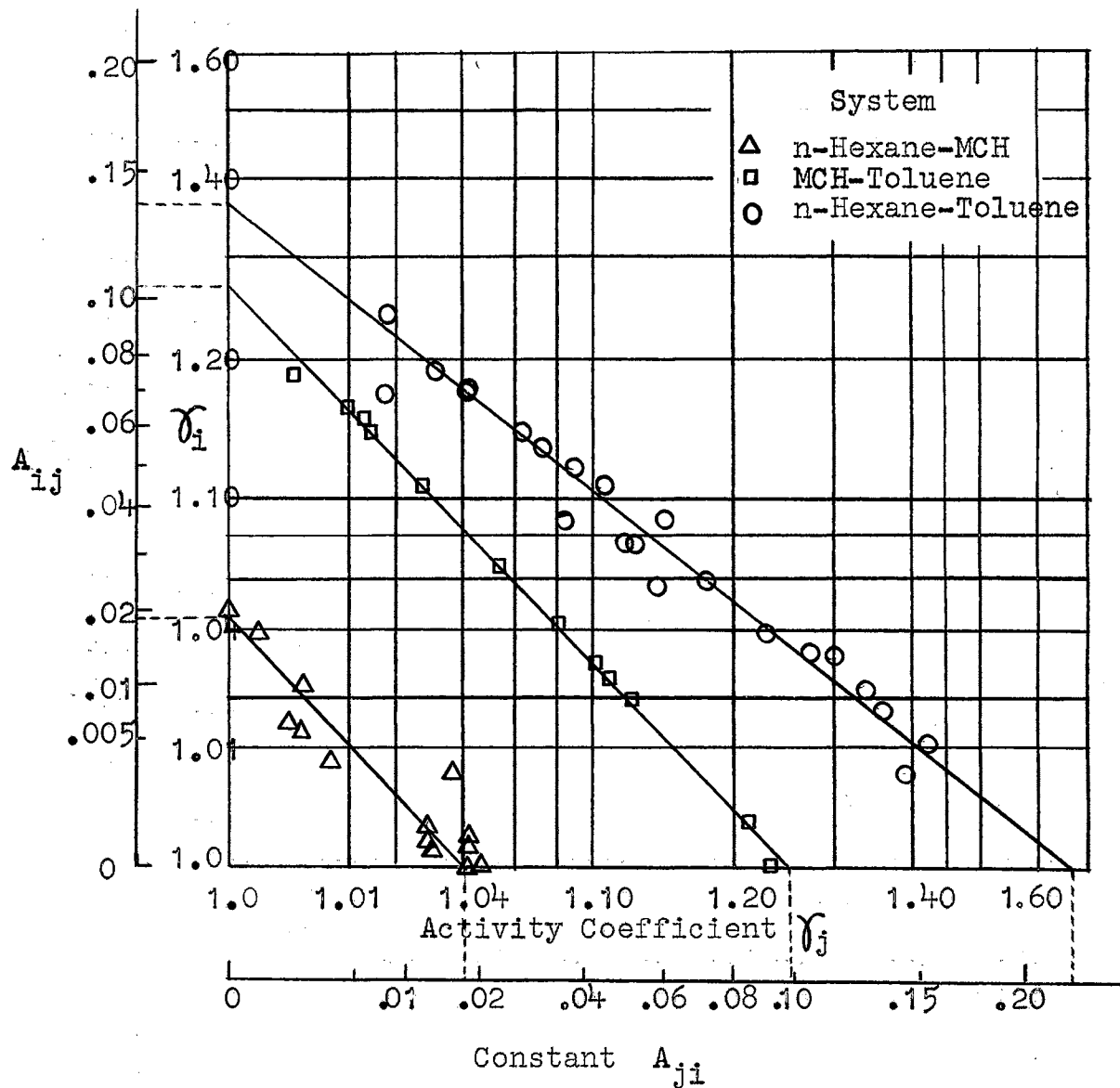


Fig. 4 Determination van Laar Constants by Method of Lu and Lavergne

$$\log \gamma_1 = \frac{(.0162 x_2^2 + .35 x_3^2 + .141 x_2 x_3)}{(x_1 + .945 x_2 + 1.598 x_3)^2} \quad (3-4)$$

$$\log \gamma_2 = \frac{.893 (.094 x_3^2 + .019 x_1^2 - .00827 x_1 x_3)}{(x_1 + .945 x_2 + 1.598 x_3)^2} \quad (3-5)$$

$$\log \gamma_3 = \frac{2.55 (.0857 x_1^2 + .109 x_2^2 + .198 x_1 x_2)}{(x_1 + .945 x_2 + 1.598 x_3)^2} \quad (3-6)$$

The computations of γ_1 , γ_2 , γ_3 were done on an I.B.M. 650 computer, using the same liquid mole-fractions as in the experimental ternary data. The calculated activity coefficients are compared with those obtained from the experimental work in Tables XIII to XVIII (Appendix B).

Scatchard-Hildebrand Method

Edmister(19) has developed the familiar van Laar equation from the Scatchard-Hildebrand(8,9) relationships. This development is also given in the Appendix. The equations can be used not only for binary but for multicomponent mixtures (22).

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B} \frac{x_1}{x_2}\right)^2} \quad (3-7)$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A} \frac{x_2}{x_1}\right)^2} \quad (3-8)$$

The subscripts 1 and 2 in Eq.(3-7), and (3-8) denote the

solute and the solvent, respectively. The solvent is considered to be the total of all the other components except the solute. The constants A and B are defined as

$$A = \frac{V_1}{2.303 RT} (\delta_1 - \delta_2)^2 \quad (3-9)$$

$$B = \frac{V_2}{2.303 RT} (\delta_1 - \delta_2)^2 \quad (3-10)$$

where V_1 and V_2 are liquid molar volume of solute and solvent
 δ_1 and δ_2 are solubility parameter of solute and solvent.

The liquid volume and solubility parameter for a multi-component system are the average V and δ values for the components of the mixture. The volume V_2 is a molar average and δ_2 is a liquid volume average. The expressions for the binary solvent of a ternary system are

$$V_2 = V_i \frac{\frac{x_i}{d_i}}{\frac{x_i}{d_i} + \frac{x_j}{d_j}} + V_j \frac{\frac{x_j}{d_j}}{\frac{x_i}{d_i} + \frac{x_j}{d_j}} \quad (3-11)$$

$$\delta_2 = \delta_i \frac{\frac{x_i M_i}{d_i}}{\frac{x_i M_i}{d_i} + \frac{x_j M_j}{d_j}} + \delta_j \frac{\frac{x_j M_j}{d_j}}{\frac{x_i M_i}{d_i} + \frac{x_j M_j}{d_j}} \quad (3-12)$$

where x = liquid mol fraction of pure component in solvent
 d = density of pure component in solvent

M = molecular weight of pure component is solvent
The subscripts i and j refer to pure components i and j .

Equations (3-7), and (3-8) have the following three advantages: (1) A and B can be estimated from physical properties, (2) the effect of concentration on the activity coefficient is included, and (3) the effect of temperature on A and B is included.

A disadvantage of Eq. (3-7) and (3-8) is that the values of V and δ can not be calculated directly for all substances and conditions. Several attempts (9, 20) have been made to calculate the values of V and δ , two of the typical ways are as follows:

$$\frac{d \ln \delta}{d T} \approx - 1.25 \alpha \quad (3-13)$$

$$V_i = (V_1 \omega_1)_i \left(5.7 + 3.0 \frac{T}{T_{ci}} \right) \quad (3-14)$$

where

α = coefficient of thermal expansion

$(V_1)_i$ = liquid molar volume at a low reference temperature T_1 of component i

$(\omega_1)_i$ = expansion factor at low reference temperature T_1 of component i

T = absolute temperature

T_{ci} = critical temperature of component i

Prausnitz, et al(20) indicated the temperature has little effect or no significance on δ , therefore, a constant value of δ at all temperatures is satisfactory. In equation (3-14) the product $(V_1 \omega_1)_i$ is a constant for each component.

Recommended values of δ and $V_1\omega_1$ for twenty-three hydrocarbons are reported by Prausnitz, et al(20). The constants may be considered tentative and subject to revision to improve the correlation through experimental data. Values of the constants used in this work in Table IV where the densities are taken at 60°F as the low reference temperature.

TABLE IV
CONSTANTS FOR SCATCHARD-HILDEBRAND EQUATION

Component	$V_1\omega_1$ (cc/gm mole)	(cal/ml) $^{\frac{1}{2}}$	d(gm/cc)
n-hexane	16.52	7.30	.66405
methylcyclohexane	16.51	7.85	.77398
toluene	14.15	8.90	.87190

For easy distinction, equations (3-7) and (3-8) may be written in following forms for a ternary system:

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B} \frac{x_1}{x_{23}}\right)^2} \quad (3-15)$$

$$\log \gamma_{23} = \frac{B}{\left(1 + \frac{B}{A} \frac{x_{23}}{x_1}\right)^2} \quad (3-16)$$

Equation (3-15) is for the calculation of activity coefficients for component 1, while components 2 and 3 together are taken as the solvent, as represented by the subscript 23 (where $x_{23} = 1 - x_1 = x_2 + x_3$). Similar equations are obtained for

calculating the values of γ_2 and γ_3 . The six equations derived in this way involve three real γ 's and three hypothetical ones:

<u>γ to be calculated</u>	<u>Solute</u>	<u>Solvent</u>	<u>γ of Solvent</u>
γ_1	n-hexane	2 and 3	γ_{23} (hypothetical)
γ_2	MCH	1 and 3	γ_{13} "
γ_3	toluene	1 and 2	γ_{12} "

The activity coefficients γ_1 , γ_2 , and γ_3 have real meaning and values. Coefficients γ_{23} , γ_{13} , γ_{12} , are hypothetical terms that have no physical significants. It is expedient to put the equation in this form.

Values of the liquid activity coefficients calculated in this way, using an I.B.M. 650 computer, are listed in Tables XIII to XVIII in the Appendix B. The activity coefficients derived from the experimental data are plotted on Figures 21, 22 and 23.

Applicability of the Van Laar Equation

The van Laar equations can be used to indicate qualitatively the deviations from ideality encountered in liquid mixtures. Therefore, it is interesting to compare the data predicted from the equations with the data directly calculated from the experimental work.

For easy comparison, the ternary activity coefficients from three sources (experimental, Wohl's method, Scatchard-Hildebrand method) were plotted in Figures 24 through 27.

The activity coefficient of each component is plotted as a function of its concentration in the liquid mixture containing a constant ratio of the other two components. The experimental activity coefficients at constant ratio in Fig. 24 through 27 obtained by cross-plotting the values listed in Tables VII to XII. The activity coefficients for other two sources are calculated from equations (3-1), (3-2), (3-3) and (3-7) by assuming a constant ratio of the other two components.

The results of the above method are shown in Fig. 21 to 27. The unsatisfactory agreement among the data from the three sources is obvious. The deviations may be explained by three possibilities:

- (1) The experimental data do not represent true equilibrium.
- (2) Incorrect binary data were used for the determination of the constants for the Wohl's ternary van Laar equation.
- (3) The relations used to evaluate the physical properties to be used in the Scatchard-Hildebrand equation need adjustment.

Discussion of these three possibilities is presented in the next section.

Thermodynamic Consistency of the Experimental Data

Equilibrium measurements are always subject to error, depending on the equilibrium cell used and the accuracy of the various measurements. The preliminary judging of the experimental data -- the smoothness of temperature-compo-

sition curves, shown in Fig. 13 to 20 -- illustrated that the data were without large random errors. However, the reliability of the results may be poor because of systematic errors which do not show up as a scattering of the measured points. The consistency of the measured data must, therefore, be determined by the use of thermodynamically exact relations.

The vapor-liquid equilibrium data of the binary systems, n-hexane-methylcyclohexane(10), methylcyclohexane-toluene(11), and n-hexane-toluene(12) were used in this work to determine the van Laar constants in the Wohl's equation. The data were first checked for thermodynamic consistency.

A suitable method for testing the binary systems, which follows the Gibbs-Duhem equation, was proposed by Redlich and Kister(2) in following equation:

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad (3-17)$$

where γ_1 = the activity coefficient of component 1
 γ_2 = the activity coefficient of component 2
 x_1 = the liquid mol fraction of component 1

The equation was suggested to apply only over a moderate boiling interval. The boiling intervals for n-hexane-toluene, n-hexane-methylcyclohexane, are somewhat large for the strict validity of Eq. (3-17), but any likely deviation from Eq. (3-17) would increase the discrepancy of test.

Equation (3-17) is easily applied by plotting the

logarithm of γ_1/γ_2 (calculated from the measured data) as a function of x_1 . It follows from Eq.(3-17) that the total area under the curve (with respect to the abscissa) must be equal to zero, otherwise the data are not thermodynamically consistent. The binary data from the literature were treated in this way, as shown in Fig. 10, 11, and 12. Deviations from Eq.(3-17) are noticeable.

Herington(5) suggested that at isobaric conditions (no matter what the temperature interval is) the areas above the abscissa and below need not be the same. The measured data are still consistent if the following condition holds:

The algebraic sum of the two areas is represented by I.

$$I = \int_0^1 \log \frac{\gamma_1}{\gamma_2} dx_1 \quad (3-18)$$

If A denotes the sum of the magnitudes of the two areas (i.e., without regard to sign), the percentage deviation D is expressed by the equation

$$D = \frac{100 I}{A} \quad (3-19)$$

Compare this percentage deviation D with a second quantity J, which is a function of the overall range of boiling points of the system at the given pressure.

$$J = \frac{150 B}{T_{\min}} \quad (3-20)$$

where B = overall range of boiling points in °C

T_{\min} = the lowest measured boiling temperature in °K

If the condition $D < J$

is fulfilled, it can be assumed that the measured data are consistent (Herington states that if $D - J < 10$, the data can still be considered to be correct).

The systems n-hexane-toluene, methylcyclohexane-toluene were tested in this way. The results do not satisfy Herington's condition. The data are given in Table V.

TABLE V

CHECK ON THE CONSISTENCY OF THE MEASURED DATA
BY THE HERINGTON METHOD

System(P=760 mmHg)	B	T _{min}	A	D	J	D - J
n-hexane-toluene	41.87	341.70	.1564	39.7	18.40	21.30
MCH-toluene	9.75	373.85	.0977	21.6	3.92	17.68

There is no convenient way for testing the consistency of data for ternary systems, or multicomponent systems. The application of the Gibbs-Duhem relation(4) and the method suggested by Herington(5) may be used to test the thermodynamic consistency for ternary systems, but the procedures are very lengthy and require the experimental determination of a large amount of ternary data.

The author, in this work, proposes a method for testing ternary and multicomponent systems. The tests presented are similar to those described by Redlich and Kister(2), but different in meaning:

$$\int_0^1 \log \frac{\gamma_1}{\gamma_{23}} dx_1 = 0 \quad (3-21)$$

where γ_1 = activity coefficient of solute component 1
 γ_{23} = activity coefficient of solvent, component 2
 and 3 in this case

x_1 = liquid mol fraction of component 1.

The equation is also to be applied to data obtained in a moderate boiling interval.

Since this is the first time this method for the examination of ternary isobaric data has been proposed, a discussion of the underlying theory is presented. To test whether the equation is applicable, the activity coefficients calculated by the van Laar equation expressed by Edmister(19), by which the values of activity coefficient of solvent can be directly evaluated, were used. The data obtained from the thermodynamic relations should show thermodynamic consistency. This was done by plotting $\log \frac{\gamma_3}{\gamma_{12}}$ against x_3 . Good agreement is shown in Fig. 5, in which the area above the abscissa is equal to that below. The slight deviation at the lowest and highest temperatures in Fig. 5 can be explained as being due to the high boiling interval of the system n-hexane-methylcyclohexane-toluene.

However, for treatment of the experimental data, there are some difficulties. The activity coefficient of solvent, γ_{23} in Eq. (3-21), can not be evaluated directly (e.i., a relation of γ_{23} to γ_2 and γ_3 has not yet been described) from the experimental data. Therefore, the following simplifications have been made in order to evaluate γ_{23} .

The van Laar equations expressed by Edmister are rearranged the following forms(21):

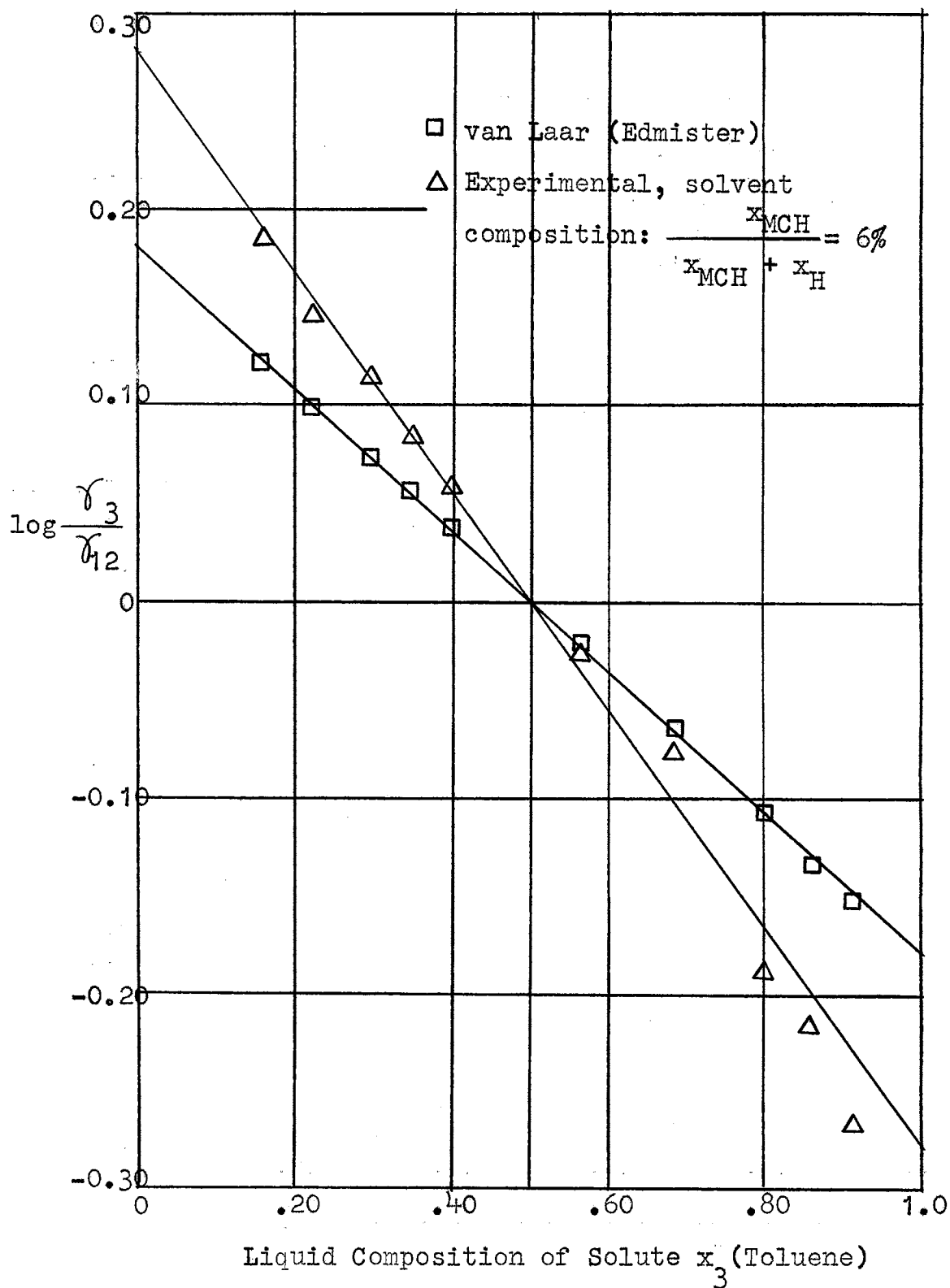


Fig. 5 Dependence of $\log \frac{\gamma_3}{\gamma_{12}}$ on the Liquid
 Composition of Solute (x_3)

$$\frac{1}{\sqrt{\log \gamma_1}} = \frac{1}{\sqrt{A}} + \frac{\sqrt{A}}{B} \left(\frac{x_1}{x_{23}} \right) = b + m \left(\frac{x_1}{1 - x_1} \right) \quad (3-22)$$

where

$$b = \frac{1}{\sqrt{A}}$$

$$m = \frac{\sqrt{A}}{B}$$

According to Eq. (3-11), (3-12), at constant ratio of component 2 to component 3, the solubility parameter of solvent γ_{23} and the liquid molar volume of solvent V_{23} are constants. Therefore, for the moderate temperature interval, A and B are constants and they are readily calculated from the values of the individual slope (m) and intercept (b) obtained by plotting $1/\sqrt{\log \gamma_1}$ as a function of $x_1/(1 - x_1)$.

$$A = \frac{1}{b^2} \quad (3-23)$$

$$B = \frac{1}{mb} \quad (3-24)$$

by rearrangement and combination of Eq. (3-15) and (3-16)

$$\frac{\log \gamma_1}{\log \gamma_{23}} = \frac{B}{A} \left(\frac{x_{23}}{x_1} \right)^2 \quad (3-25)$$

or,

$$\log \gamma_{23} = \frac{A}{B} \left(\frac{x_1}{x_{23}} \right)^2 \cdot \log \gamma_1 \quad (3-26)$$

Subtracting each side from $\log \gamma_1$,

$$\log \frac{\gamma_1}{\gamma_{23}} = \left[1 - \frac{A}{B} \left(\frac{x_1}{1-x_1} \right)^2 \right] \log \gamma_1 = \left[1 - \frac{m}{b} \left(\frac{x_1}{1-x_1} \right)^2 \right] \log \gamma_1 \quad (3-27)$$

Equations (3-22), (3-24), (3-27) constitute the convenient forms to be used in calculating the $\log \frac{\gamma_1}{\gamma_{23}}$ from the experimental values of x_1 and γ_1 . The procedure is summarized as follows:

- (1) Using liquid activity coefficients and composition data of solute at constant mixture ratio of solvent, plot

$$\frac{1}{\sqrt{\log \gamma_1}} \quad \text{against} \quad \frac{x_1}{1-x_1} .$$

- (2) A and B are determined from slope and the intercept using Eq. (3-23) and (3-24).
 (3) $\log \gamma_1 / \gamma_{23}$ is readily calculated from Eq. (3-27).

The experimental data may not show an exact straight line relation when treated as procedure (1) described. It is suggested the values of A and B be determined from different slopes using a common intercept for each point.

Group 1 (Table VII) experimental data were treated in the above way to obtain an intercept of 2.35 and an average slope of 1.855 (Fig. 6). In order to avoid any modification of the experimental data, different slopes of each point were used in calculating the $\log \frac{\gamma_1}{\gamma_{23}}$ values. The consistency of the experimental data are shown by a plot of the log of the activity coefficient ratio as a function of liquid composition (Fig. 5).

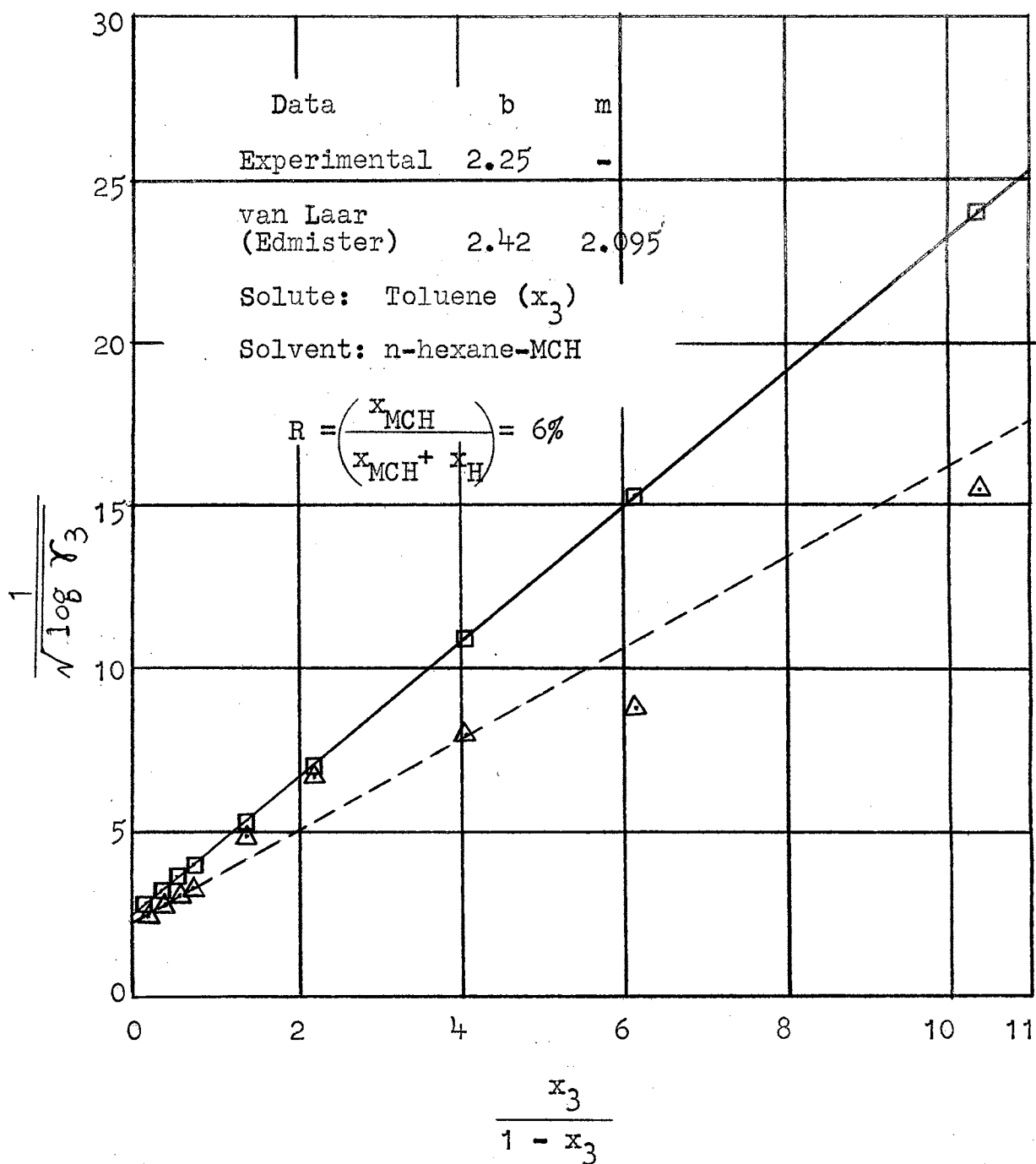


Fig. 6 Correlation Plot of van Laar Equation(Edmister) at Constant Solvent Composition For Determining the Activity Coefficient of Solvent.

CHAPTER IV

DISCUSSION OF RESULTS

The vapor-liquid equilibrium data for the ternary system n-hexane-methylcyclohexane-toluene at normal atmospheric pressure are listed in Tables VII to XII, and also shown in Fig. 13 to 18. The boiling point data (ternary diagrams of temperature-composition) are plotted in Fig. 19 and 20, which were obtained by cross-plotting of the experimental data.

The smooth curves of the temperature-composition data shown in Fig. 13 through 18 do not indicate systematic errors; therefore, the results of the equilibrium measurements must be examined for thermodynamic consistency. This was done by the method suggested by the author in the previous section, and good agreement was shown (Fig. 5). Group 1 experimental data were used in this calculation, the reason being that this was the only group of experiments in which a constant ratio of n-hexane to methylcyclohexane (90:10) was treated by adding different amounts of toluene in the determination of the vapor-liquid equilibria. In order to save chemicals, other runs were operated continuously. Each sample contained a relatively high mole-fraction of the more volatile component (n-hexane). Continuous sampling reduce the composition of the n-hexane slightly, and the ratio of n-hexane to

methylcyclohexane was not maintained constant. Therefore, the first group of experimental data were the best data for correlating and comparing because the desired conditions were obtained directly in the experiments.

The thermodynamic consistency of the experimental data shown in Fig. 5 does not constitute, in itself, a proof of equilibrium, but it does constitute powerful presumptive evidence of equilibrium. From the preliminary judging of the experimental data -- the smooth temperature-composition curves -- in addition to the thermodynamic consistency, the experimental data in this work are considered to be correct.

Deviations from ideality of the mixture components are represented by their activity coefficients. The coefficients were compared with the values predicted from the van Laar equation, in one case based on binary data (as expressed by Wohl), and in the other as estimated from their physical properties (as suggested by Edmister). The results are given in Tables XIII to XVIII.

The experimental results for n-hexane, from Tables XIII to XVI, are seen to be somewhat irregular, and at low naphthene-aromatic concentrations negative deviations from Raoult's law (activity coefficients less than one) were obtained. This may be due to analytical error, to small errors in observed equilibrium temperature, or to the fact that n-hexane associates in the liquid phase.

For easy comparison, a method of plotting ternary activity coefficients is shown in Fig. 21 to 27, in which the

activity coefficient of one component is plotted as a function of its liquid composition with a constant ratio of the other two components as a parameter. These figures indicated that the activity coefficients estimated from experimental do not compare well with those data predicted from the ternary van Laar equations based binary data. The lack of agreement is believed to be due to the following:

- (1) Inconsistent binary data were used.
- (2) The effect of changing temperature was not included.

The first of the above reasons was discussed in the previous section, where the vapor-liquid equilibria for the binary systems, n-hexane-methylcyclohexane, methylcyclohexane-toluene, and n-hexane-toluene were checked for thermodynamic consistency by two methods. None of the binary data is satisfactory (Fig. 10 to 12, and Table V). The consistency of the experimental data may not constitute proof of equilibrium, but thermodynamically inconsistent data can not be correct.

The effect of system temperature change is believed to be relatively small. Actually, the temperature of the equilibrium mixtures varied from 72° to 107°C (i.e., 345° to 380°K), or about 9.2%.

The activity coefficients obtained from the solubility parameter and molar volume also do not agree closely with the experimental data. However, it is interesting to compare the A and B values calculated from physical properties with those obtained by simply fitting Eq.(3-7) to experimental

data. A method similar to that described in the previous section was used to fit the experimental data and evaluate A and B. The latter, as expected, are constant at constant composition of solvent for small temperature intervals.

Figure 7 shows the A and B values from the three sources for group 1 data. The values obtained from physical properties are closer to the experimental data, and they are easily adjusted to fit the experimental data by slightly changing the intercept and slope values.

Recall the van Laar equations as expressed by Edmister, for toluene:

$$\log \gamma_3 = \frac{A}{\left(1 + \frac{A}{B} \frac{x_3}{x_{12}}\right)^2} \quad (4-1)$$

$$\log \gamma_{12} = \frac{B}{\left(1 + \frac{B}{A} \frac{x_{12}}{x_3}\right)^2} \quad (4-2)$$

where

$$A = \frac{V_3}{2.303 RT} (\delta_3 - \delta_{12})^2 \quad (4-3)$$

$$B = \frac{V_{12}}{2.303 RT} (\delta_3 - \delta_{12})^2 \quad (4-4)$$

and

$$\frac{A}{B} = \frac{V_3}{V_{12}} \quad (4-5)$$

$$V_3 = (V_1 \omega_1)_3 \left(5.7 + 3.0 \frac{T}{T_{c3}}\right) \quad (4-6)$$

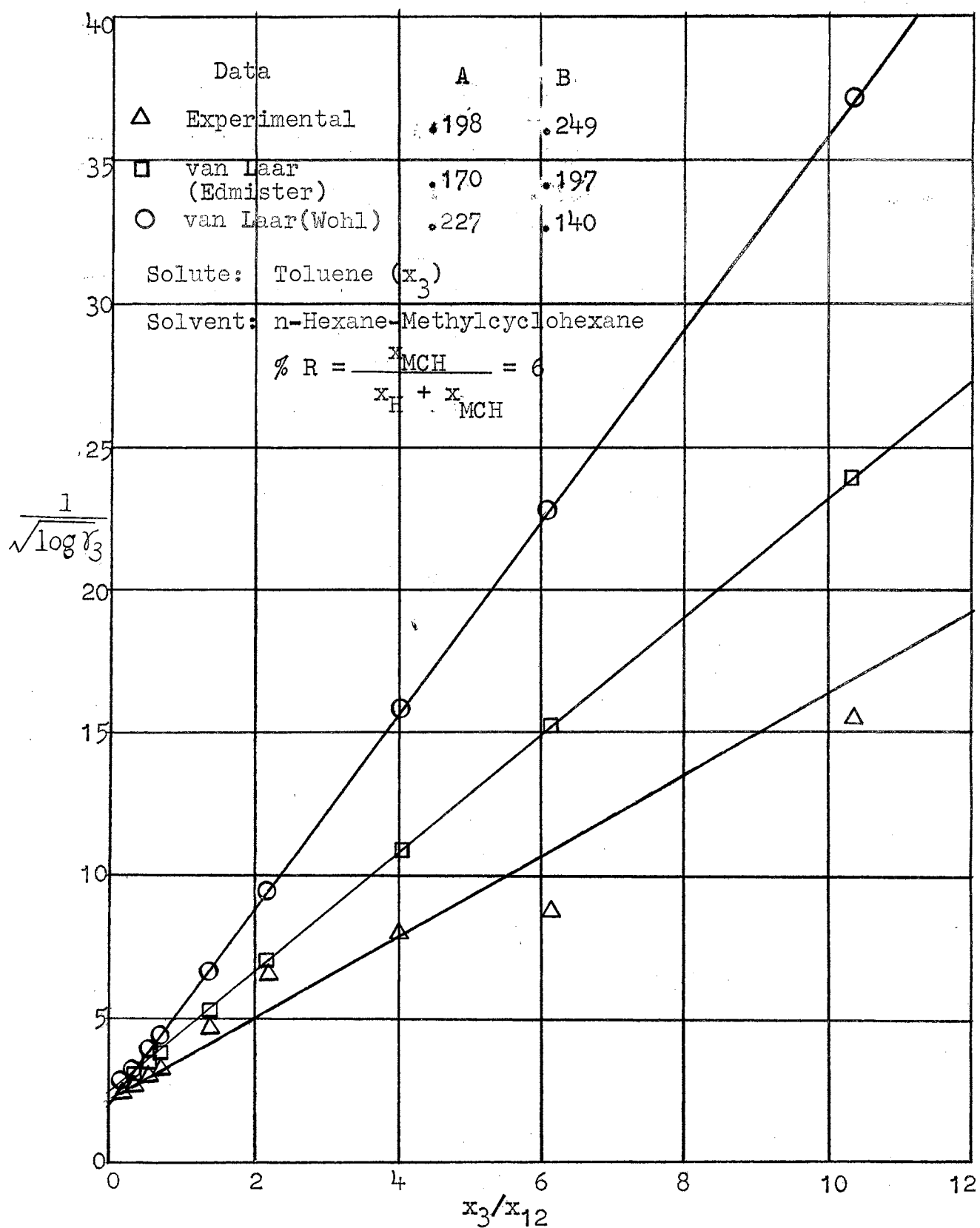


Fig. 7 Correlation Plot of van Laar Equation at Constant Solvent Composition For Determining the A, B Constants

If, in Fig. 7, the intercept b and slope m both change but the ratio m/b is maintained constant, the value of A/B is then constant (by Eq.(3-23) and (3-24)). Therefore, by Eq.(3-27), the value of the log of the ratio of activity coefficients does not alter (i.e., the system is still in thermodynamic consistency). The only change is in the individual activity coefficient values, which is readily observed by inspection of Eq.(4-1). The change is due to the "slope" A ; that is, if we plot $\log \gamma_3$ as a function of $\left(1 + \frac{A}{B} \frac{x_3}{x_1^2}\right)^{-2}$, the slope is A . Therefore, the shape of curve -- activity coefficients against liquid composition(at constant ratio of solvent) -- remains unchanged.

From this point of view, it is suggested that the values of A and B be changed at a constant ratio in order to fit the experimental data. From Eq.(4-3), (4-4), and (4-5) it is observed that such a change will not affect the square root of solubility parameter difference, because the compositions are constant. Therefore, the only parameter to be changed is the molar volume, or the product $V_1 \omega_1$ of Eq.(4-6).

A complete discussion of the molar volumes used in the correlation of experimental data is beyond the scope of this work. Therefore, only the toluene is discussed. The case of toluene may be assumed to be a typical one.

From Fig. 7, the van Laar equation was assumed to have the same slope and intercept as the experimental data. Values of the slope m and intercept b were thus changed

from the original 2.095 and 2.426 to 1.86 and 2.15, respectively. Note that the ratio $m/b = 2.095/2.15$ is constant. A and B were then calculated from Eq.(3-23) and (3-24). The values are compared with the experimental values in Table VI.

TABLE VI
CORRELATION OF VAN LAAR CONSTANTS

	b	m	A	B
Experimental	2.25	1.855	.198	.239
van Laar(Edmister)	2.42	2.095	.170	.1965
van Laar(modified)	2.15	1.86	.216	.2495

Equation (4-6) must be modified as follows:

$$V_3 = 1.27 (V_1 \omega_1)_3 \left(5.7 + 3.0 \frac{T}{T_{c3}} \right) \quad (4-7)$$

The multiplying factor 1.27 was back-calculated from the modified A and B values. The activity coefficient values calculated by using Eq.(4-7), show good agreement with the experimental values (Fig. 8).

To sum up, the Scatchard-Hildebrand form of the van Laar equation is tentative and subject to revision in order to improve the correlation of experimental data. The equation is independent of binary data when used in calculating for multicomponent systems, and it is a simple function of three characterizing constants for both solute and solvent (δ , $V_1 \omega_1$, and T_c), of temperature and of concentration. The solubility parameters are considered to be

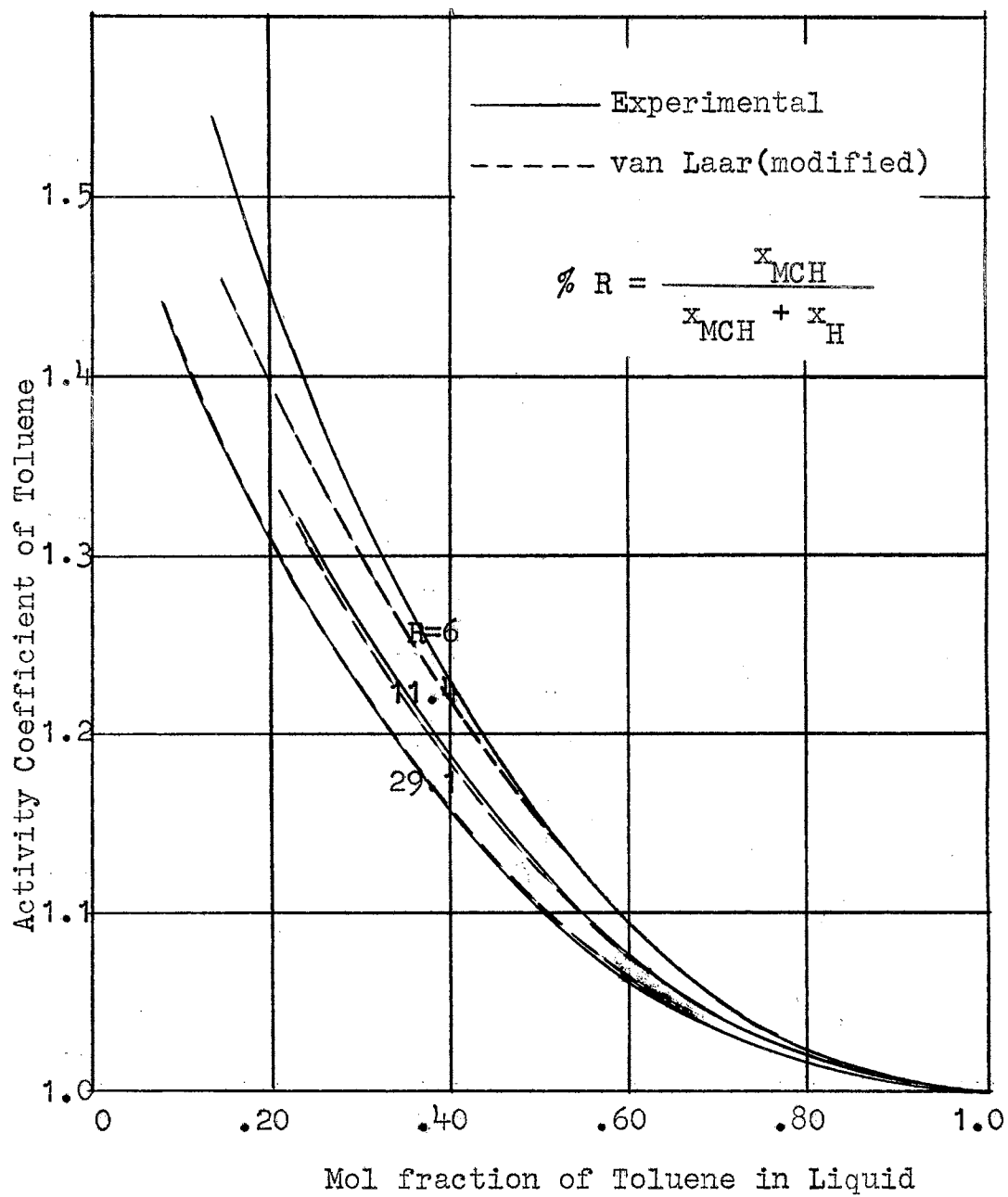


Fig. 8 Toluene Activity Coefficients
System: n-Hexane-Methylcyclohexane-Toluene

constant. The factor affected is the molar volume or $V_1\omega_1$ in Eq.(4-6). If sufficient experimental data are available, the correction factor (i.e., 1.27 in this work) may be taken from the average values. It is suggested that recorrelation of the $V_1\omega_1$ values be attempted using binary data.

CHAPTER V

SUMMARY AND CONCLUSIONS

Vapor-liquid equilibria have been determined at 739 to 745 mm Hg pressure for the ternary system n-hexane-methylcyclohexane-toluene. Triangular temperature-composition diagrams were constructed by cross-plotting the experimental data.

Moderate deviations from ideal solution law were observed, the activity coefficients for n-hexane, methylcyclohexane, and toluene at infinite dilution vary about 1.5, 1.5, and 1.95, respectively. For the system of a paraffin-naphthene-aromatic, this result is as expected.

The experimental activity coefficient data do not compare well with the data predicted from the van Laar equations based on binary data. The lack of agreement is believed to be due to the doubtful binary data. The latter have been checked by thermodynamic consistency tests. None of the binary data satisfied this test.

A convenient new method for testing the thermodynamic consistency of experimental data for ternary and multi-component systems is suggested and demonstrated. This method should be of value to chemical engineers as in pro-

vides an accurate and rapid means of checking ternary or multicomponent equilibrium data for use in extractive and fractional distillation design calculations.

With the new experimental vapor-liquid equilibria data obtained on the n-hexane-methylcyclohexane-toluene system, a convenient method for applying the van Laar equation to ternary systems is demonstrated. In this method the van Laar coefficients, A and B, are evaluated from the physical properties, i.e. liquid molar volume and solubility parameter, of the mixture components. The ternary system is treated as a binary mixture of a single solute and a mixed (2 components) solvent. This treatment is applied three times, with each component being the solute in turn.

The experimental activity coefficient data for toluene are nearly coincident with the activity coefficients computed by this "physical properties" form of the van Laar equation, provided that the latter equation is modified by increasing the molar volume of toluene by 27%.

A SELECTED BIBLIOGRAPHY

1. Chu, Ju-Chin, et al. "Vapor-Liquid Equilibrium Data" Ann Arbor (1956).
2. Redlich O., Kister A. T. Chem. Eng. Progr. Symp. Ser. 48, No. 2, 49 (1952).
3. Herington, E. F. G. Research, 1950, 3, 41.
4. Steinhauser, H. H., White R. R. Ind. Eng. Chem. 41 2912 (1949).
5. Herington, E. F. G. J. Inst. Petrol. 37 457 (1951).
6. van Laar, Z. Physik. Chem., 72, 723 (1910).
7. Wohl K., Trans. Amer. Inst. Chem. Engrs. 42 215 (1946)
8. Scatchard, G. Trans Faraday Soc. 33 160 (1937)
9. Hildebrand, J. H. and Scott, "Solubility of Non-Electrolytes" Reinhold (1950).
10. Myers, H. S. Petroleum Refiner March 1957.
11. Sieg L., Chem. Ing. Tech. 22 322 (1950).
12. Quiggle and Fenske: J. Am. Chem. Soc. 59 1829 (1937).
13. _____, "Phillip 66 Hydrocarbons" 5th Edition Phillips Petroleum Company (1958).
14. Gillespie, D. T., Ind. Eng. Chem., Anal. Ed. 18 575 (1946).
15. Drehman, L. E., "Vapor-Liquid Equilibria among the C₆ Hydrocarbons" M.S. Thesis, Oklahoma State University, 1959.
16. Webster, J. L., "Principles And Properties of Gas Chromatography" M.S. Thesis, Oklahoma State University, 1961.
17. Rossini, F. D., et al. "Selected Values of Physical And Thermodynamic Properties of Hydrocarbons And Related Compounds" Pittsburgh (1953).

18. Lu, C. Y. and Lavergne, B. A. Chem. Eng. 65 132
August 1958.
19. Edmister, W. C., "Theoretical Methods for Obtaining
Vapor-Liquid K values" Notes, Oklahoma State
University, Vapor-Liquid Equilibrium Conference,
April 1959.
20. Prausnitz, J. M., W. C. Edmister, and K. C. Chao,
AIChE Journal June (1960).
21. Robinson C. S., Gilliland E. R. "Elements of Frac-
tional Distillation" 4th Edition, McGraw-Hill
(1950).
22. Edmister, W. C. Petroleum Refiner 159- Dec. 1960.

APPENDIX A

DERIVATION OF THE VAN LAAR EQUATIONS

Van Laar Equation for Van der Waals Fluid

Van Laar based his derivation on the thermodynamic changes occurring on the mixing of pure liquids, using the van der Waals equation ($P = RT/(V - b) - a/V^2$) applied to each of the components and to the mixture, both as liquid and as vapor. The van der Waals constants of the mixture are calculated from the constants of the pure constituents. Two additional assumptions were made:

- (1) The change in entropy on mixing is equal to that of an ideal solution.
- (2) No volume change on mixing.

The equation is developed on page 56-58 of Robinson and Gilliland "Elements of Fractional Distillation" (McGraw-Hill, 1950).

$$\ln \gamma_1 = \frac{B^1/T}{\left(1 + A^1 \frac{x_1}{x_2}\right)^2} \quad (\text{A-1})$$

$$\ln \gamma_2 = \frac{A^1 B^1/T}{\left(A + \frac{x_2}{x_1}\right)^2} \quad (\text{A-2})$$

where γ_1 = activity coefficient of component 1
 γ_2 = activity coefficient of component 2

The constants are defined by

$$A' = \frac{b_1}{b_2} \quad (A-3)$$

$$B' = \frac{b_1}{R} \left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 \quad (A-4)$$

where a and b are van der Waals constants, the subscripts 1 and 2 denote component 1 and 2, and R is the universal gas constant.

By algebraic manipulations, Eq.(A-1) and (A-2) can be put into a more symmetrical form.

Let

$$A = \frac{B'}{2.303 T} = \frac{b_1}{2.303 RT} \left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 \quad (A-5)$$

$$B = \frac{B'}{2.303 A' T} = \frac{b_2}{2.303 RT} \left(\frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2 \quad (A-6)$$

Then substitute into Eq.(A-1) and (A-2).

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A x_1}{B x_2} \right)^2} \quad (A-7)$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B x_2}{A x_1} \right)^2} \quad (A-8)$$

It will be recalled that the van der Waals constants are found from the critical constants, where

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad \text{and} \quad b = \frac{RT_c}{8P_c}$$

The van der Waals method for evaluating the van Laar constants is only an approximation, to be used when no other information is available.

Van Laar Equation from Wohl's Excess Free Energy Expression

Wohl(7) expressed the dependence of molar excess free energy of mixing, ΔF^* , on the composition of the liquid phase by the following general expression:

$$\frac{\Delta F^*}{2.303 RT} = \left(\sum_i q_i x_i \right) \left[\sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} + \dots \right] \quad (\text{A-9})$$

where R = universal gas constant

T = absolute temperature

q_i , q_j , q_k ... = constants which Wohl called the effective molar volumes of the constituents i , j , k ,

a_{ij} , a_{ijk} = empirical constants

The subscripts of a , a_{ij} for instance, indicates that a_{ij} appears in a term which contains the product $x_i x_j$, therefore $a_{ij} = a_{ji}$. The effective volumetric fraction z for any component i is defined by the relation

$$z_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2 + \dots + x_n q_n} \quad (\text{A-10})$$

Obviously $\sum z_i = 1$

Equation (A-9) can be used to derive activity coefficients for a mixture of any number of components, provided we first relate the excess free energy of mixing with the activity coefficient.

The change of free energy on mixing of three pure liquid components to form a solution is given by the relation

$$\Delta F_{\text{mix}} = \sum_1^3 n_i \mu_i - \sum_1^3 n_i \mu_i^0 = \sum_1^3 n_i (\mu_i - \mu_i^0) \quad (\text{A-11})$$

where μ_i = the chemical potential (partial molar free energy) of component i in the solution

μ_i^0 = the chemical potential of pure component i

n_i = the moles of component i , $i = 1, 2, \text{ or } 3$

and $\sum n_i = n$ which is constant.

From the definition of activity,

$$RT \ln a_i = \mu_i - \mu_i^0 \quad (\text{A-12})$$

where a_i = the activity of component i , defined by

$$a_i = \gamma_i x_i$$

equation (A-11) becomes

$$\Delta F_{\text{mix}} = \sum n_i RT \ln(\gamma_i x_i) = \sum n_i RT \ln \gamma_i + \sum n_i RT \ln x_i \quad (\text{A-13})$$

For ideal solutions $\gamma_i = 1$ or $\ln \gamma_i = 0$

$$\Delta F_{\text{mix}}^0(\text{ideal}) = \sum n_i RT \ln x_i \quad (\text{A-14})$$

Let the excess free energy between ΔF_{mix} and ΔF_{mix}^0 be

$$\text{denoted by } \Delta F^e = \Delta F_{\text{mix}} - \Delta F_{\text{mix}}^0 = \sum n_i RT \ln \gamma_i \quad (\text{A-15})$$

Differentiating with respect to moles of component i at constant temperature and constant pressure,

$$\left(\frac{\partial \Delta F^e}{\partial n_i} \right)_{T,P, n \neq i} = RT \ln \gamma_i + RT \left[n_1 \frac{\partial \ln \gamma_1}{\partial n_i} + n_2 \frac{\partial \ln \gamma_2}{\partial n_i} + n_3 \frac{\partial \ln \gamma_3}{\partial n_i} \right] \quad (\text{A-16})$$

The last part of equation (A-16) is zero, as can be proved by using the Gibbs-Duhem equation.

$$VdP - SdT = \sum n_i d\mu_i \quad (\text{A-17})$$

At constant temperature and pressure,

$$\sum n_i d\mu_i = \sum n_i (RT d \ln a_i) = RT \left(\sum n_i d \ln \gamma_i n_i \right) = 0 \quad (\text{A-18})$$

$$\text{or } \sum n_i d \ln \gamma_i + \sum n_i d \ln n_i = 0 \quad (\text{A-19})$$

Here, $\sum n_i = n$, which is constant, and $\sum n_i d \ln n_i = \sum d n_i = 0$. This reduces equation (A-19) to

$$\sum n_i d \ln \gamma_i = 0 \quad (\text{A-20})$$

For a ternary mixture Eq.(A-20) becomes

$$n_1 \frac{\partial \ln \gamma_1}{\partial n_i} + n_2 \frac{\partial \ln \gamma_2}{\partial n_i} + n_3 \frac{\partial \ln \gamma_3}{\partial n_i} = 0 \quad (\text{A-21})$$

Therefore, Eq.(A-16) becomes

$$\left(\frac{\partial \Delta F^e}{\partial n_i} \right)_{T,P, n \neq i} = RT \ln \gamma_i \quad (\text{A-22})$$

The molar excess free energy, ΔF^* , is given by
 $\Delta F^* = \Delta F^e / \sum n_i$. Substituting the latter into equation
 (A-22), and rearranging

$$\ln \gamma_i = \frac{1}{RT} \frac{\partial}{\partial n_i} \left(\sum n_i \cdot \Delta F^* \right)_{T,P, n \neq i} \quad (\text{A-23})$$

Wohl's expression for a ternary system is

$$\begin{aligned} \frac{\Delta F^*}{2.303RT} &= (q_1 x_1 + q_2 x_2 + q_3 x_3) \left[2z_1 z_2 a_{12} + 2z_1 z_3 a_{13} \right. \\ &\quad \left. + 2z_2 z_3 a_{23} \right] \\ &= q_1 \left(x_1 + \frac{q_2}{q_1} x_2 + \frac{q_3}{q_1} x_3 \right) \left[\frac{2a_{12} (x_1 x_2 q_1 q_2 / q_1^2)}{\left(x_1 + \frac{q_2}{q_1} x_2 + \frac{q_3}{q_1} x_3 \right)^2} + \dots \right] \end{aligned} \quad (\text{A-24})$$

By introducing the following new constants, the latter equation can be simplified. Let

$$\begin{aligned} A_{12} &= q_1 2a_{12} & A_{21} &= q_2 2a_{12} \\ A_{13} &= q_1 2a_{13} & A_{31} &= q_3 2a_{13} \\ A_{23} &= q_2 2a_{23} & A_{32} &= q_3 2a_{23} \end{aligned}$$

The new constants are first substituted into Eq. (A-24), then combining with Eq. (A-23) and simplifying:

$$\log \gamma_1 = \frac{\left[x_2^2 A_{12} \left(\frac{A_{21}}{A_{12}} \right)^2 + x_3^2 A_{13} \left(\frac{A_{31}}{A_{13}} \right)^2 + x_2 x_3 \left(A_{12} + A_{13} - A_{32} \frac{A_{13} A_{21} A_{31}}{A_{31} A_{12} A_{13}} \right) \right]}{\left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2} \quad (\text{A-25})$$

$$\log \gamma_2 = \frac{\left(\frac{A_{21}}{A_{12}}\right)^2 \left[x_3^2 A_{23} \left(\frac{A_{32}}{A_{23}}\right)^2 + x_1^2 A_{21} \left(\frac{A_{12}}{A_{21}}\right)^2 + x_1 x_3 (A_{23} + A_{21} - A_{13}) \frac{A_{21}}{A_{12}} \frac{A_{32} A_{12}}{23 \ 21} \right]}{\left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2} \quad (\text{A-26})$$

$$\log \gamma_3 = \frac{\left(\frac{A_{31}}{A_{13}}\right)^2 \left[x_1^2 A_{31} \left(\frac{A_{13}}{A_{31}}\right)^2 + x_2^2 A_{32} \left(\frac{A_{23}}{A_{32}}\right)^2 + x_1 x_2 (A_{31} + A_{32} - A_{21}) \frac{A_{32}}{A_{23}} \frac{A_{13} A_{23}}{A_{31} A_{32}} \right]}{\left(x_1 + x_2 \frac{A_{21}}{A_{12}} + x_3 \frac{A_{31}}{A_{13}} \right)^2} \quad (\text{A-27})$$

This is the van Laar equation for ternary system. Equations (A-25), (A-26), and (A-27) are easily reduced to the binary van Laar equation by setting one of the x 's equal to zero. For a binary system of components 1 and 2, for instance, let $x_3 = 0$. Equations (A-25), and (A-26) become

$$\log \gamma_1 = \frac{A_{12}}{\left(1 + \frac{A_{12} x_1}{A_{21} x_2} \right)^2} \quad (\text{A-28})$$

$$\log \gamma_2 = \frac{A_{21}}{\left(1 + \frac{A_{21} x_2}{A_{12} x_1} \right)^2} \quad (\text{A-29})$$

This is the same van Laar equation expressed in Eq. (A-7) and (A-8), which was evaluated by assuming the validity of the van der Waals fluid relationship. The constants A_{12} , A_{21} used above are usually referred to as A and B. Therefore they also can be expressed in terms of van der Waal

constants.

Van Laar Equation from Solubility Parameter and Molar Volume

Scatchard and Hildebrand obtained a similar expression for the liquid activity coefficient without assuming the van der Waals fluid or free energy expression. The development is described on page 159 of Edmister "Applied Hydrocarbon Thermodynamics" Petroleum Refiner, December 1960 and is also given in Hildebrand and Scott, "Solubility of Non-Electrolytes", Reinhold (1950). The following equations are obtained for the liquid activity coefficients:

$$\log \gamma_1 = \frac{V_1}{2.303 RT} (\delta_1 - \delta_2)^2 X_{V_2}^2 \quad (\text{A-30})$$

$$\log \gamma_2 = \frac{V_2}{2.303 RT} (\delta_1 - \delta_2)^2 X_{V_1}^2 \quad (\text{A-31})$$

where V_1 and V_2 = the molar volumes of components 1 and 2
 X_{V_1} , X_{V_2} = the liquid volume fraction of component 1, 2 . Which is defined by

$$X_{V_i} = \frac{x_i V_i}{x_1 V_1 + x_2 V_2}$$

δ_1 , δ_2 = solubility parameter of component 1, 2.

Equations (A-30) and (A-31) are frequently referred to as the Scatchard-Hildebrand relationships. Edmister has rearranged this equation and put them into the familiar van Laar form by defining the two constants A and B as follows:

$$A = \frac{V_1}{2.303RT} (\delta_1 - \delta_2)^2 \quad (\text{A-32})$$

$$B = \frac{V_2}{2.303RT} (\delta_1 - \delta_2)^2 \quad (\text{A-33})$$

Combining Eq.(A-30) with (A-32), and Eq. (A-31) with (A-33); replacing X_{V_i} by its equivalent $(x_i V_i)/(x_1 V_1 + x_2 V_2)$; and rearranging gives

$$\log \gamma_1 = \frac{A}{\left(1 + \frac{A}{B} \frac{x_1}{x_2}\right)^2} \quad (\text{A-34})$$

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B}{A} \frac{x_2}{x_1}\right)^2} \quad (\text{A-35})$$

Equations (A-34) and (A-35) are similar to Eq.(A-7) and (A-8) in form, but different in meaning. The constants A and B, given by Eq.(A-34) and (A-35), are functions of the component physical properties and temperature. Also, the subscripts 1 and 2 can denote the solute and solvent, where the solvent may be a multicomponent mixture. Then γ_2 and x_2 denote the activity coefficient and liquid mol fraction of the solvent (22), respectively. The values of V_2 and δ_2 are the average V and δ values for the components of the mixture(not including the solute). The value, V_2 , is a molar average and δ_2 is a liquid volume average.

Equations (A-34) and (A-35) have an obvious advantage when used for ternary or multicomponent systems, since the A and B constants can be estimated directly from physical properties, and are not dependent on the binary systems included.

APPENDIX B
EXPERIMENTAL DATA AND FIGURES

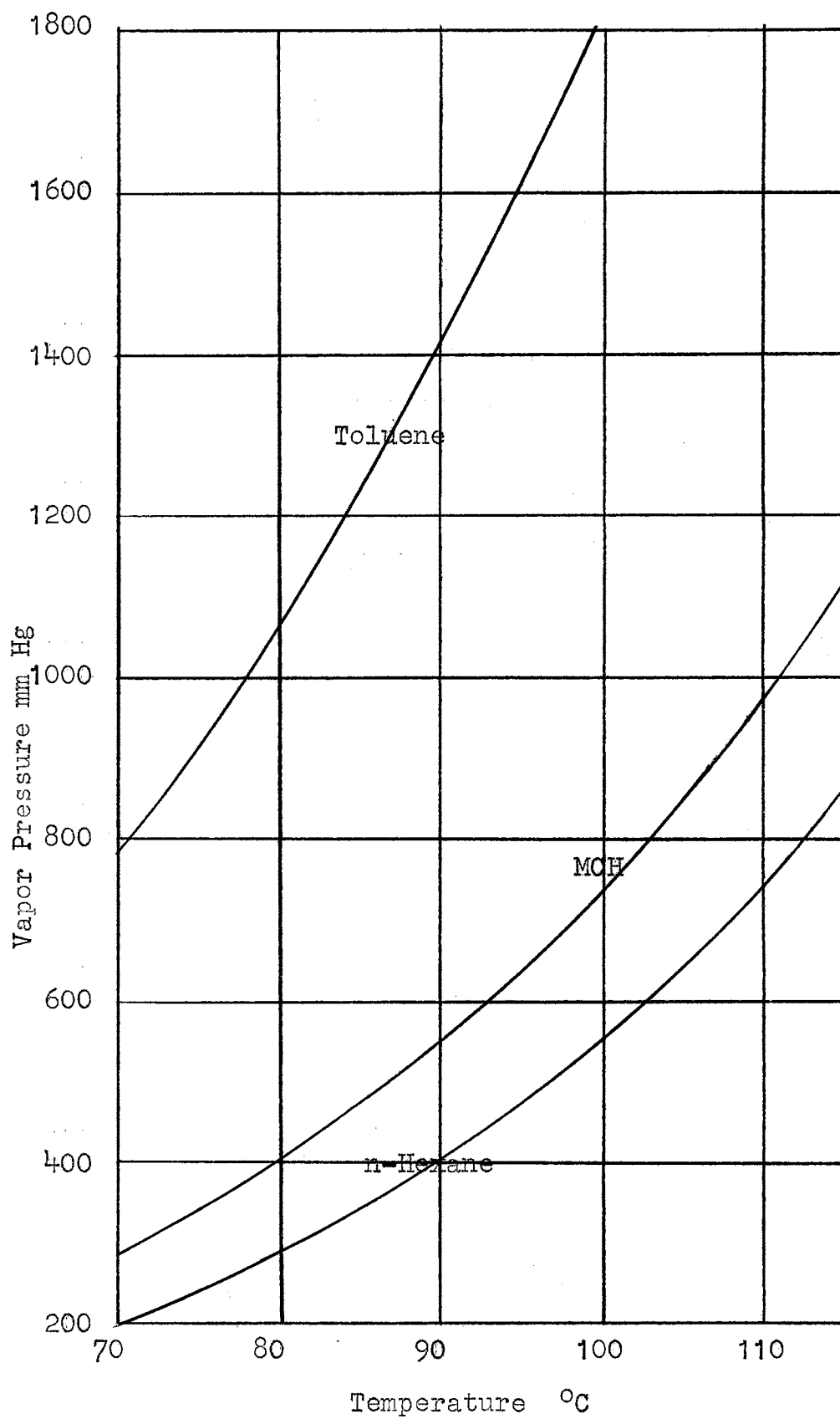


Fig. 9 Typical Vapor-Pressure Temperature Curves

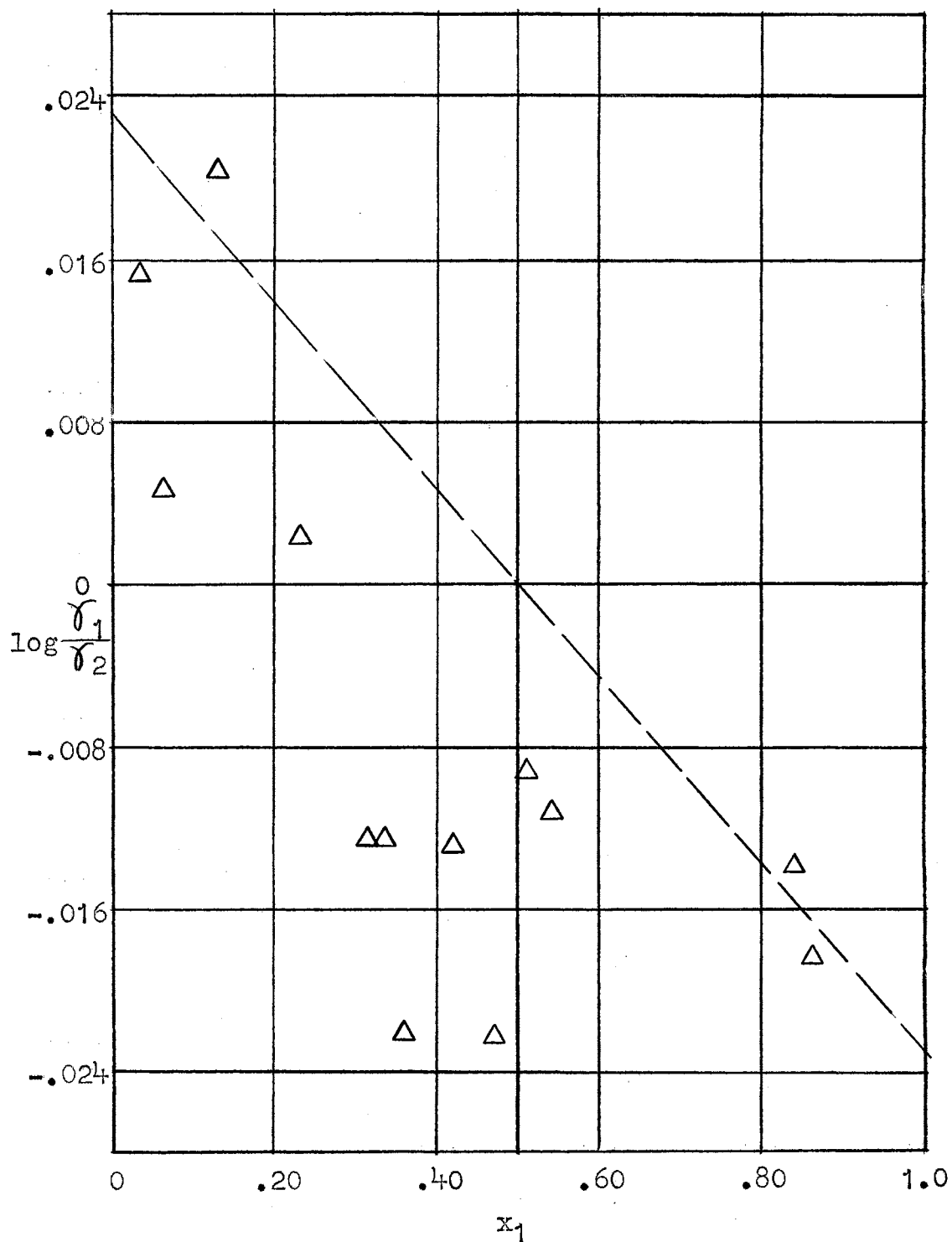


Fig. 10 Dependence of $\log \frac{\gamma_1^0}{\gamma_2}$ on the liquid Composition (x_1).

System: n-Hexane-Methylcyclohexane(Myers)

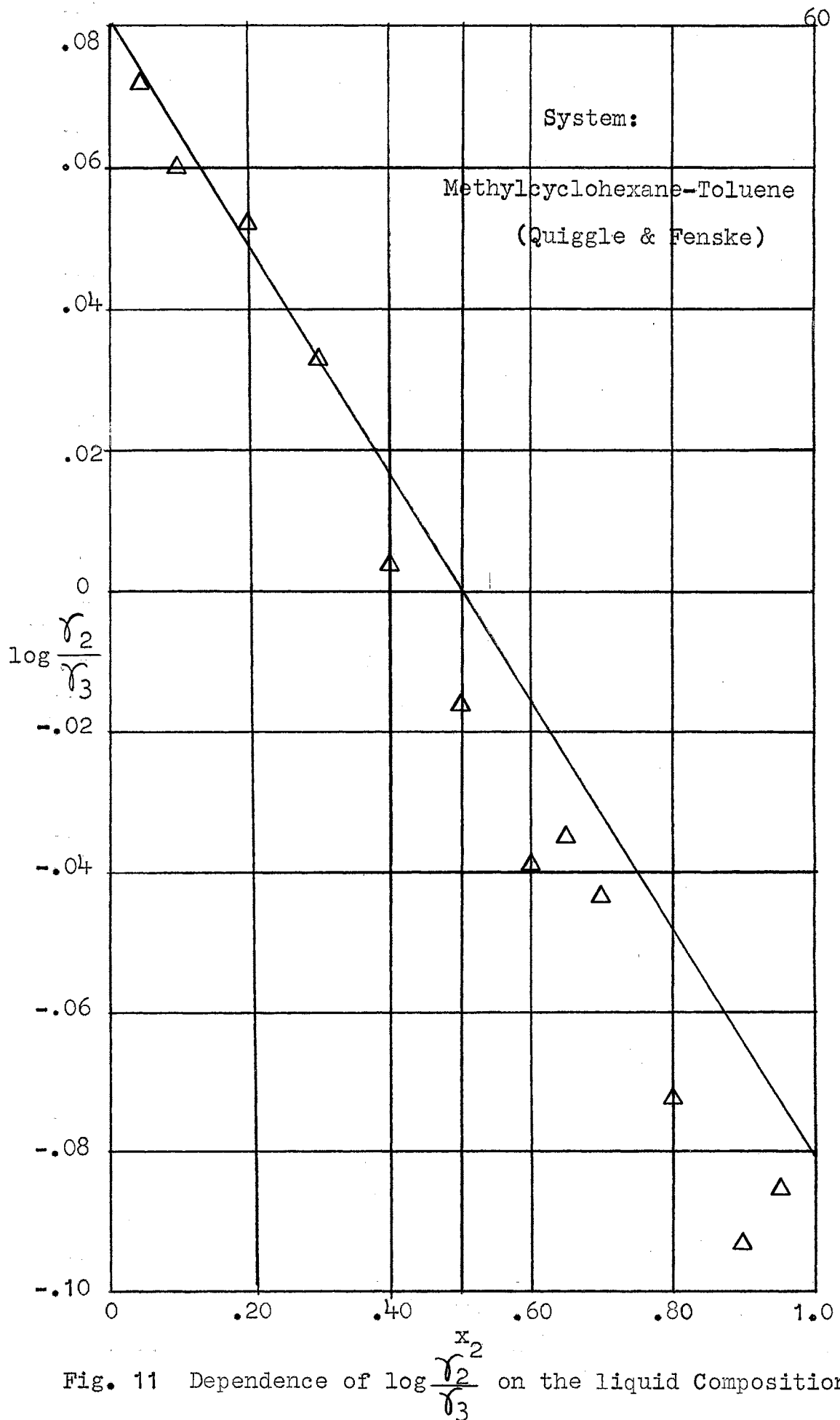


Fig. 11 Dependence of $\log \frac{\gamma_2}{\gamma_3}$ on the liquid Composition

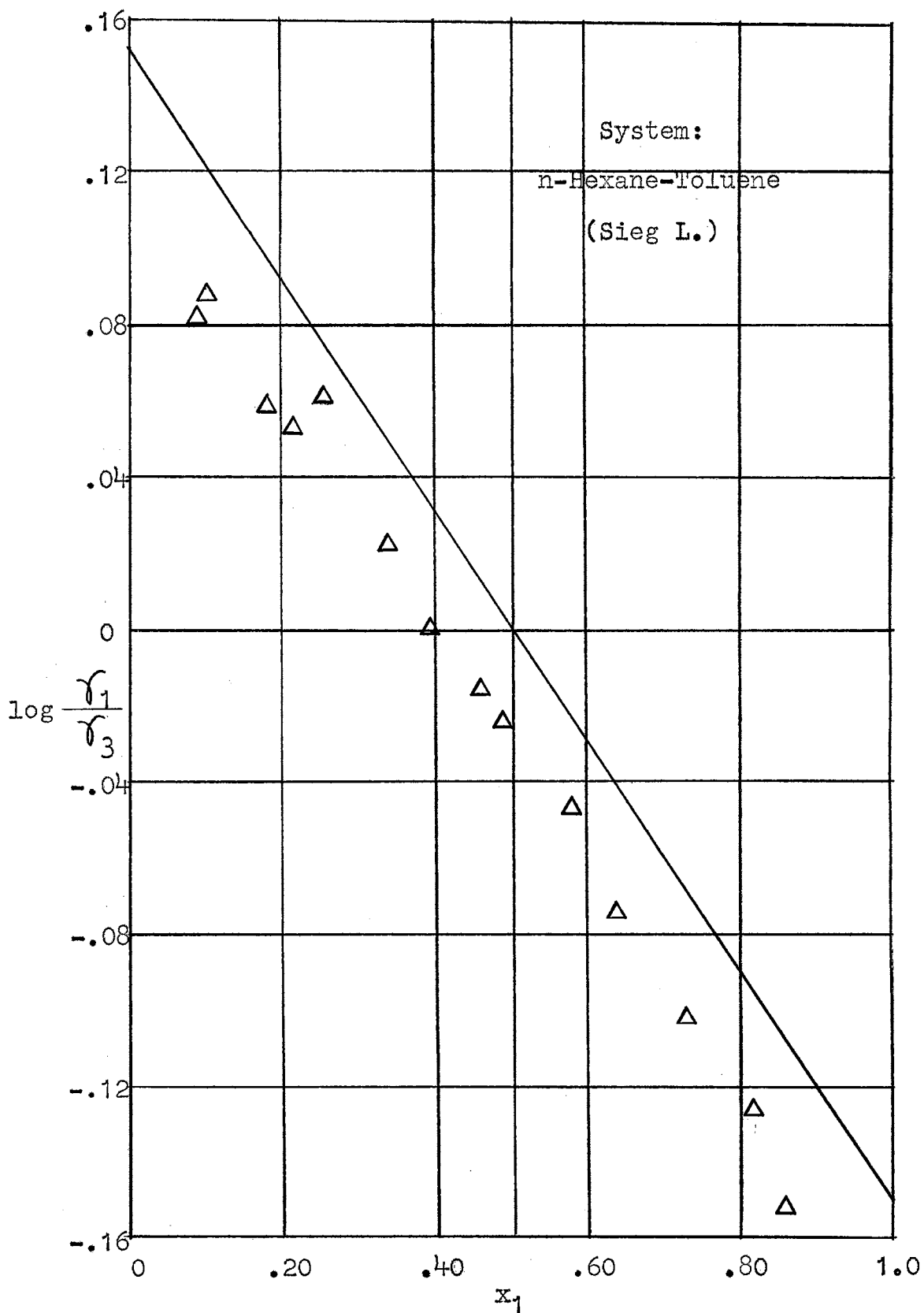


Fig. 12 Dependence of $\log \frac{\gamma_1}{\gamma_3}$ on the liquid Composition (x_1)

TABLE VII

VAPOR-LIQUID EQUILIBRIUM DATA FOR n-HEXANE-MCH-TOLUENE SYSTEM

GROUP 1 - VOLUME RATIO n-HEXANE : MCH = 90 : 10

PRESSURE = 744.2(\pm 2.3) mm Hg

Temp. °C	Composition, Mole%						Activity Coefficients		
	Liquid			Vapor			H	MCH	T
	H	MCH	T	H	MCH	T			
99.25	8.32	0.49	91.19	31.65	1.07	67.28	1.564	2.244	1.009
96.60	13.11	0.91	85.98	39.07	1.21	59.72	1.313	1.473	1.031
93.95	18.43	1.37	80.20	46.48	1.36	52.16	1.191	1.189	1.049
89.20	29.43	2.03	68.54	59.59	1.98	38.43	1.088	1.346	1.053
86.50	36.53	2.52	60.95	65.81	2.23	31.96	1.043	1.326	1.077
84.90	40.25	2.92	56.83	68.70	2.26	29.04	1.033	1.220	1.107
83.10	45.86	3.27	50.87	71.94	2.36	25.70	1.000	1.202	1.162
81.30	52.08	3.35	44.57	75.53	2.39	22.08	.973	1.258	1.211
79.95	56.45	3.40	40.15	78.06	2.42	19.52	.965	1.311	1.246
78.60	61.55	3.59	34.86	80.90	2.45	16.65	.954	1.312	1.281
77.00	66.87	4.08	29.05	83.53	2.47	14.00	.951	1.227	1.367
76.40	68.81	4.27	26.92	84.88	2.61	12.51	.956	1.266	1.346
75.20	73.52	4.55	21.93	87.00	2.62	10.38	.951	1.241	1.431
73.60	79.55	4.80	15.65	89.82	2.66	7.52	.952	1.258	1.542
71.80	85.99	5.30	8.71	93.45	2.70	3.85	.967	1.23	1.523

TABLE VIII

VAPOR-LIQUID EQUILIBRIUM DATA FOR n-HEXANE-MCH-TOLUENE SYSTEM

GROUP 2 - VOLUME RATIO n-HEXANE : MCH = 80:20

PRESSURE = 742.7(\pm 0.5) mm Hg

Temp. °C	Composition, Mole%						Activity Coefficients		
	Liquid			Vapor			H	MCH	T
	H	MCH	T	H	MCH	T			
106.00	1.80	.65	97.55	7.16	.98	91.86	1.376	1.280	1.051
100.95	5.89	1.63	92.48	24.65	2.28	73.07	1.644	1.366	1.025
93.80	19.26	3.48	77.25	48.53	3.57	47.90	1.218	1.260	1.028
88.80	29.65	4.72	65.63	61.00	4.07	34.93	1.117	1.203	1.011
85.75	39.18	5.51	55.31	68.19	4.31	27.50	1.026	1.199	1.045
83.60	45.73	6.35	47.92	72.82	4.38	22.80	.998	1.129	1.074
82.90	48.16	6.63	45.21	74.26	4.54	21.20	.986	1.145	1.083
81.60	52.28	7.05	40.67	76.21	4.65	19.14	.968	1.150	1.136
80.85	54.69	7.26	38.05	77.06	4.68	18.26	.956	1.151	1.189
79.50	59.31	7.67	33.02	79.17	4.71	16.12	.941	1.145	1.267
78.80	61.80	7.84	30.36	80.33	4.73	14.94	.936	1.151	1.309
77.20	66.78	8.38	24.84	83.10	4.76	12.14	.940	1.142	1.374
75.60	73.08	8.85	18.07	86.14	4.94	8.92	.934	1.184	1.468
73.60	79.97	9.75	10.28	89.59	5.06	5.35	.943	1.173	1.667
72.15	85.46	10.45	4.09	92.51	5.10	2.39	.951	1.162	1.981

TABLE IX

VAPOR-LIQUID EQUILIBRIUM DATA FOR n-HEXANE-MCH-TOLUENE SYSTEM

GROUP 3 - VOLUME RATIO n-HEXANE : MCH = 60 : 40

PRESSURE = 742.6(\pm 0.2) mm Hg

Temp. °C	Composition, Mole%						Acticity Coefficients		
	Liquid			Vapor			H	MCH	T
	H	MCH	T	H	MCH	T			
106.40	1.54	1.48	96.98	5.31	2.18	92.51	1.181	1.236	1.052
102.95	4.26	3.55	92.32	15.86	5.04	79.10	1.400	1.311	1.047
99.80	6.90	5.03	88.07	25.61	6.25	68.14	1.502	1.253	1.038
96.30	11.54	6.92	81.54	36.79	7.76	55.46	1.413	1.251	1.016
92.50	19.91	9.78	70.31	47.04	8.79	44.17	1.157	1.121	1.058
89.45	27.40	12.10	60.50	55.31	9.74	34.94	1.074	1.100	1.073
87.60	32.70	13.54	53.76	59.80	10.57	29.63	1.024	1.129	1.089
86.40	36.42	15.06	48.52	62.84	10.85	26.31	1.002	1.080	1.115
85.60	38.30	16.10	45.60	64.81	11.20	23.99	1.002	1.070	1.110
85.10	39.56	16.99	43.45	65.96	11.29	22.76	1.001	1.038	1.125
83.25	45.83	18.59	35.58	69.72	11.58	18.70	.963	1.030	1.199
82.20	49.03	20.20	30.78	71.86	12.31	15.83	.956	1.042	1.217
80.20	55.82	22.52	21.66	76.20	12.53	11.27	.943	1.015	1.318
77.80	64.68	24.30	11.02	81.18	13.12	5.71	.931	1.064	1.426
76.75	68.67	25.83	5.50	82.98	13.95	3.07	.924	1.103	1.594

TABLE X

VAPOR-LIQUID EQUILIBRIUM DATA FOR n-HEXANE-MCH-TOLUENE SYSTEM

GROUP 4 - VOLUME RATIO n-HEXANE : MCH = 40 : 60

PRESSURE = $741.5(\pm 0.3)$ mm Hg

Temp. °C	Composition, Mole%						Activity Coefficients		
	Liquid			Vapor			H	MCH	T
	H	MCH	T	H	MCH	T			
106.00	1.34	2.44	96.22	4.97	3.49	91.54	1.281	1.212	1.060
103.80	3.06	5.17	91.77	11.05	7.38	81.57	1.318	1.286	1.057
101.65	4.82	7.90	87.28	17.30	10.67	72.03	1.382	1.295	1.047
99.60	6.77	10.88	82.35	23.48	13.34	63.18	1.408	1.243	1.034
97.05	9.86	14.85	75.29	30.53	16.97	52.50	1.343	1.245	1.017
95.80	12.29	18.00	69.71	34.24	18.63	47.13	1.249	1.169	1.024
93.95	15.85	22.71	61.44	39.06	21.06	39.88	1.160	1.107	1.043
92.60	18.26	26.46	55.28	42.46	23.23	34.31	1.134	1.090	1.040
91.30	21.23	30.89	47.88	45.83	24.91	29.26	1.090	1.038	1.069
90.60	22.92	32.70	44.38	47.38	26.11	26.51	1.064	1.052	1.068
89.10	26.91	38.69	34.40	51.28	27.74	20.98	1.023	.989	1.144
88.40	29.09	40.49	30.42	53.00	28.48	18.53	1.000	.992	1.171
85.60	37.50	45.08	17.42	59.85	29.60	10.56	.944	1.008	1.278
84.40	40.42	47.76	11.82	62.11	30.54	7.34	.940	1.019	1.362
82.10	43.98	50.68	5.34	65.14	31.65	3.20	.967	1.065	1.420

TABLE XI

VAPOR-LIQUID EQUILIBRIUM DATA FOR n-HEXANE-MCH-TOLUENE SYSTEM

GROUP 5 - VOLUME RATIO n-HEXANE : MCH = 20 : 80

PRESSURE = 740.5(\pm 4.3) mm Hg

Temp. °C	Composition, Mole%						Activity Coefficients		
	Liquid			Vapor			H	MCH	T
	H	MCH	T	H	MCH	T			
107.70	0.45	2.54	97.01	1.59	4.65	93.76	1.168	1.480	1.024
105.05	2.12	8.66	89.22	5.73	11.36	82.91	.955	1.140	1.063
103.40	3.36	12.56	84.08	8.80	16.13	75.07	.964	1.168	1.073
100.60	5.42	20.44	74.14	14.68	24.70	60.62	1.071	1.188	1.069
99.10	6.30	26.41	67.29	18.47	29.69	51.84	1.203	1.154	1.054
98.10	7.69	31.48	60.83	20.40	33.40	46.20	1.118	1.120	1.071
97.30	8.03	35.83	56.14	22.13	36.30	41.57	1.186	1.095	1.070
96.60	8.62	39.45	51.93	23.62	38.39	37.99	1.201	1.073	1.080
94.85	10.94	47.40	41.66	27.99	42.45	29.56	1.174	1.039	1.106
93.60	13.57	52.42	34.01	31.93	44.35	23.72	1.116	1.019	1.132
92.40	16.16	57.88	25.96	35.58	46.28	18.14	1.078	.997	1.177
91.30	18.25	63.77	17.98	39.09	47.83	13.08	1.080	.964	1.271
90.40	20.19	67.74	12.07	42.21	48.85	8.94	1.080	.955	1.331
89.20	23.35	71.77	4.88	46.30	49.96	3.74	1.060	.956	1.432

TABLE XII

VAPOR-LIQUID EQUILIBRIUM DATA FOR n-HEXANE-MCH-TOLUENE SYSTEM

GROUP 6 - VOLUME RATIO n-Hexane : MCH = 10 : 90

PRESSURE = 739.7(\pm 0.6) mm Hg

Temp. °C	Composition, Mole%						Activity Coefficients		
	Liquid			Vapor			H	MCH	T
	H	MCH	T	H	MCH	T			
107.90	0.14	3.93	95.93	0.40	5.56	94.04	.940	1.136	1.032
106.40	0.44	8.38	91.18	1.41	12.19	86.40	1.093	1.216	1.041
105.00	0.90	13.07	86.03	2.55	18.55	78.90	1.001	1.234	1.050
103.20	1.45	20.06	78.49	4.50	26.64	68.86	1.160	1.213	1.059
102.00	1.93	26.70	71.37	5.63	33.07	61.30	1.111	1.170	1.076
101.10	2.35	32.30	65.35	6.77	37.39	55.84	1.123	1.121	1.099
100.45	2.81	37.05	60.14	7.60	41.64	50.76	1.072	1.108	1.107
100.05	2.98	40.29	56.72	7.95	44.64	47.41	1.069	1.105	1.110
99.20	4.10	45.51	50.39	9.80	49.22	40.98	.978	1.106	1.107
98.40	4.68	51.55	43.77	11.53	53.09	35.38	1.029	1.077	1.128
97.80	5.30	56.64	38.06	12.99	56.89	30.12	1.039	1.069	1.125
96.90	6.43	64.82	28.75	15.15	61.42	23.43	1.023	1.034	1.191
96.05	7.32	73.79	18.89	16.98	66.17	16.85	1.030	1.003	1.338
95.25	8.01	79.85	12.14	18.98	70.74	10.29	1.074	1.015	1.304

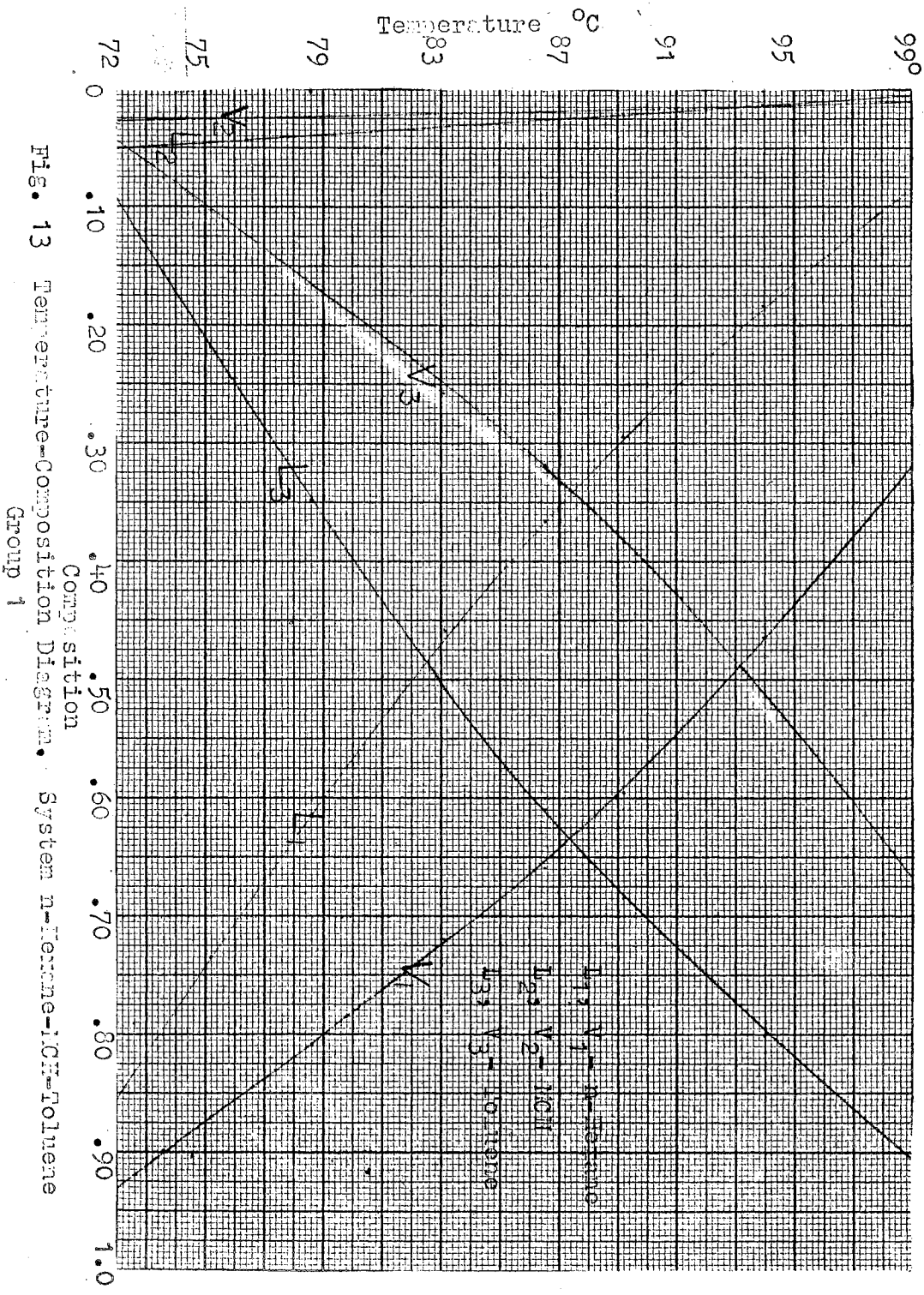


Fig. 13 Temperature-Composition Diagram, System n-Terpane-ICH-Toluene Group 1

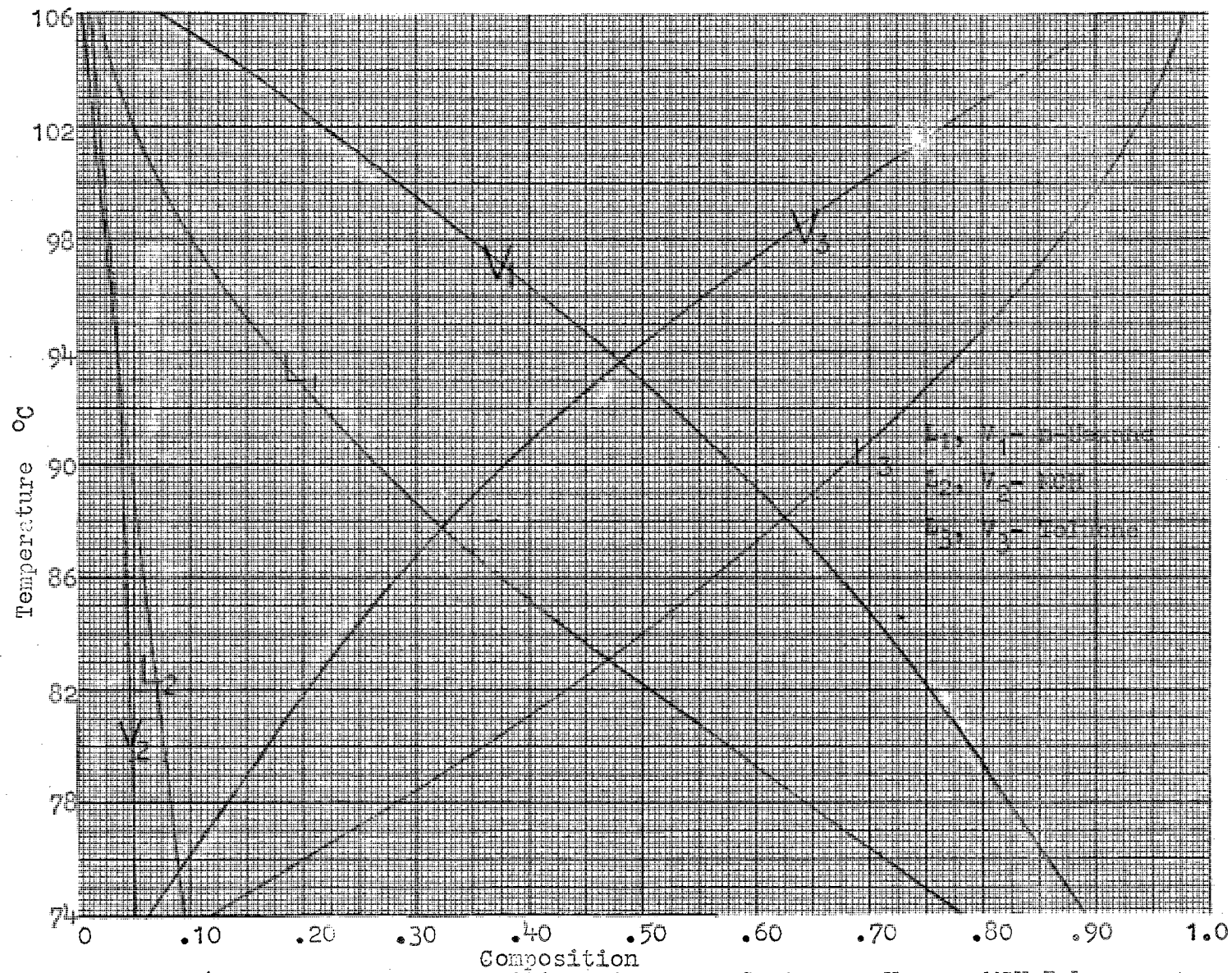


Fig. 14 Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene
Group 2

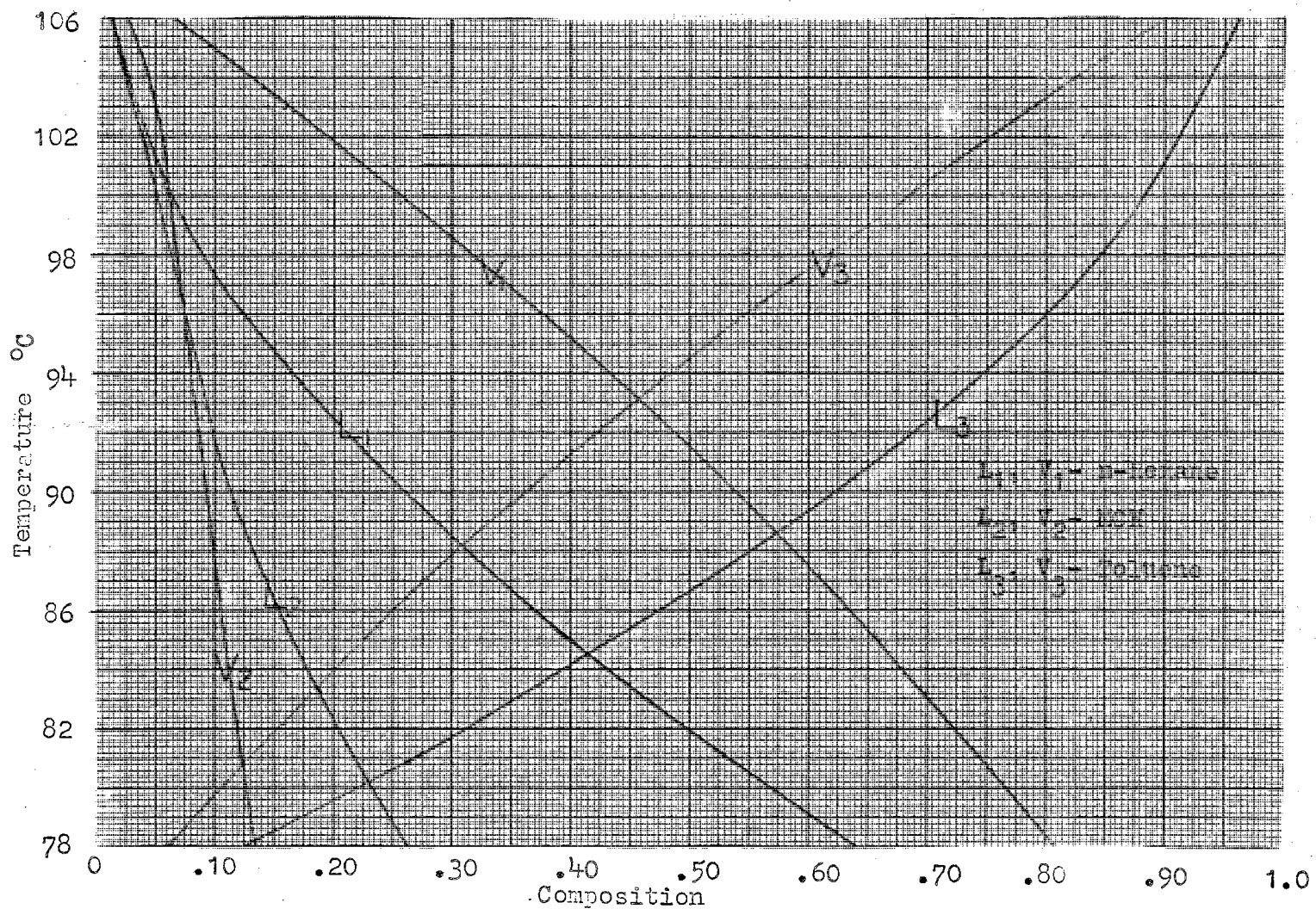


Fig. 15 Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene
Group 3

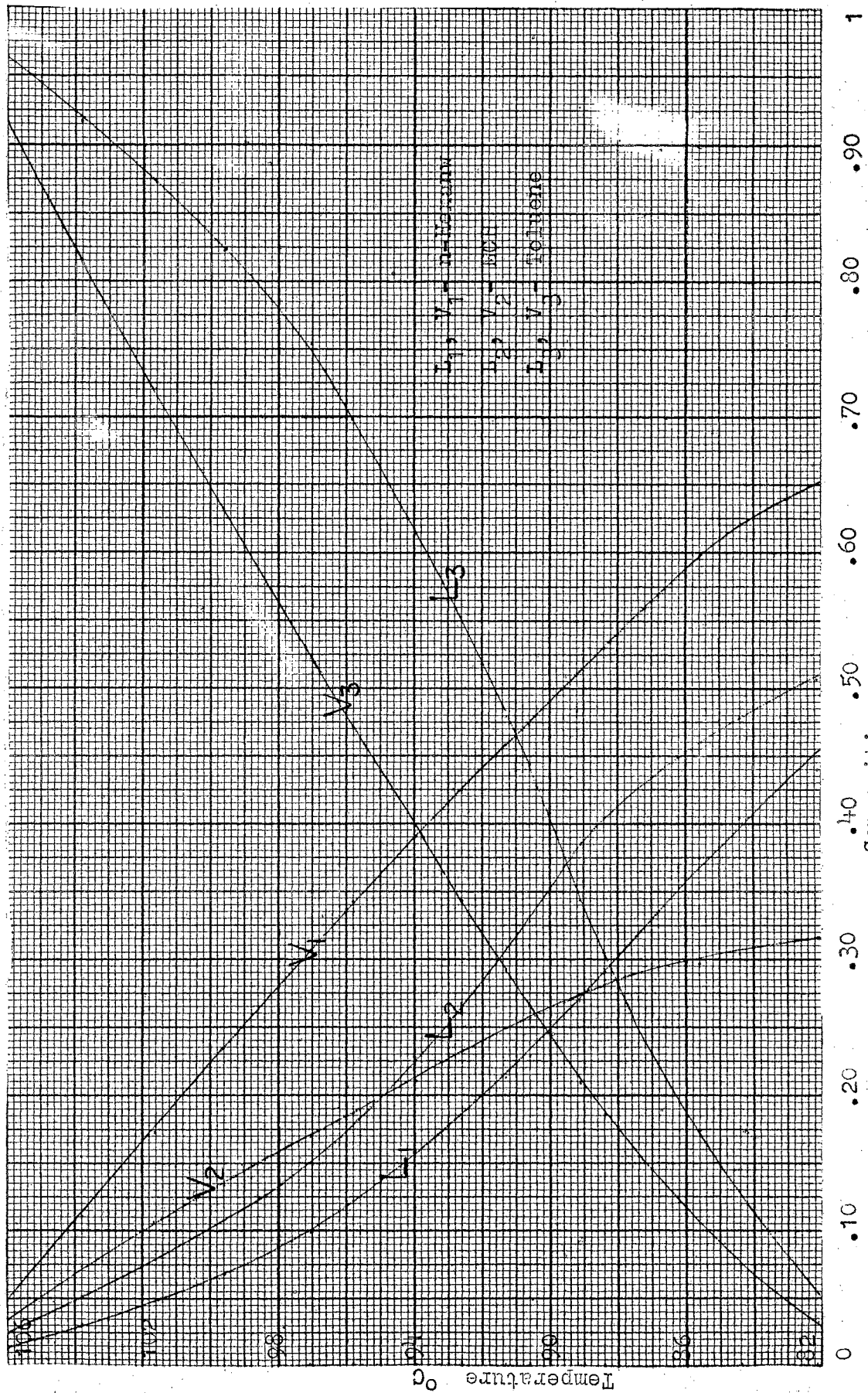


Fig. 16 Temperature-Composition Diagram. System: n-Hexane-tCH-Toluene
Group 4

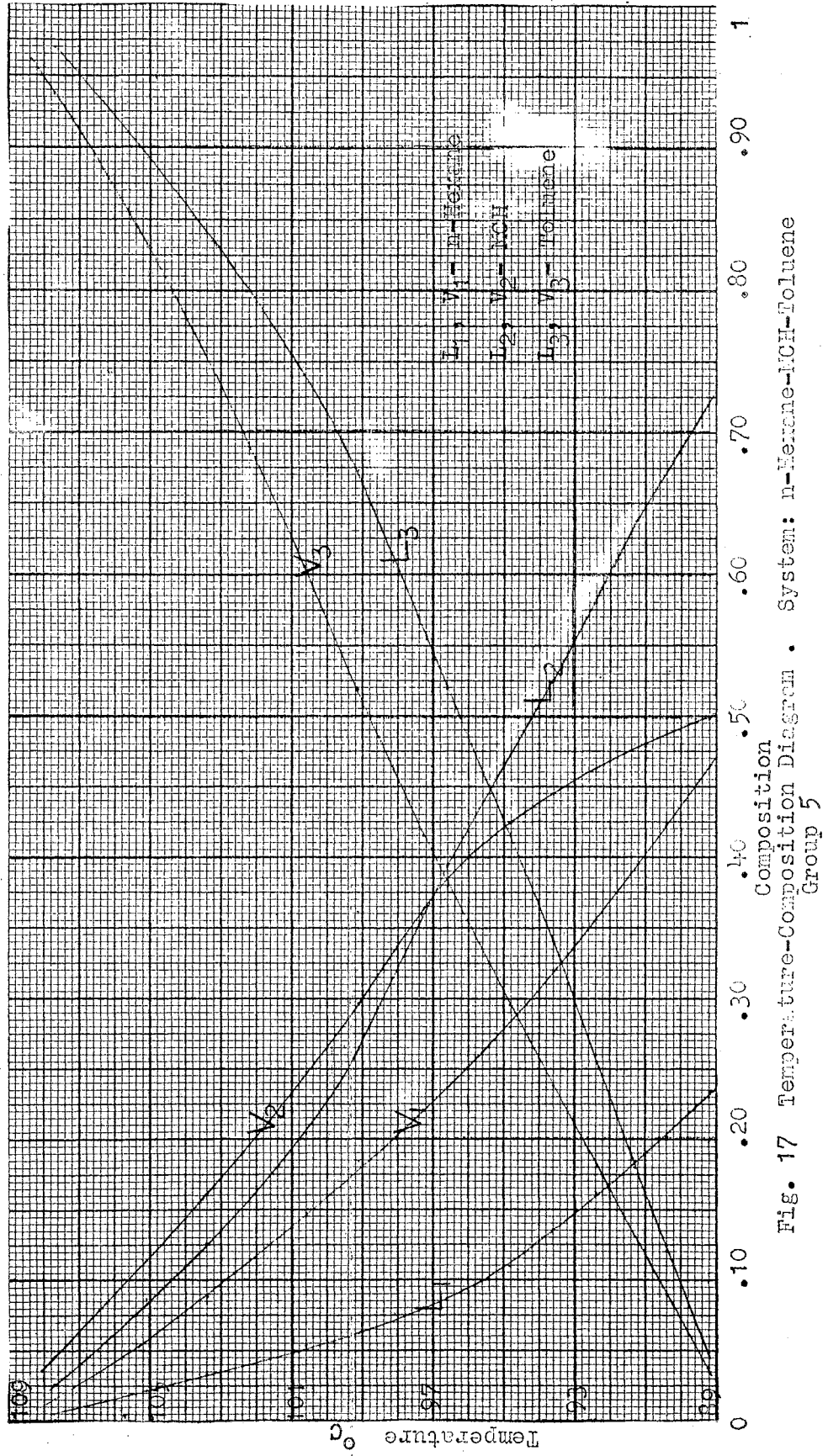


Fig. 17 Temperature-Composition Diagram . System: n-Heptane-MCH-Toluene Group 5

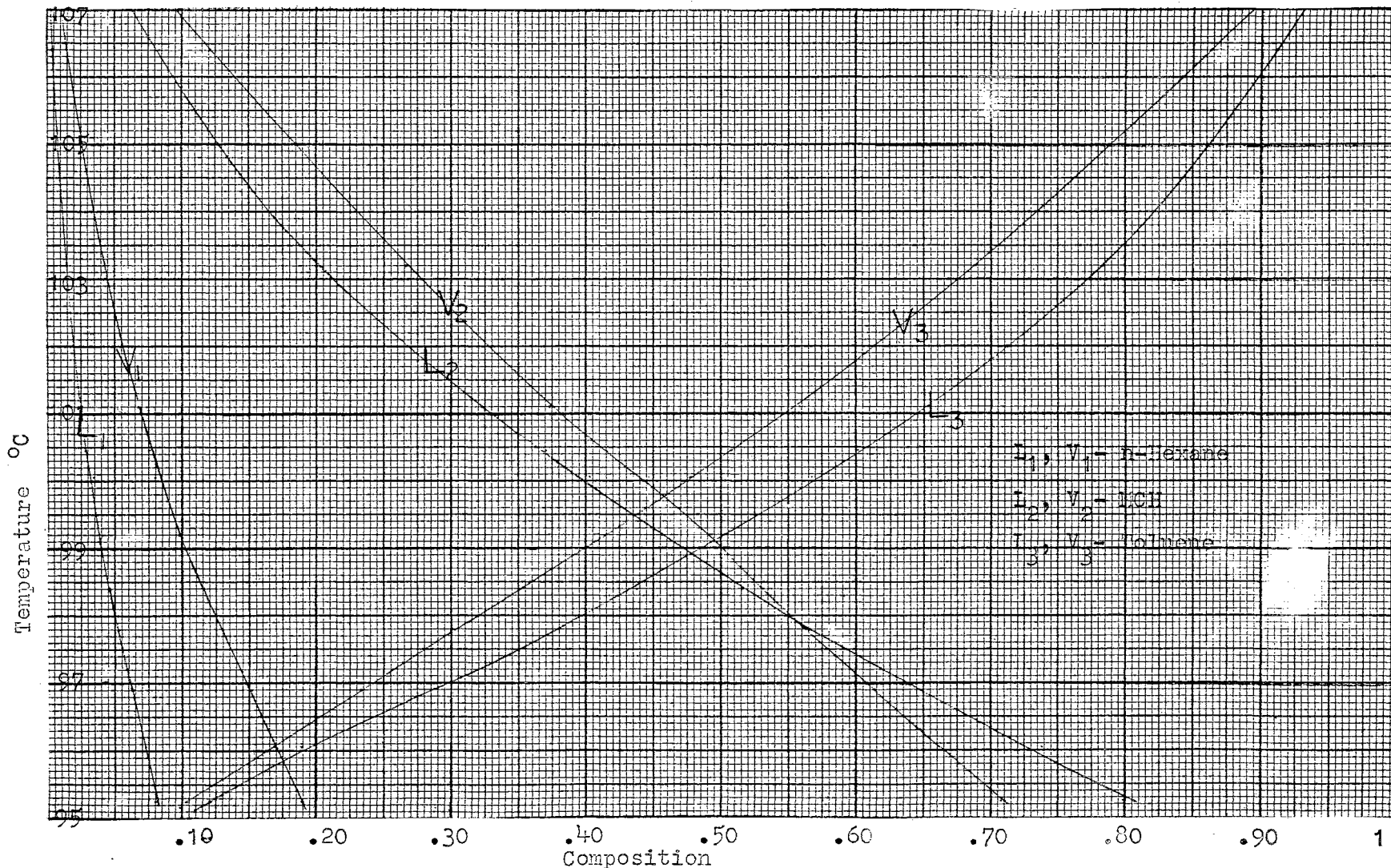


Fig. 18 Temperature-Composition Diagram. System: n-Hexane-MCH-Toluene
Group 6

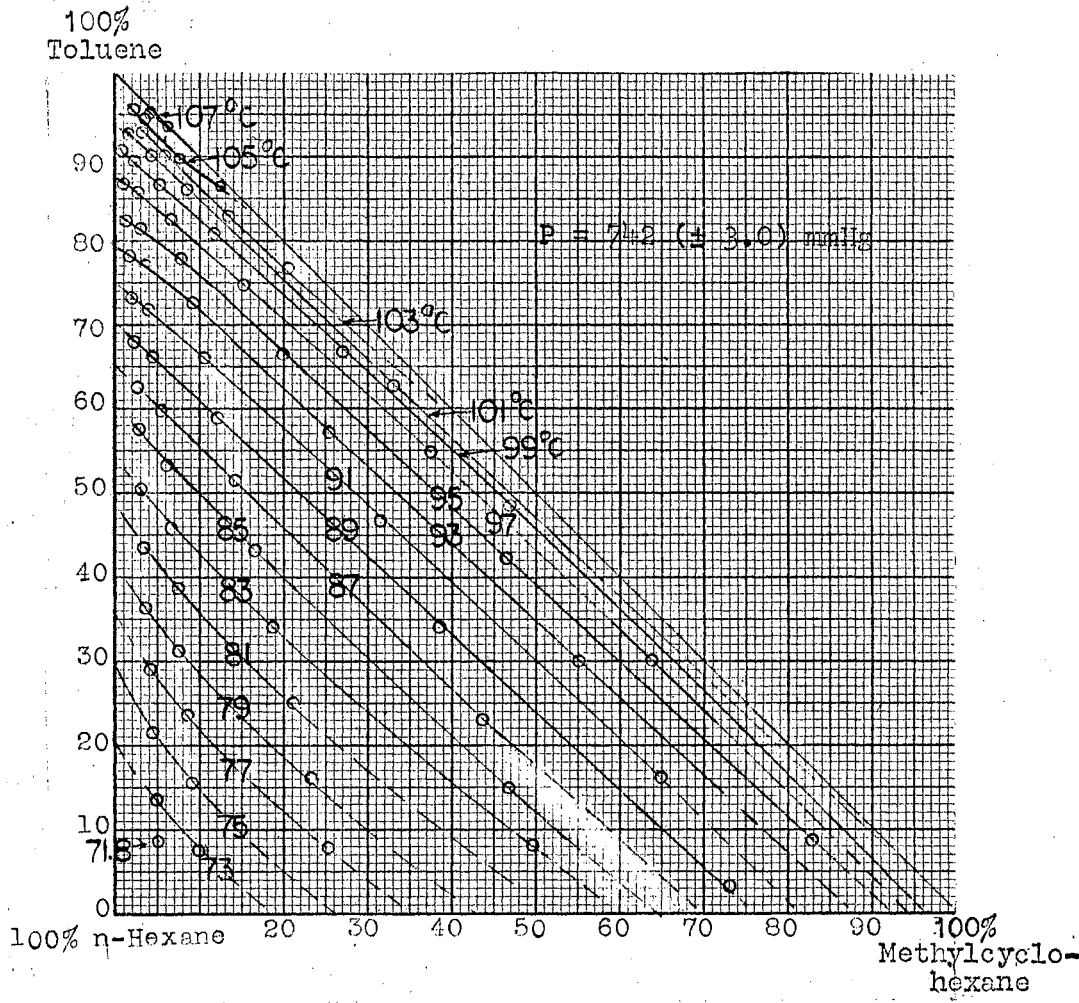


Fig.19 Temperature-Liquid Composition Diagram for Ternary System: n-Hexan-MCH-Toluene

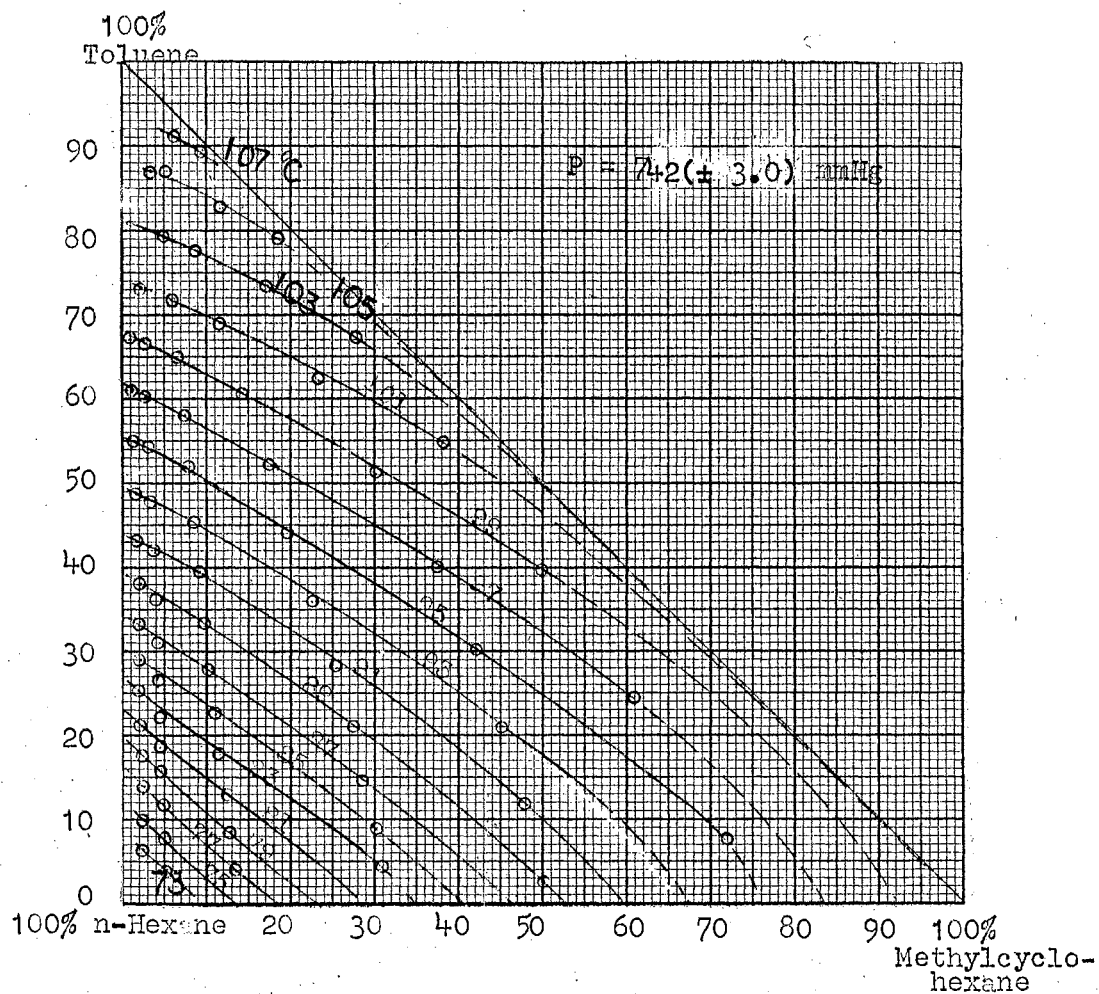


Fig. 20 Temperature-vapor Composition Diagram for Ternary System: n-Hexane-MCH-Toluene

TABLE XIII

LIQUID ACTIVITY COEFFICIENTS (GROUP 1)

Liquid Comp. Mole%		Liquid Activity Coefficients								
H	MCH	Experimental			van Laar (Wohl)			van Laar (Edmister)		
		H	MCH	T	H	MCH	T	H	MCH	T
8.32	0.49	1.564	2.244	1.009	1.437	1.142	1.004	1.325	1.069	1.002
13.11	0.91	1.313	1.473	1.031	1.374	1.113	1.009	1.298	1.064	1.004
18.43	1.37	1.191	1.189	1.049	1.311	1.085	1.019	1.269	1.058	1.009
29.43	2.03	1.088	1.346	1.053	1.208	1.042	1.047	1.212	1.047	1.026
36.53	2.52	1.043	1.326	1.077	1.156	1.023	1.072	1.178	1.040	1.043
40.25	2.92	1.033	1.220	1.107	1.131	1.015	1.087	1.160	1.037	1.055
45.86	3.27	1.000	1.202	1.162	1.100	1.007	1.112	1.134	1.032	1.076
52.08	3.35	.973	1.258	1.211	1.073	1.001	1.143	1.108	1.028	1.103
56.45	3.40	.965	1.311	1.245	1.057	1.000	1.166	1.091	1.026	1.127
61.55	3.59	.954	1.312	1.281	1.041	1.000	1.196	1.072	1.024	1.161
66.87	4.08	.951	1.227	1.367	1.026	1.003	1.232	1.054	1.023	1.207
68.81	4.27	.956	1.266	1.346	1.022	1.004	1.246	1.047	1.022	1.226
73.52	4.55	.951	1.241	1.431	1.013	1.009	1.280	1.033	1.022	1.278
79.55	4.80	.953	1.258	1.542	1.006	1.018	1.327	1.019	1.023	1.359
85.99	5.30	.967	1.230	1.523	1.001	1.030	1.383	1.007	1.027	1.475

TABLE XIV

LIQUID ACTIVITY COEFFICIENTS (GROUP 2)

Liquid Comp.		Liquid Activity Coefficients								
Mole%		Experimental			van Laar (Wohl)			van Laar (Edmister)		
H	MCH	H	MCH	T	H	MCH	T	H	MCH	T
1.80	0.65	1.376	1.280	1.051	1.525	1.186	1.000	1.359	1.076	1.000
5.89	1.63	1.644	1.366	1.025	1.457	1.153	1.002	1.334	1.070	1.001
19.26	3.48	1.218	1.260	1.028	1.285	1.075	1.023	1.258	1.055	1.013
29.65	4.72	1.117	1.203	1.011	1.187	1.038	1.052	1.200	1.048	1.030
39.18	5.51	1.026	1.199	1.045	1.121	1.014	1.089	1.156	1.035	1.061
45.73	6.35	.998	1.129	1.074	1.085	1.005	1.120	1.126	1.030	1.090
48.16	6.63	.986	1.145	1.083	1.073	1.003	1.133	1.115	1.028	1.103
52.28	7.05	.968	1.150	1.136	1.056	1.000	1.155	1.097	1.026	1.127
54.69	7.26	.956	1.151	1.189	1.048	1.000	1.169	1.087	1.024	1.143
59.31	7.67	.941	1.145	1.267	1.033	1.000	1.198	1.070	1.022	1.178
61.80	7.84	.936	1.151	1.310	1.027	1.001	1.214	1.061	1.021	1.200
66.78	8.38	.940	1.142	1.374	1.016	1.005	1.248	1.044	1.020	1.252
73.08	8.85	.934	1.184	1.468	1.007	1.012	1.296	1.026	1.021	1.333
79.97	9.75	.943	1.173	1.667	1.002	1.023	1.354	1.011	1.023	1.456
85.46	10.45	.951	1.162	1.982	1.000	1.035	1.405	1.003	1.028	1.587

TABLE XV

LIQUID ACTIVITY COEFFICIENTS (GROUP 3)

Liquid Comp. Mole%		Liquid Activity Coefficients								
H	MCH	Experimental			van Laar (Wohl)			van Laar (Edmister)		
		H	MCH	T	H	MCH	T	H	MCH	T
1.54	1.48	1.181	1.237	1.052	1.519	1.184	1.000	1.237	1.075	1.000
4.23	3.55	1.401	1.311	1.047	1.460	1.156	1.002	1.336	1.070	1.001
6.90	5.03	1.502	1.254	1.039	1.411	1.133	1.005	1.317	1.066	1.003
11.54	6.92	1.413	1.251	1.016	1.337	1.101	1.013	1.286	1.060	1.009
19.91	9.78	1.157	1.121	1.059	1.229	1.057	1.034	1.234	1.048	1.025
27.40	12.10	1.074	1.100	1.073	1.154	1.030	1.060	1.190	1.039	1.048
32.70	13.54	1.025	1.129	1.090	1.113	1.017	1.083	1.160	1.033	1.070
36.40	15.06	1.002	1.080	1.115	1.087	1.010	1.102	1.139	1.029	1.092
38.30	16.10	1.002	1.070	1.110	1.073	1.007	1.113	1.128	1.027	1.107
39.56	16.99	1.001	1.038	1.125	1.065	1.005	1.122	1.120	1.026	1.119
45.83	18.59	.963	1.030	1.200	1.038	1.000	1.158	1.090	1.021	1.170
49.03	20.20	.956	1.042	1.217	1.025	1.000	1.181	1.074	1.018	1.210
55.82	22.52	.944	1.015	1.318	1.010	1.003	1.231	1.045	1.015	1.309
64.68	24.30	.931	1.064	1.426	1.002	1.013	1.301	1.019	1.016	1.477
68.67	25.83	.925	1.103	1.594	1.000	1.020	1.338	1.009	1.018	1.600

TABLE XVI

LIQUID ACTIVITY COEFFICIENTS (GROUP 4)

Liquid Comp. Mole%		Liquid Activity Coefficients								
H	MCH	Experimental			van Laar (Wohl)			van Laar (Edmister)		
		H	MCH	T	H	MCH	T	H	MCH	T
1.34	2.44	1.281	1.212	1.060	1.513	1.181	1.000	1.355	1.075	1.000
3.06	5.17	1.318	1.286	1.057	1.461	1.157	1.002	1.337	1.070	1.002
4.82	7.90	1.382	1.295	1.047	1.412	1.134	1.005	1.318	1.066	1.004
6.77	10.88	1.408	1.243	1.035	1.360	1.113	1.010	1.298	1.061	1.008
9.86	14.85	1.343	1.245	1.017	1.292	1.085	1.019	1.268	1.054	1.017
12.29	18.00	1.249	1.170	1.025	1.243	1.067	1.028	1.245	1.048	1.028
15.85	22.71	1.160	1.107	1.043	1.180	1.044	1.045	1.211	1.040	1.049
18.26	26.46	1.134	1.090	1.041	1.140	1.031	1.059	1.186	1.034	1.070
21.23	30.89	1.090	1.038	1.069	1.100	1.018	1.080	1.158	1.028	1.104
22.92	32.70	1.064	1.053	1.069	1.083	1.014	1.090	1.144	1.025	1.124
26.91	38.69	1.023	.989	1.145	1.045	1.004	1.124	1.108	1.017	1.198
29.09	40.49	1.000	.992	1.171	1.033	1.002	1.140	1.094	1.015	1.236
37.50	45.08	.944	1.008	1.278	1.008	1.001	1.201	1.051	1.009	1.408
40.42	47.76	.940	1.020	1.362	1.003	1.003	1.229	1.035	1.008	1.516
43.98	50.68	.968	1.069	1.421	1.001	1.007	1.264	1.021	1.008	1.679

TABLE XVII

LIQUID ACTIVITY COEFFICIENTS (GROUP 5)

Liquid Comp.		Liquid Activity Coefficients								
Mole%		Experimental			van Laar (Wohl)			van Laar (Edmister)		
H	MCH	H	MCH	T	H	MCH	T	H	MCH	T
.45	2.54	1.169	1.481	1.024	1.523	1.187	1.000	1.360	1.076	1.000
2.12	8.66	1.955	1.140	1.064	1.441	1.148	1.003	1.330	1.068	1.003
3.36	12.56	.965	1.168	1.073	1.390	1.125	1.007	1.310	1.063	1.007
5.42	20.44	1.071	1.188	1.069	1.303	1.089	1.017	1.272	1.053	1.020
6.30	26.41	1.203	1.254	1.054	1.253	1.069	1.026	1.247	1.046	1.035
7.69	31.48	1.118	1.121	1.071	1.207	1.052	1.037	1.222	1.040	1.053
8.03	35.83	1.186	1.095	1.070	1.180	1.043	1.046	1.206	1.035	1.071
8.62	39.45	1.202	1.073	1.080	1.157	1.035	1.054	1.190	1.032	1.090
10.94	47.40	1.175	1.039	1.107	1.102	1.019	1.079	1.152	1.022	1.151
13.57	52.42	1.116	1.019	1.132	1.067	1.010	1.102	1.124	1.016	1.215
16.16	57.88	1.078	.997	1.177	1.038	1.004	1.128	1.096	1.011	1.306
18.25	63.77	1.080	.964	1.271	1.018	1.001	1.156	1.070	1.006	1.433
20.19	67.74	1.080	.955	1.331	1.008	1.000	1.179	1.053	1.004	1.558
23.35	71.77	1.060	.956	1.432	1.001	1.001	1.211	1.034	1.002	1.760

TABLE XVIII

LIQUID ACTIVITY COEFFICIENTS (GROUP 6)

Liquid Comp. Mole%	Liquid Activity Coefficients									
	Experimental			van Laar (Wohl)			van Laar (Edmister)			
	H	MCH	T	H	MCH	T	H	MCH	T	
.14	3.93	.940	1.136	1.032	1.515	1.182	1.000	1.357	1.075	1.000
.44	8.38	1.093	1.216	1.041	1.469	1.160	1.002	1.340	1.070	1.002
.90	13.07	1.001	1.234	1.050	1.421	1.138	1.004	1.321	1.065	1.005
1.45	20.06	1.160	1.213	1.059	1.358	1.110	1.010	1.294	1.057	1.014
1.93	26.70	1.111	1.170	1.076	1.305	1.087	1.018	1.269	1.050	1.026
2.35	32.30	1.123	1.121	1.099	1.265	1.070	1.026	1.247	1.045	1.041
2.81	37.05	1.072	1.108	1.107	1.231	1.057	1.033	1.228	1.039	1.057
2.98	40.29	1.069	1.105	1.110	1.212	1.050	1.039	1.216	1.036	1.070
4.10	45.51	.978	1.106	1.107	1.174	1.037	1.051	1.192	1.030	1.100
4.68	51.55	1.029	1.077	1.128	1.141	1.026	1.065	1.169	1.024	1.140
5.30	56.64	1.040	1.069	1.125	1.115	1.018	1.079	1.149	1.019	1.185
6.43	64.82	1.024	1.034	1.191	1.076	1.009	1.103	1.117	1.012	1.282
7.32	73.79	1.030	1.003	1.338	1.042	1.003	1.131	1.085	1.006	1.435
8.01	79.85	1.074	1.015	1.304	1.022	1.001	1.152	1.065	1.003	1.585

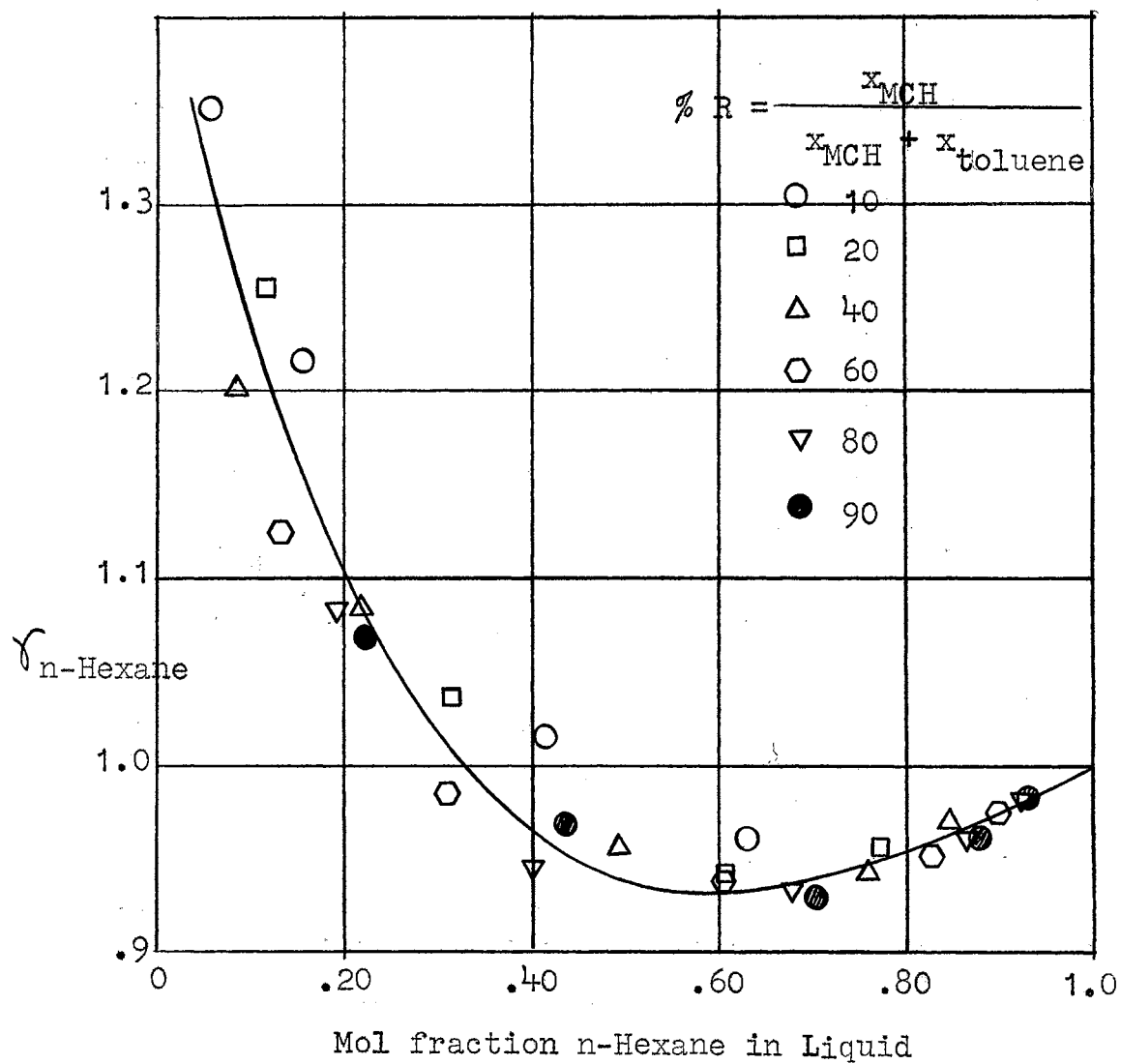


Fig. 21 Experimental n-Hexane Activity Coefficients
 System: n-Hexane-Methylcyclohexane-Toluene

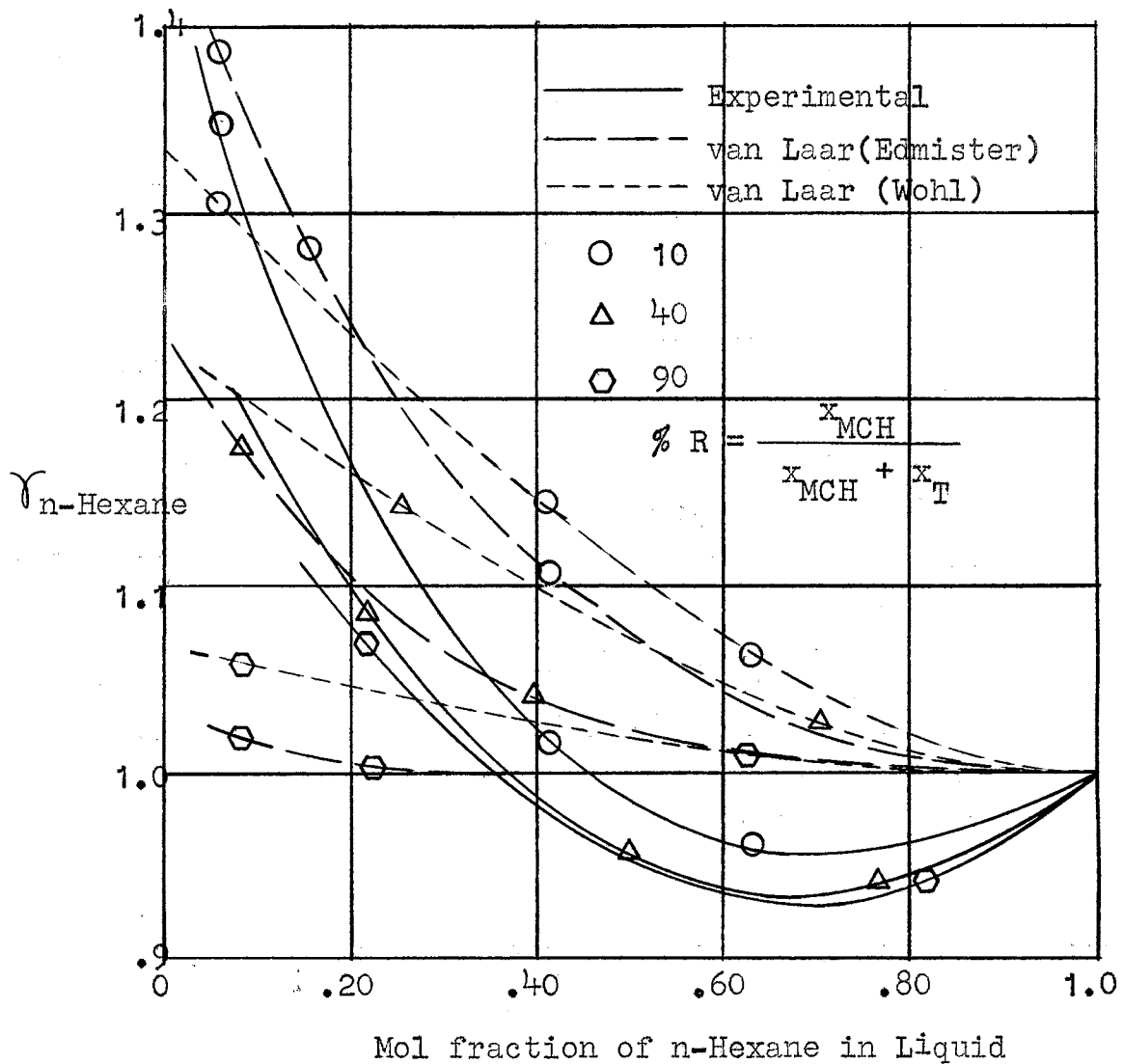


Fig. 22 Comparisons of n-Hexane Activity Coefficients
System: n-Hexane-Methylcyclohexane-Toluene

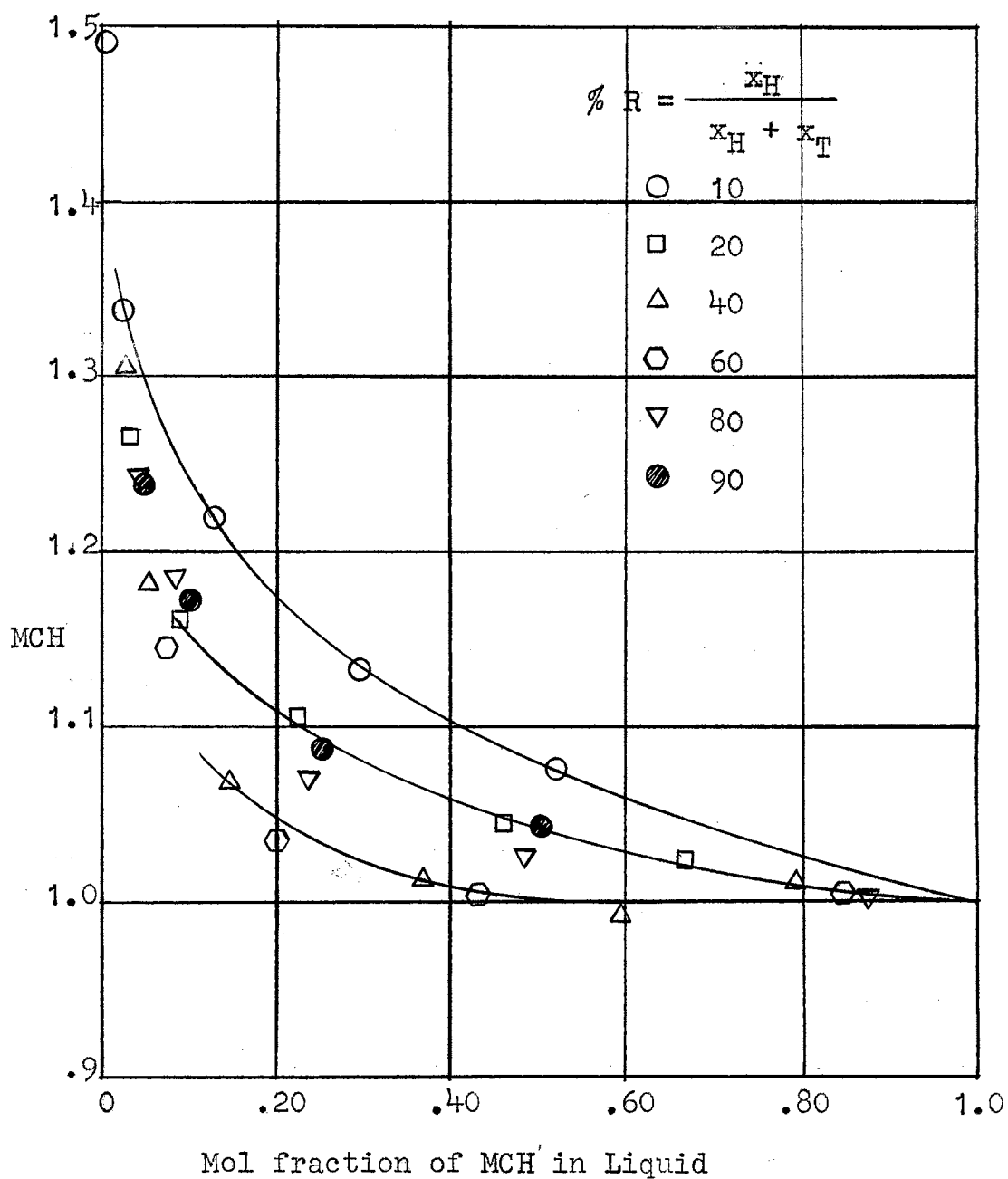


Fig. 23 Experimental Methylcyclohexane Activity Coefficients

System: n-Hexane-Methylcyclohexane-Toluene

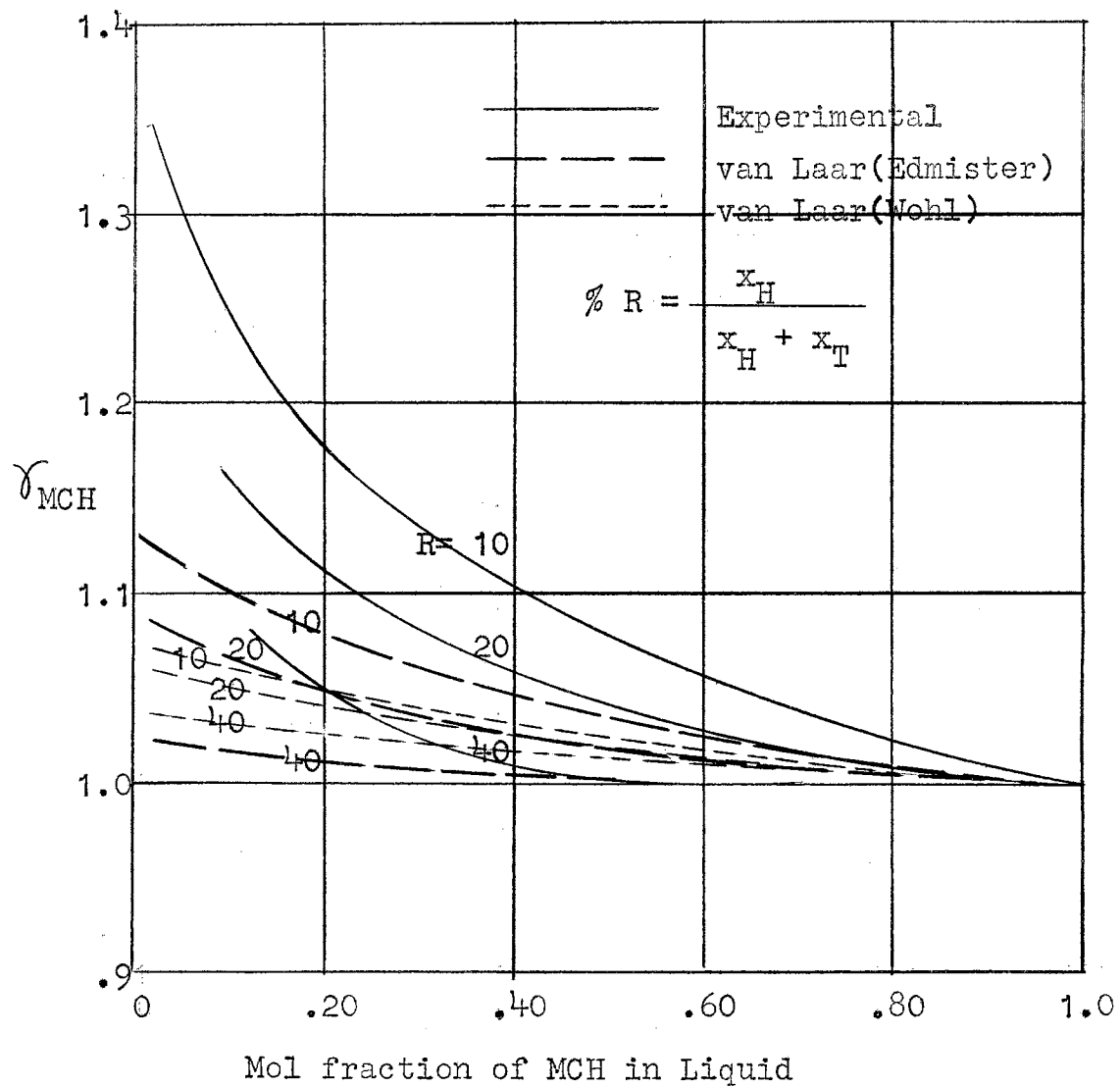


Fig. 24 Comparisons of Methylcyclohexane Activity Coefficients
 System: n-Hexane-Methylcyclohexane-Toluene

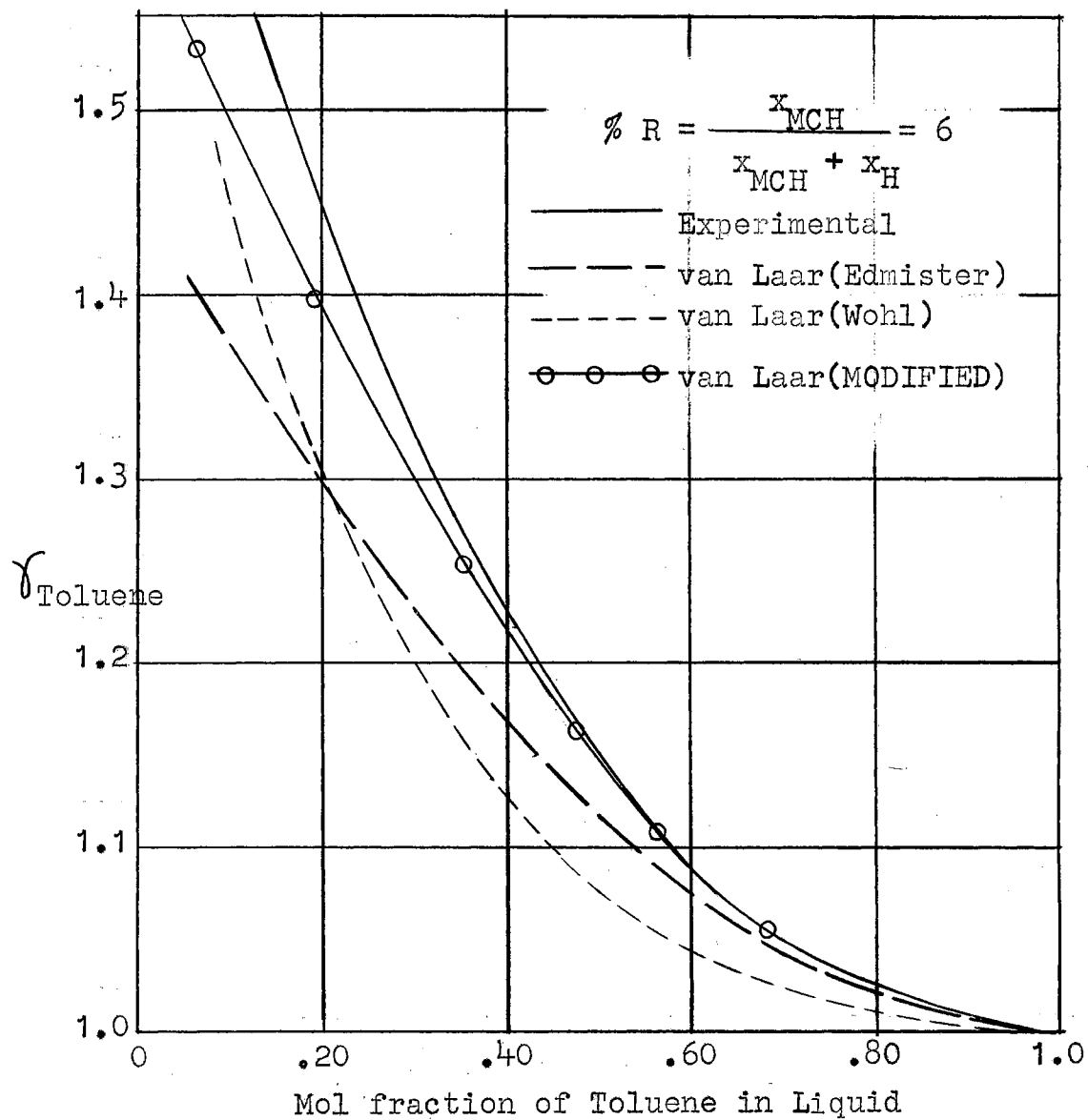


Fig. 25 Comparisons of Toluene Activity Coefficients
 System: n-Hexane-Methylcyclohexane-Toluene,
 at $R = 6$.

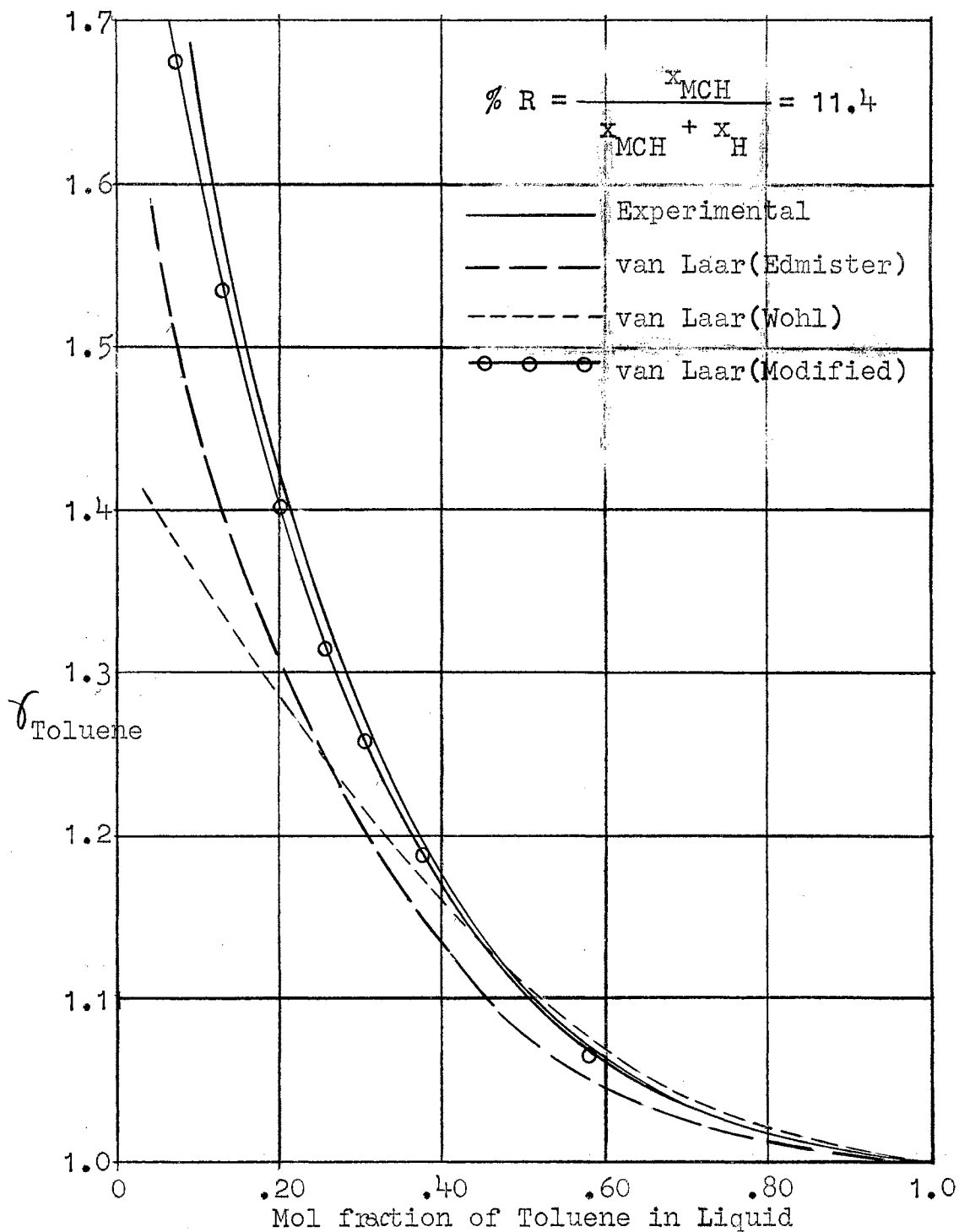


Fig. 26 Comparisons of Toluene Activity Coefficients
 System: n-Hexane-Methylcyclohexane-Toluene
 at $R = 11.4$

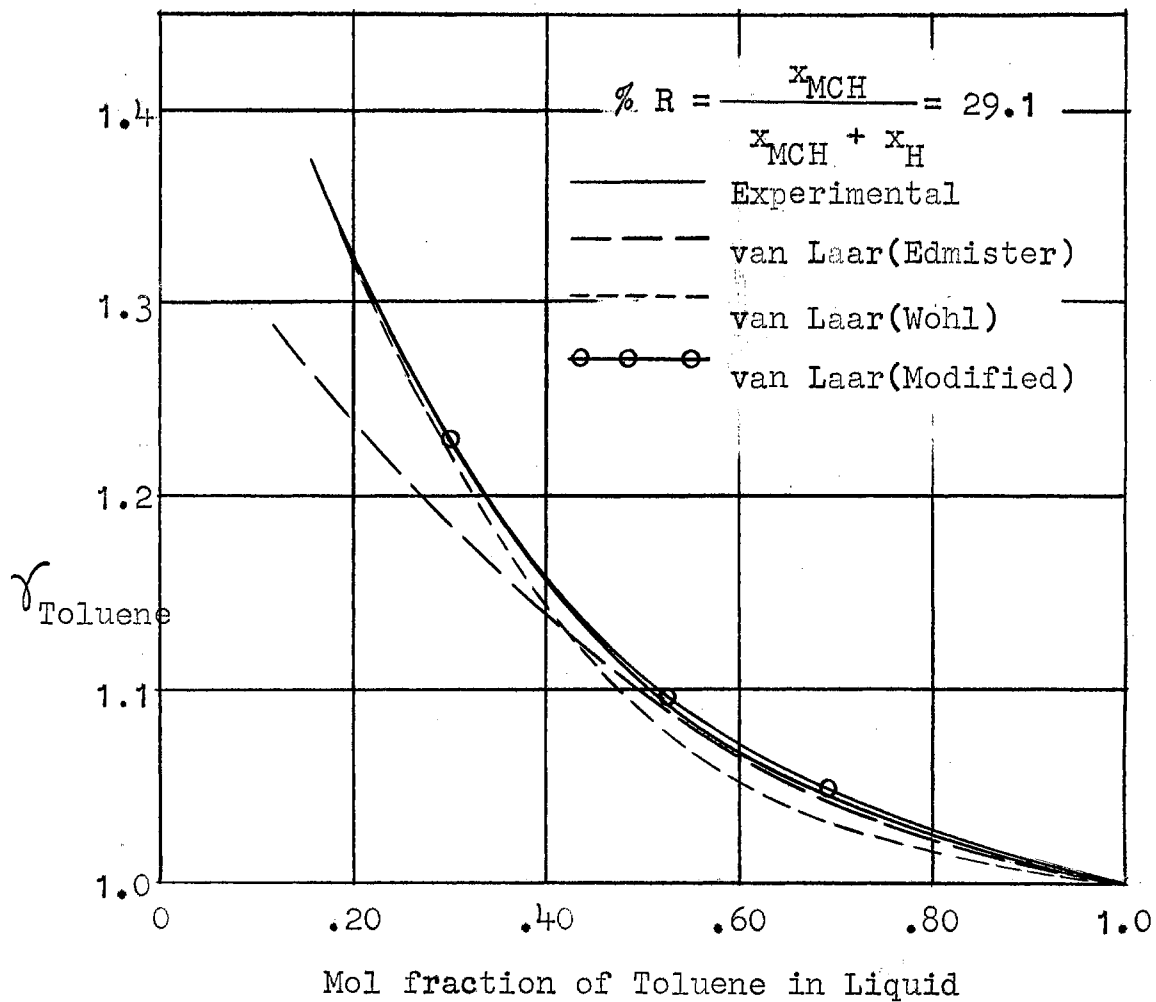


Fig. 27. Comparisons of Toluene Activity Coefficients

System: n-Hexane-Methylcyclohexane-Toluene
at $R = 29.1$

VITA

I-Der Huang

Candidate for the Degree of
Master of Science

Thesis: VAPOR-LIQUID PHASE EQUILIBRIA FOR SYSTEM N-HEXANE-
METHYLCYCLOHEXANE-TOLUENE, EXPERIMENTAL AND CORRE-
TION.

Major Field: Chemical Engineering

Biographical:

Personal data: Born at Hangchow, China, June 24, 1936
the son of C. T. Huang and B. T. Woo.

Education: Attended primary school and junior middle
school in Hangchow, China; attended high school
in Taipei, China; graduated from high school in
May, 1953; received the Bachelor of Science degree
from National Taiwan University, with a major in
Chemical Engineering, in May, 1957; completed the
requirements for the Master of Science in February,
1961.

Professional experience: Served as Second-Lieutenant
in Ordnance Engineering College, Chinese Army,
1958 to 1959.

Professional societies: Member of Chinese Chemical
Society.