PREDICTION OF LIQUID MIXTURE VISCOSITY OVER A WIDE RANGE OF TEMPERATURE USING GROUP CONTRIBUTION METHOD

By

SULEIMAN YOUSEF DIAB

Bachelor of Science
Texas A&M University
College Station, Texas
1973

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1980

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the Degree of
DOCTOR OF PHILOSOPHY
December, 1982

PREDICTION OF LIQUID MIXTURE VISCOSITY OVER A WIDE RANGE OF TEMPERATURE USING GROUP CONTRIBUTION METHOD

Thesis Approved:

R. N. Maddox
Thesis Adviser

John H Erbar

Kenneth J Bell

Gilbert J. Mains

Norman N Durham
Dean of the Graduate College

PREFACE

A model for predicting liquid mixture viscosity over wide ranges of temperature and concentration was developed. The Ratcliff-Khan Group Solution Model for predicting mixture viscosities at 25°C served as the base for this work. The model is capable of handling binary and multicomponent mixtures of straight and branched components, polar and non-polar components and components with multiple groups. The model is the first of its kind in explicitly addressing temperature in predicting liquid mixture viscosity.

Constants for eight active groups were generated. The model was tested on thirty-eight mixtures covering such groups. The model is promising and its extension to cover other groups is encouraged.

I wish to express my sincere gratitude to all the people who assisted me in this work and during my stay at Oklahoma State University. In particular, I am especially indebted to my major advisor, Dr. Robert N. Maddox, for his intelligent guidance, concern and invaluable help.

I am also thankful to the other committee members, Dr. Kenneth J. Bell, Dr. John H. Erbar, and Dr. Gilbert J. Mains for their advisement in the course of this work. Special thanks are due to Dr. Ruth C. Erbar for her kind help in providing pertinent data and her remarks.

The help of Dr. J. P. Chandler in using subroutine "MARQ" is appreciated. I am thankful to the unforgettable friendship, encouragement and company of Dr. Saed Akashah, Dr. Dulaihan Al-Harbi, Dr. Mohammad

Abul-Hamayel, Dr. Daniel Chen, Dr. Faisal Al-Juwaihel, Mahmud Rahman, Ross Fox, Fahad Al-Habdan, Beleid Kuwairi, Khaled Gasem and A. K. M. Uddin.

Special thanks are due to Fluid Properties Research, Inc. and the School of Chemical Engineering for the financial support I received during the course of this work.

My mother, my wife, Rajiya, my two sons, Labeed and Bashar deserve my deepest appreciation for their constant support, moral encouragement, and understanding.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Engineers, whether designing and operating industrial plants, discovering new materials or transporting old ones are often dealing with liquids whose properties constitute important variables. The availability of reliable data on these porpoerties and the availability of reliable techniques for predicting them are of great interest and concern for both industrialists and academicians.

The liquid state is intermediate between the solid and gaseous states. Liquid theory, is in its primitive stages compared to both the gaseous and the solid theories. Thus, experimental data and reliable predictive techniques are not only welcomed, but a necessity in this field.

Viscosity is an important property. It is a fluid resistance to flow. It is sensitive to changes in temperature and composition. Its influence is felt in many aspects of daily life, but is almost too commonplace to receive special notice. In the industrial world viscosity is important in many different fields. Oil, grease, printing inks, polymers and liquid foods are a few examples. Viscosity figures prominently in the petroleum industry all the way from producing fields to the market place.

In general, viscosity is essential in proper design of industrial plants. It is essential in proper design of the equipment for handling fluids. It is essential for proper functioning of hydraulic systems, automatic transmissions and other responsible systems for transportation.

The purpose of this work is to develop a liquid mixture viscosity prediction method based on group contributions for predicting liquid mixture viscosity. The method should be capable of predicting liquid mixture viscosity over wide ranges of temperature and concentration and capable of handling multiple groups and components. Since the model is utilizing the functional and structural gruops of the mixture, i.e., CH_3, CH_2,..., etc., certain parameters characterizing these groups will be generated and generalized using experimental viscosity data. These generalized constants will be used in predicting the viscosity of other mixtures consisting of the same groups for which data are either not readily available and expensive in time and money to get or not existing at all.

The generated constants will be tested to see their applicability for branched and polar mixtures that have the same groups. They will be tested for their interpolation and extrapolation capabilities. Eight groups will be attempted. The groups are CH_3, CH_2, COOH, CO, OH, NH_2, NH and N. Thirty-eight mixtures covering these active groups will be utilized.

CHAPTER II

DEFINITIONS AND LITERATURE SURVEY

Definitions

Viscosity, an important property of fluids, is too commonplace to receive special attention. Although it is a cornerstone in many of the design calculations that involve transporting and processing fluids, the research involved and the interest generated are far below its level of importance. With increasing energy costs, a need to revise design procedures and design parameters has arisen. So more attention is paid, and will be paid, to getting accurate and precise viscosity data through experimental investigations and predictive techniques. Such accurate data will lead ultimately to more appropriate and economical designs.

Throughout this work certain terms will be used and the following definitions to such terms apply:

Viscosity: Is the fluid resistance to flow or the shearing stress per unit area divided by the velocity gradient. Its dimensions are (force)(time)/(length)^2 or mass/length time. For scientific work, viscosities are expressed in terms of poise (P), centipoise (cP), etc.

$$\begin{aligned} 1 \text{ poise (P)} &= 1.00 \times 10^2 \text{ cP} \\ &= 1.00 \times 10^6 \ \mu\text{P} \\ &= \text{gm/cm-sec} \end{aligned}$$

= dyne-sec/cm^2

= 242 lbmass/ft-hr

= 242 Poundal-hr/ft^2

= 0.0672 lbmass/ft-sec

= 0.0672 Poundal-sec/ft^2

= 0.1 Newton-sec/m^2

Ideal mixture: A mixture that undergoes either no change of volume upon mixing or minimum changes, i.e., volume change upon mixing less than 0.1 percent.

Non-ideal mixture: A mixture with a change of volume upon mixing larger than 0.1 percent.

Miscible liquids: Liquids that dissolve in each other in all proportions.

Immiscible liquids: Liquids that are slightly soluble in each other such as oil and water but for practical purposes considered insoluble.

Partially miscible liquids: Liquids that mix with each other appreciably but in limited proportions.

The concentration throughout this work is expressed in one of the following forms:

Weight fraction $W_1 = w_1/(w_1 + w_2)$

where

w_1 = the weight of component 1

w_2 = the weight of component 2

$$\text{Mole fraction } M_1 = \frac{\text{mass}_1/\text{MW}_1}{\dfrac{\text{mass}_1}{\text{MW}_2} + \dfrac{\text{mass}_2}{\text{MW}_2}}$$

where MW_1, MW_2 are molecular weights of components 1, 2 respectively.

Volume fraction $V_1 = \frac{v_1}{v_1 + v_2}$

where

v_1 = the volume of component 1

v_2 = the volume of component 2

Notice that:

$W_1 + W_2 = 1$

$M_1 + M_2 = 1$

$V_1 + V_2 = 1$

Fluidity $\phi = 1/\mu$

ϕ = fluidity

μ = absolute viscosity

Molar volume $\overline{v} = MW/\rho$

where

MW = molecular weight

ρ = density

log = logarithm to the base$_{10}$

ln = logarithm to the base e

Literature Survey

The models for presenting and predicting the viscosity of liquid mixtures, which range form purely empirical to purely theoretical, will be classified and discussed.

Before discussing these models some points are worth stating:

1. There is no intent to survey the theories of viscosity. The reader is referred to two references which address this subject by Brush (1) and Touloukian (2).

2. Theories of mixtures also will not be discussed. For more details about such theories the following references are helpful: Scatchard (3) and Hildebrand (4) for regular solution theory; Barker (5) and Guggenheim (104, 105) for lattice theory; Rawlinson (6) and Leland and Chappelear (7) for corresponding states; Gibbons (8) for perturbation expansion; Lucassen-Reynder (9, 10, 11) for vacancy theory.

3. Mixture rules will not be discussed. Valuable information on mixture rules is presented in Nielson (12).

4. A survey of the equations for presenting and predicting the viscosity of mixtures will be stated following the Irving (21) way of classification.

Equations for Viscosity Mixtures

Most of the models stated here are applicable only to physical mixing of two homogeneous, completely miscible liquids unless otherwise stated. Equations for salt solutions are given in Doolittle (13):

I. First family: Additive equations - these can be classified into two types:

   A. Plain additive equations

$$f(\mu) = \Sigma x_i f(\mu_i)$$

where

x_i = weight, mol or volume fraction of component i

$f(\mu)$ is the viscosity function and generally is

$f(\mu) = \mu$; or $f(\mu) = \ln(\mu)$, $f(\mu) = \phi$

where

μ = absolute viscosity of the mixture

ϕ = fluidity and defined as $1/\mu$

Examples of this type of equation:

1. The Arrhenius Equation (14)

$$\ln \mu = V_1 \ln \mu_1 + V_2 \ln \mu_2$$

where

V_1 = volume fraction of component 1

V_2 = volume fraction of component 2

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

2. The Findlay Equation (15)

$$\phi = V_1 \phi_1 + V_2 \phi_2$$

where

ϕ_1 = fluidity of component 1

ϕ_2 = fluidity of component 2

V_1 = volume fraction of component 1

V_2 = volume fraction of component 2

3. The Bingham (16), and the Drucker and Kassel (17) Models.

$$\phi = W_1 \phi_1 + W_2 \phi_2$$

where

ϕ_1 = fluidity of component 1

ϕ_2 = fluidity of component 2

W_1 = weight fraction of component 1

W_2 = weight fraction of component 2

B. Additive equation with constants

1. The Lee Equation (18)

$$\phi^m = V_1\phi_1^m + V_2\phi_2^m$$

where

m = constant

V_1 = volume fraction of component 1

V_2 = volume fraction of component 2

ϕ_1 = fluidity of component 1

ϕ_2 = fluidity of component 2

2. The Kendall and Monroe Equation (19)

$$\mu^{1/3} = M_1\mu_1^{1/3} + M_2\mu_2^{1/3}$$

where

M_1 = mole fraction of component 1

M_2 = mole fraction of component 2

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

3. The Lautie Equation (20)

$$\phi^{1/3} = M_1\ \phi_1^{1/3} + M_2\ \phi_2^{1/3}$$

where

ϕ_1 = fluidity of component 1

ϕ_2 = fluidity of component 2

M_1 = mole fraction of component 1

M_2 = mole fraction of component 2

As Irving (21) stated, none of the additive equations is satisfactory. All of them fail whenever the viscosities of the pure components are widely different.

II. Second Family: Parabolic equations - the general form of this family has an interaction parameter added to the additive form:

$$f(\mu) = x_1 f(\mu_1) + x_2 f(\mu_2) + 2\ x_1 x_2 C$$

where $f(\mu)$ and the x's have the same definitions as in the First Family. C = the interaction parameter.

Replacing x_1 with $(1-x_2)$ and rearranging gives:

$$f(\mu) = (1-x_2)f(\mu_1) + x_2 f(\mu_2) + 2(1-x_2)x_2 C$$

collecting like terms:

$$f(\mu) = -2Cx_2^2 + x_2[f(\mu_1) - f(\mu_2) + 2C] + f(\mu_1)$$

this is of the form

$$f(\mu) = Ax_2^2 + Bx_2 + C$$

The following equations are examples of this family.

A. The Van der Wyke Equation (22)

$$\ln\ (\mu) = M_1^2 \ln\ (\frac{\mu_1\ \mu_2}{\mu_{12}}) + 2M_1 \ln\ (\frac{\mu_2}{\mu_1}) + \ln(\mu_2)$$

where

$\ln(\mu_1)$ = absolute viscosity of component 1

$\ln(\mu_2)$ = absolute viscosity of component 2

M_1 = mole fraction of component 1

$\ln(\mu_{12})$ = interaction coefficient

B. The Mato-Hernandez-Dolezalek Equation (23, 24, 25)

$$\mu = V_1^2\mu_1 + V_2^2\mu_2 + 2V_1V_2C$$

where

V_1 = volume fraction of component 1

V_2 = volume fraction of component 2

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

C = constant

This is the original form proposed by Dolezalek (23) and revived by Mato and Hernandez (24, 25) who show the applicability of this equation at equimolar concentrations.

C. The Sachanov and Rjachowsky Equation (26)

$$\mu = M_1^2\mu_1 + M_2^2\mu_2 + 2M_1M_2C$$

where

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

M_1 = mole fraction of component 1

M_2 = mole fraction of component 2

The interaction coefficient here is C and defined as

$$C = \sqrt{\mu_1\mu_2}$$

D. The Grunberg and Nissan Equation (27)

$$\ln(\mu) = M_1\ln(\mu_1) + M_2\ln(\mu_2) + 2M_1M_2C$$

μ's and M's have the same definitions as above; C is a characteristic constant of the system. It can be positive or negative which allows for the maximum and minimum viscosity that occurs for some mixtures.

E. The Hind, McLaughlin and Ubbelohde Equation (28)

$$\mu = M_1^2\mu_1 + M_2^2\mu_2 + 2M_1M_2C$$

where

M_1 = mole fraction of component 1

M_2 = mole fraction of component 2

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

This is similar to the Sachanov and Rjachowsky equation. C is the interaction coefficient defined as μ_{12} and approximately is $0.5(\mu_1 - \mu_2)$.

According to Irving (21) the equations of this family using ln (μ) (as the Van der Wyke and the Grunberg equations) are to be preferred. Although the Hind et al. and the Sachanov et al. equations have been theoretically derived by Bearman and Jones (29) from statistical mechanical theory, they are not sufficiently accurate for prediction purposes. This supports the claim of the experimentalists that theoretical developments have to be modified to suit experimental results.

III. Third Family: Equations of mixture density - this family of equations requires mixture density. It is subdivided into two kinds:

A. Viscosity-Density Equation - such as:

1. The Chakrabertty and Ganguly Equation (30)

$$\ln(\mu) - 1/3 \ln \rho = C_1 + C_2 M_2$$

where

C_1 and C_2 are constants

ρ = density of the mixture

M_2 = mole fraction of component 2

This equation is intended for non-polar liquids. It is deduced from Andrade's equation (68) with allowance made to account for the change in volume upon mixing.

2. The Spells Equation (31)

$$\mu = \mu_L \left(\frac{\mu}{\mu_L}\right)^{1/3} \exp \beta(\rho - \rho_L)$$

where

$\mu_L = \mu_1 + r(\mu_2 - \mu_1)$

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

r = concentration by volume of liquid 2 in the mixture of components.

$\rho_L = \rho_1 + r(\rho_2 - \rho_1)$

ρ_1 = density of component 1

ρ_2 = density of component 2

β is a function of concentration for each binary mixture, but Spells simplified it and considered it a constant that characterizes the mixture. It can be evaluated from experimental data on viscosity and density. By differentiating Spells main equation the following expression for "β" is given:

$$\beta = \frac{\ln(\mu) - \ln(\mu_L) - \frac{1}{3}(\ln \rho_L - \ln \rho)}{\rho - \rho_L}$$

A single value of β is chosen so as to give best agreement with observation over the whole range of concentration.

This equation and the MaCleod equation to be stated later are based on the assumption that a perfect mixture undergoing no volume change on mixing would give a linear law for viscosity - concentration. (The relation between the density and concentration expressed as volume of solute per unit volume of mixture being a straight line.) There is no theoretical justification for this assumption. Plots of alkane-alkane and alcohol-alcohol mixtures in the next chapter do not agree with this assumption.

3. The Srinivasan Equation (32)

$$\mu^{1/3} = \frac{\rho}{100}[(\mu_1)^{1/3}v_1 + (\mu_2)^{1/3}v_2](\frac{\rho}{\rho_c})^n$$

where

n = a constant

$\rho_c = \frac{100}{v_1 + v_2}$, v_1 and v_2 are the volumes of pure components 1 and 2 in 100 grams of mixture.

This equation was claimed to handle non-ideal binaries. The same author derived another equation from the Andrade equation (68) to account for the variation of viscosity with temperature at constant composition.

4. The Bhagwat and Mandloi Equation (33)

$$\rho^{1/3} = \frac{\rho}{M_1MW_1 + M_2MW_2}[\frac{M_1MW_1\mu_1^{1/3}}{\rho_1} + \frac{M_2MW_2\mu^{1/3}}{\rho_2}]$$

where

ρ = is the density of the mixture

M_1= mole fraction of component 1

M_2= mole fraction of component 2

MW_1 = molecular weight of component 1

MW_2 = molecular weight of component 2

ρ_1 = density of component 1

ρ_2 = density of component 2

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

This equation assumes that component rheochors follow a linear law. (Rheochor was proposed by Fried, et al. (34) and defined as $R = (MW\mu^{1/3})/\rho$.

5. The Chacravarti Equation (35)

$$\mu^{1/8} = \frac{\rho}{W_1MW_1 + W_2MW_2}\left[\frac{W_1MW_1\mu^{1/8}}{\rho_1} + \frac{W_2MW_2\mu^{1/8}}{\rho_2}\right]\left[\frac{\rho}{W_1MW_1 + W_2MW_2}\right]^m$$

where all terms are the same as above for the Bhagwat and Madloi equation and:

W_1 = weight fraction of component 1

W_2 = weight fraction of component 2

m = constant

This equation is an extension of Bhagwat et al. work using weight fractions instead of mole fractions. It was proposed to handle non-ideal mixtures.

As is commented by Irving (21), the mixture density are of academic interest only rather than of practical interest. This can be easily seen since such equations require mixture density. Data on mixture density are not usually available and their measurement requires considerable care if the small changes in volume on mixing are to be satisfactorily detected.

B. Free Volume Equations

These equations also require mixture density. They are based on, and derived from, the Bachinskii equation (36) which is restricted to pure liquids.

$$\mu = \frac{C}{v - v_o}$$

where C is a constant, sometime referred to as the specific modulus of viscosity. (It is the contraction per unit volume deduced from the density of the mixture.)

v = the specific volume of the liquid = $1/\rho$

v_o = the limiting specific volume (a constant)

The Bachinskii equation simply says that the viscosity is inversely proportional to the free-volume.

1. Meyer and Mylius Equation (37)

$$\phi = \frac{1}{C}(W_1C_1\phi_1 + W_2C_2\phi_2)$$

where

ϕ = the fluidity = $1/\mu$

W_1= weight fraction of component 1

W_2= weight fraction of component 2

C_1= viscosity modulus of component 1

C_2= viscosity modulus of component 2

ϕ_1= fluidity of component 1

ϕ_2= fluidity of component 2

This equation is obtained by assuming that the free volume is additive and that there is no change of volume in mixing. Meyer and Mylius also derived another equation for the limiting volume v_o. C, the viscosity modulus, depends on composition. In this equation they did not show how the equation depends on composition.

2. The Macleod Equation (38)

$$\mu = \mu_1 M_1 \frac{x_1}{x} + \mu_2 M_2 \frac{x_2}{x}$$

where

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

x_1 = free space of component 1 defined as $C_1\phi_1$

x_2 = free space of component 2 defined as $C_2\phi_2$

x = free space of the mixture defined as $C\phi$

(C's are constants and ϕ's = $1/\mu$)

M_1 = mole fraction of pure component 1

M_2 = mole fraction of pure component 2

The Macleod equation can be expressed in terms of the Bachiniskii constants as follows:

$$\phi = 1/C(V_1C_1\phi_1 + V_2C_2\phi_2 + \Delta V)$$

where

$\phi = 1/\mu$ the fluidity

V_1, V_2 = volume of fractions introduced by the Macleod definition of free volume of the mixture "X", defined as $V_1X_1 + V_2X_2 + \Delta V$, and X_1, X_2 are free spaces of components 1, 2.

ΔV = the change of volume on mixing

$C = M_1C_1 + M_2C_2$

As Irving (21) noted, the Macleod equation is equivalent to defining the Bachinskii "modulus of viscosity" as:

$$C = M_1C_1 + M_2C_2$$

3. The Gugel Equation (39)

$$\phi = 1/C(W_1C_1\phi_1 + W_2C_2\phi_2 + \Delta v)$$

This equation is exactly the same as the Meyer and Mylius equation with the addition of Δv, the change of volume on mixing.

4. The Luchinskii Equation (40)

$$\phi = 1/C(M_1C_1\phi_1 + M_2C_2\phi_2)$$

where the terms are as above in the Gugel Equation. The equation is for an ideal mixture where there is no change in volume upon mixing. "C" is assumed to follow the additive rule and the limiting specific volume as well. (This assumption was rejected by Bachinskii himself later.)

5. The Kottler Equation (41)

$$\phi = (1/C)[MW_1M_1\phi_1C_1 + MW_2M_2\phi_2C_2 + MW\Delta V]$$

where "MW" is defined as $M_1MW_1 + M_2MW_2$

M_1, M_2 are mole fractions of components 1 and 2 and MW_1, MW_2 are molecular weights of componetns 1 and 2, and "C" the Bachinskii modulus of viscosity is defined as in

$$\ln(C) = M_1\ln(C_1) + M_2\ln(C_2) + M_1M_2\ln(C_{12})$$

This equation is similar to the previous equations except that the units are expressed in molar units. What is new here is the clarity of the assumptions of Kottler. He assumes that the limiting specific volumes "v's" are additive and proposes that the logarithms of the Bachinskii moduli of viscosity are additive.

Kottler states that in case of ideality both v and MC_{12} are zero.

6. The Doolittle Equation (42)

$$\ln\mu = \gamma + a \text{ EXP } \left(-\frac{\beta}{(\bar{M})^{1/4}}\right)$$

or, as expressed by him later (43)

$$\ln(\mu) = A \text{ EXP } \left(\frac{\beta}{v_f/v_o}\right)$$

where

$v_f/v_o = (v-v_o)/v_o$

v_f = volume of free-space per gram of liquid at any temperature

v_o = volume of 1 gram of liquid extrapolated to absolute zero without change of phase.

v = volume of 1 gram of liquid at any temperature

A and B are the same constants in both forms.

$\overline{MW}_a$ is the weighted average molecular weight and defined as:

$$\overline{MW}_a = MW_1 + \frac{MW_2 + MW_1}{[1 + (\frac{W_1}{W_2})(\frac{MW_2}{MW_1})^{a-1}]}$$

where "a" lies between 0 and 1 and depends upon the difference between the molecular weights of the components. The larger the difference, the closer "a" is to 1.0, and the smaller the difference the closer "a" is to 0.0.

β has to be found from a previous knowledge of the individual components. Its value need not be precise.

For "γ" and "a" a trial and error procedure is required. Different values for "a" are assumed and a plot of ln μ vs $EXP(-\beta/(\overline{MW}_a)^{1/4}$ is constructed to produce a straight line. "a" is the slope of the line and "γ" is the y intercept.

The best equation of this family is the Doolittle equation which was obtained empirically and later derived semi-theoretically by Turnbull, et al. (44).

$$\ln \mu = A + B\frac{v_o}{v_f}$$

where v_o is the limiting specific volume, v_f is the free-volume equal to the difference between the specific volume and the limiting specific volume. A and B are the same as "γ" and "a".

The drawbacks of the equations of this family are three:

a. They can be applied only when the specific volume of mixture is known.

b. They require knowledge of the Bachinskii constants for the pure components. They must be obtained from viscosity and density data over a range of temperature.

c. Bachinskii's Law holds only at temperatures away from the freezing point.

Most of the equations of this family are similar in considering the limiting specific volume of the mixture to be linear with composition. They are different in their definition of the viscosity modulus C. The assumption that the Bachinskii constant "C" follows a simple additive law was not justified by experimental evidence and was rejected by Bachinskii himself (45).

IV. Fourth Family: Kinematic Viscosity Equations - Viscosity usually is reported as absolute or dynamic viscosity. This family of equations predicts kinematic viscosity. To convert the kinematic to absolute (dynamic) viscosity, the corresponding density is required: (Kinematic viscosity $\nu = \mu/\rho$)

A. The Wilson Equation (46)

This equation is intended for mineral oil blends. It uses volume fraction and a constant which varies according to the paraffinic or naphthenic content of the components.

$$\nu^w = V_1\nu_1^w + V_2\nu_2^w$$

where

ν_1 and ν_2 = the kinematic viscosities of pure components 1 and 2

V_1 and V_2 = volume fractions of pure components 1 and 2

w = a constant which varies according to the paraffinic or napthenic content of the pure components 1 and 2.

B. The American Society for Testing and Materials Equation (ASTM D341-443, 1932)

This equation is the basis of the ASTM chart for predicting kinematic viscosity.

$$W = \log[\log(\nu + 0.6)]$$

$$W = v_a \log[\log(\nu_1 + 0.6)] + v_b \log[\log(\nu_2 + 0.6)]$$

where

v_a and v_b are functions of volume fractions V_1 and V_2 of components 1 and 2

$v_b = 11.68 \log (1 + 0.28 V_2)$

The parameter W is calculated from the above equation. Using this calculated parameter the viscosity of the mixture is found from the chart. The new modified kinematic viscosity ASTM is the Wright equation (47):

$\log (\log Z) = A - B \log T$

where

T = absolute temperature K

$Z = \nu + 0.7 - C - D + E - F + G - H$

ν = kinematic viscosity centistokes

$C = \mathrm{Exp}(-1.14883 - 2.65868\ \nu)$

$D = \mathrm{Exp}(-0.0038138 - 12.5645\ \nu)$

$E = \mathrm{Exp}(5.4649 - 37.6289\ \nu)$

$F = \mathrm{Exp}(13.0458 - 74.6851\ \nu)$

$G = \mathrm{Exp}(37.5619 - 192.643\ \nu)$

$H = \mathrm{Exp}(80.4945 - 400.468\ \nu)$

C. The Nederbragt Equation (48)

$\log (\log \nu) = v_1 \log (\log \nu_1) + v_2 \log (\log \nu_2)$

where

ν = kinematic viscosity in centistokes

The equation is as effective as the ASTM viscosity equation and also can be used for mineral oil blends.

D. The Reed and Taylor Equation (49)

$$\ln (MW\nu) = W_1 \ln (MW_1 \nu_1) + W_2 \ln (MW_2 \nu_2)$$

where

ν_1, ν_2 = kinematic viscosities of pure components 1, 2

MW_1, MW_2 = molecular weights of pure components 1, 2

W_1, W_2 = weight fractions of pure components 1, 2

This equation was derived from the rate process theory of Eyrning et al.(50).

5. The McAllister Equation (51)

$$\begin{aligned}\ln \nu = {} & M_1^3 \ln \nu_1 + 3M_1^2 M_2 \ln \nu_{12} \\ & + 3M_1 M_2^2 \ln \nu_{21} + M_2^3 \ln \nu_2 \\ & - \ln \frac{[M_1 + M_2\ MW_2]}{MW_1} \\ & + 3M_1^2\ M_2 \ln \left[\frac{2 + MW_2/MW_1}{3}\right] \\ & + 3M_1\ M_2^2 \ln \left[\frac{1 + (2MW_2/MW_1)}{3}\right] \\ & + M_2^3 \ln \left(\frac{MW_2}{MW_1}\right)\end{aligned}$$

M's and MW's are mole fractions and molecular weights respectively. This equation has shown to give good results when the component molecules are of great difference in size such as water - ethylene glycol systems. It was recommended by Reid and Sherwood (52) for mixtures of such components provided that ν_{12}, ν_{21} are available.

ν_{12} and ν_{21} are parameters that must be evaluated from experimental viscosity data for the mixture.

6. The Katti and Chaudri Equation (53)

$$\ln\nu\ MW = M_1 \ln\nu_1\ MW_1 + M_2 \ln\ \nu_2\ MW_2 + M_1 M_2 C$$

where $MW = M_1\ MW_1 + M_2\ MW_2$

$$C = \frac{W_{visc}}{RT}$$

R is the gas constant and T absolute temperature.

W_{visc} is a parameter calculated for an equimolar mixture from experimental data.

This equation was reported to predict the viscosity of alcohol mixtures satisfactorily. This equation also can be classified under the Fifth family of equations, "Equations with Constant(s)".

7. The Cronauer, Rothfus and Kermode Equation (54)

$$\ln\nu = m_1\ \ln\ \nu_1 + m_2\ \ln\ \nu_2$$

This is an additive type using kinematic viscosity and mole fractions.

8. The Auslander Equation (55)

$$\nu = \frac{W_1 k_1 V_1 + W_2 k_2 V_2}{W_1 k_1 + W_2 k_2}$$

where k for each component is defined at the temperature of the mixture as:

$$k = -\frac{1}{\sqrt{d\nu/dT}}$$

k_1, k_2 are found from the viscosity-temperature behavior of pure components. Irving (21) suggested that the results of this equation can be improved by using log instead of ν and d (log ν/dT) instead of dν/dT. The equation is applicable to oil mixtures and hydrocarbon mixtures where pure component viscosities are not widely different. It will not show a maximum or minimum on the viscosity curve.

9. The Heric and Brewer Equations (56, 57)

   They have two equations; the first one uses the mole fractions of the pure components. The second one uses the absolute viscosities of pure components instead of kinematic viscosity.

   a. $\ln\nu\,MW = M_1 \ln\nu_1 MW_1 + M_2 \ln\nu_2 MW_2 + M_1 M_2 \overline{C}$

   where $\overline{C}$ is a power series.

$$\overline{C} = C_o + C_1(M_1 - M_2) + C_2(M_1 - M_2)^2 + \ldots$$

$$\ldots + C_n(M_1 - M_2)^n + \ldots$$

$$MW = M_1 MW_1 + M_2 MW_2$$

where

M_1, M_2 = mole fractions of components 1 and 2

MW_1, MW_2 = molecular weights of components 1 and 2

Irving (21) reported that three constants in the power series expansion are sufficient to provide a fit to better than 0.5 per cent. This equation is similar to the Katti et al. equation but differs from it by expressing the constant C as a power series.

b. $\mu = M_1\mu_1 + M_2\mu_2 + M_1M_2\overline{C}$

where

μ_1, μ_2 = absolute viscosities of pure components 1 and 2

$\overline{C}$ = a power series as above.

Irving (21) reported that this equation is entirely empirical and much simpler than the kinematic form. Also, he reported that it gives better fit than the kinematic one.

These two equations are considered as part of the coming family, equations with constants, but are stated here for the sake of continuity.

By using the congruence concept they are also a pioneer work in the direction of a good group contribution method. The congruence concept was introduced by Bronsted et al. (80). It stays that a mixture of components k_1, k_2, ...n, containing C_1, C_2, ...n, carbon atoms per molecule, respectively, and present in the mixture in mole fractions x_1, x_2, ... may be characterized by an index C given by:

$C = x_1C_1 + x_2C_2 + \ldots.$

Mixtures with same index are designated as congruent.

10. The Krishnan and Laddha Equation (58)

This is another kinematic equation having the same terms as the Heric equation but differing in the constant.

$$\ln \nu MW = M_1 \ln \nu_1 MW_1 + M_2 \ln \nu_2 MW_2 - 2.303\, M_1M_2[A + B(M_1 - M_2)]$$

The authors stated that A and B are constants that are predicted from vapor liquid equilibrium data.

Of this Family, Irving (21), has recommended the Heric and Brewer equations for predicting mixture viscosities.

V. Fifth Family: Equations with constants.

A. The Flory Equation (78)

$$\log \mu = A + B \sqrt{Z}$$

The Flory equation is intended for mixtures of polymers with widely different molecular weights.

A and B are constants and Z is the weight average chain length of the two components defined as

$$Z = W_1 Z_1 + W_2 Z_2$$

where

W_1, W_2 = weight fraction of components 1 and 2

Z_1, Z_2 = number of atoms in the chain skeletan of components 1 and 2.

Irving (21), stated that the Flory equation is effective in predicting the viscosity of a blend of two polymers.

B. The Saraiya and Winnick Equation (59)

$$\ln \mu = \ln A + \frac{E^*}{RT} + \alpha \frac{v_o}{v_f}$$

This equation has combined the free-volume principle (v_o/v_f) and the energy principle (E^*/RT).

It was proposed by Litovitz et al. (60) for pure liquids and was applied to liquids ranging from fused silica to liquid argon. Saraiya and Winnick applied it to mixtures and assumed that ln A and E* (the energy vaporization) are additive with respect to mole fractions. Free volume is determined by Goldhammer's rule (61).

C. The Samu and Lima Equation (62)

$$\log (\log \mu) = [\frac{M_1I_1 + M_2I_2}{M_1MW_1 + M_2MW_2}]\rho - 2.9$$

where I_1, I_2 are the Souders constants for components 1 and 2 defined as:

$I = \overline{m}\ MW$

where MW is the molecular weight and $\overline{m}$ is defined as

$$\frac{\log(\log \mu) + 2.9}{\rho}$$

This is an empirical equation developed by Souders (63) who listed "I" values for over 100 organic polar liquids. He avoided the strongly polar liquids because his model did not work for them. Souders work is one of the very early works which considered group effects.

Other equations of this family are the Doolittle equation which was discussed earlier under the Free Space Family equations and the Ishikawa equation (64). According to Irving (21), the Ishikawa equation is not recommended. The Flory equation is limited to polymers and the Sariaya and Winnick equation is difficult to use.

VI. Sixth Family: Unclassified Equations - Equations that do not fit under any of the above families.

A. The Cragoe Equations (65)

Cragoe has two equations:

1. $$\frac{1}{\ln 20\mu} = \frac{1}{V_1(\ln 20\mu_1)} + \frac{1}{V_2(\ln 20\mu_2)}$$

2. $$\frac{1}{\ln 20\mu} = \frac{1}{V_1(\ln 20\mu_1)} + \frac{1}{V_2(\ln 20\mu_2)} + V_1V_2C$$

where

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

C = is a constant

V_1 = mole fraction of component 1

V_2 = mole fraction of component 2

The last term in equation 2 is to account for the maximum or minimum that occurs in some mixtures. Equation 2 is applicable to mineral oils.

B. The Lederer Equation (66)

$$\ln \mu = \frac{M_1}{M_1 + M_2S} \ln \mu_1 + \frac{M_2S}{M_1 + M_2S} \ln \mu_2$$

where

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

M = mole fraction

S = is a constant defined as the degree of association between the component molecules and is very similar to the interaction coefficient in other equations. It is calculated from the following relationship:

$$S = [\frac{M_1(\ln\mu_1 - \ln \mu_2)}{\ln \mu - \ln \mu_2} - M_1] \frac{1}{M_2}$$

Blok (67) has critized the theoretical assumptions that led to this expression.

C. The Ganguly and Chakrabertty Equation (30)

$$\ln \mu = \ln \mu_1 + C_1M_2 + C_2$$

where

μ_1 = absolute viscosity of component 1

M_2 = mole fraction of component 2

C_1 and C_2 are constants

This equation is deduced from the Andrade Equation (68) and later was extended by the same authors (30) to have a density form (Family 3A eq. 1).

D. The Glasstone, Laidler and Eyring Equation (50)

$$\mu = \frac{hN}{V} \exp \frac{\Delta F^{\ddagger}}{RT}$$

where

h = Plank's constant

N = Avogadro's number

R = the gas constant

V = the molar volume

$\Delta F^{\ddagger}$ = the standard free energy activation per mole, often replaced by ΔG^*, the excess Gibbs molar free energy of activation.

This equation is derived by statistical mechanics from the reaction rate. When it is applied to mixtures it becomes:

$$\mu = \frac{hN}{v_{12}} \exp\left(\frac{M_1\Delta F_1^{\ddagger} + M_2\Delta F_2^{\ddagger}}{RT}\right)$$

where

v_{12} = the average molar volume

$\Delta F_1^{\ddagger}, \Delta F_2^{\ddagger}$ = the energies of activation of the components are found from plotting ln μ as a function of 1/T or by using the following relationship using the latent heat of vaporization:

$$\Delta F^{\ddagger} = \frac{E_{vap}}{2.45}$$

More than six theoretical or semi-theoretical mixture equations are based on Erying's fundamental reaction law.

E. The Tuomikoski Equation (69)

$$\frac{\mu - \mu_i}{\mu} = 1 - \left(\frac{\left(\frac{V_1}{V_2}\right)^{V_1}}{V_1 \frac{V_1}{V_2} + V_2} \right)^p$$

where μ_i is the ideal viscosity, defined as:

$\mu_i = (\mu_1)^{v1}(\mu_2)^{v2}$

V_1 = volume fraction of component 1

V_2 = volume fraction of component 2

p = is a constant

According to Irving (21) this equation can not be used for associated or partly associated liquids.

F. The Roegiers and Roegiers Equation (70)

$$\mu = \mu_2 \left(\frac{\mu_1}{\mu_2}\right)^{\overline{w}}$$

where

$$\bar{w} = \frac{x_1\alpha}{x_1\alpha + x_2}$$

where

$x_1 = 1 - x_2$ and can be either weight, mole or volume fraction

α = is a constant. It is a blending factor (the equation was originally used with data on lubricating oil mixtures).

If the logrithms of this equation are taken, it is similar to the Lederer equation (66).

G. The Tamura and Kurata Equation (71)

$$\mu = M_1V_1\mu_1 + M_2V_2\mu_2 + 2(M_1M_2V_1V_2)^{1/2}C$$

where

C = is a constant

μ_1, μ_2 = absolute viscosities of components 1 and 2

M_1, M_2 = mole fraction of components 1 and 2

V_1, V_2 = volume fraction of component 1 and 2

This equation is semi-empirical and was recommended for mixtures where the difference in pure component viscosities is not large.

H. The Fried, Hala and Pick Equation (72)

$$\ln\mu = W_1\ln\mu_1 + W_2 \ln\mu_2 + W_1W_2[B+C(W_1-W_2)+D(W_1-W_2)^2 \ldots]$$

where

W_1 = weight fraction of component 1

W_2 = weight fraction of component 2

C = is a constant

The constants here are the coefficients of the power series expansion of $(W_1 - W_2)$.

I. The Roelands Equation (73)

The original form of the Roeland's equation is:

$$\log(\log\mu) = V_1 \log(\log \mu_1) + V_2 \log(\log \mu_2)$$

where

V_1, V_2 = volume fraction for components 1 and 2

μ_1, μ_2 = absolute viscosities for components 1 and 2

In deriving this form Roelands used Souders formula and assumed that Souders "I" obeys the additive law using the mole fractions. Also, he assumed that there is negligible volume change upon mixing. Later the same author developed another form of this equation.

$$\log(\log\mu + 1.2) = V_1 \log(\log \mu_1 + 1.2) + V_2(\log \mu_2 + 1.2) + V_1V_2C$$

where the terms are as above.

The constant C is evaluated by substituting values at 50% by volume, or by a fit over the whole range of concentration and optimizing C.

J. The Cullinan Equation (74)

$$\ln \mu = M_1 \ln \mu_1 + M_2 \ln \mu_2 + \ln\frac{\bar{\bar{V}}_A}{\bar{\bar{V}}_G}$$

where

M_1 = mole fraction of component 1

M_2 = mole fraction of component 2

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

$\overline{V}_A$ = is the arithmetic mean molar volume, defined as:

$$\overline{V}_A = M_1\overline{v}_1 + M_2\overline{v}_2$$

$\overline{V}_G$ = is the geometric mean molar volume, defined as:

$$\ln \overline{V}_G = M_1 \ln\overline{v}_1 + M_2 \ln\overline{v}_2$$

$\overline{v}_1$ and $\overline{v}_2$ are the molar volumes of pure components 1 and 2 defined as:

$$\overline{v}_1 = \frac{MW_1}{\rho_1} \text{ and } \overline{v}_2 = \frac{MW_2}{\rho_2}$$

This equation is based on statistical mechanics. Irving (21) reported that this equation is good for mixtures with no volume changes and no inflection points on the viscosity curve.

K. The Cokelet, Hollander and Smith Equation (75)

$$\mu = \mu_1 - \frac{M_2}{aM_2-b}$$

where

μ_1 = absolute viscosity of component 1

M_2 = mole fraction of component 1

a, b = constants to be evaluated from experimental data

L. The Mikhail and Kimel Equation (76)

$$\mu = \mu_2 + a_1W_1 + a_2W_2^2 + a_3W_1^3 + a_4W_1^4 + a_5W_1^5$$

where

μ_2 = absolute viscosity for component 2

W = weight fraction

a = constant of the power series

Mikhail and Kimel reported that using weight fraction for alcohol water mixtures produced a better fit to the experimental data than mole fractions.

Irving (21) commented the following on this family:

> The Glasstone, Laidler and Erying equation is the most significant one among the equations of this family, because it served as the parent equation of many others. The Roelands equation is applicable to mineral oil mixtures. The Tamura and Kurata equation has general applications and is more reliable than other equations of its type (p 27).

VII. Seventh Family: Group Contribution equations - This type of equation will be discussed in Chapter III. Examples of this family are the Ratcliff and Khan equation (83) and this work which is based on the Ratcliff et al. work.

As seen from this quick survey, there is no general equation that can predict the viscosities of different mixtures. This author believes that the last family of equations, namely Group Contribution Family, has the potential for general applicability to predict mixture viscosity. It is not limited to binaries as is the case for most of the previous equations. It is capable of handling multiple and multicomponent systems as well. It is capable of handling different kinds of components such as straight chains, branched chains, polar mixtures, non-polar mixtures, ..., etc. So this family of equations has the potential for general applicability if the temperature effect on mixture viscosity is incorporated. Experimental data covering wide ranges of temperature and concentration are needed to generate the group constants.

Once the group constants are generated, they are used to predict the viscosity of other mixtures consisting of the same groups for which data are either, not readily available or not existing at all.

CHAPTER III

MODEL DEVELOPMENT

Theoretical Background

Any solution is made up of components. These components are made up of chemical groups such as CH_3, CH_2, CO, COOH, OH, NH, etc. According to the theory of group contributions, these groups are the major contributors to the physical, thermophysical and thermodynamic properties of pure components and mixtures.

The number of pure components which now exists is very large. The number of mixtures which are combinations of these pure components is still larger. However, the number of groups that constitutes these compounds is relatively small. If the different properties of the components in the mixtures are related to group behavior or contributions, then a relatively small number of parameters need be generated. These parameters may be used to predict the properties correlated covering large numbers of mixtures containing the same groups.

The concept of correlating and then predicting the properties of mixtures from group contributions is not new. It goes back to Langmuir (77) in the early 1920's. He stated that in a liquid solution of polymeric molecules, it is not the interactions of molecules, but the interactions of functional groups comprising the molecules which are important. Significant progress in this direction has been made since the two independent publications of both Flory and Huggins (78, 79) in 1940. They used quasi-lattice theory to derive an expression for the entropy of mixing in a thermal solution. They discovered a size effect contribution to the excess free energy of mixing. Recent work has showed the residual free energy can nearly be correlated in terms of group contribution. Bronsted et al. (80) in 1946 formulated the principle of congruence which states that, at constant temperature and pressure, the properties of a mixture of hydrocarbon chain molecules from a given homologous series depend only on the average chain length of the mixture.

Lima (62) in 1951 (his equation was discussed earlier) used the Souders viscosity constant I which was calculated from the atomic and structural contributions for pure components to predict mixture viscosities. Griest et al. (81) in 1958 concluded from their study that viscosity is an additive function of the constituent groups, independent of whether these parts are combined in the same or different molecules as long as the basic molecular symmetry is unchanged. Dixon (82) also concluded in 1959 that the difference in viscosities, densities and refractive indices could be attributed to a fundamental difference in the behavior of molecules having rotational barriers at the bonds between adjacent branched carbon atoms.

All of these authors either showed or hinted that viscosity is a function of structural groups. Their observations and hints fell short of proposing a law to state how the groups contribute to viscosity.

Heric and Coursey (103) used the congruence concept and extended it to the viscosity of n-hexadecane and 1-n-chloralkane mixtures. To account for the presence of the chloride group the authors resolved the excess Gibbs free energy into contributions related to chain length and contributions related to chlorine concentration. To evaluate the effect of chlorine concentration, they compared mixtures of n-hexadecane and n-alkanes to mixtures of n-hexadecane and other halides at indentical n-hexadecane molar concentrations. As seen from the work of Ratcliff et al. (83), the principle of congruence is a method available when dealing with mixtures of homologous series. When different types of molecules are mixed, the method becomes complicated. Ratcliff and Khan (83) explicitly proposed a group solution model to predict the excess viscosity. This model was used by Wedlake (84, 85) and extended to cover multigroup binaries.

Ratcliff - Khan - Wedlake Model

Their group solution model considers the liquid state to be a mixture of structural groups rather than molecules. Interactions between these basic units are hten assumed to contribute to the overall properties of the mixture. The model defined an ideal viscosity equation and then accounted for the excess viscosity due to non-ideality. The model does not differentiate between intermolecular and intramolecular interactions. It attributes the effects to the manner in which the groups are joined together to form molecules. In the original version, Ratcliff and Khan (83) restricted their work to n-alcohol/n-alkane and n-alcohol/water mixtures where interactions between parts of like and unlike molecules are nearly identical. The original version of the model was for constant temperature. Wedlake (84) expanded it to cover a range of temperatures between 10-40°C. He also differentiated between CH_3 and CH_2 groups which was not done before, and generalized it to cover multi-groups in binary systems. The details of the formulation of the model are discussed below.

The Group Solution Model

The viscosity of any mixture is defined as the ideal mixture viscosity plus some excess viscosity due to non-ideality. Ratcliff et al. (83) defined an ideal mixture as one where the interactions between the different groups of the mixture are alike. The viscosity of an ideal mixture is defined as:

$$(\ln \mu)_{ideal} = \Sigma x_i \ln \mu_i$$

For a real mixture the viscosity is defined as:

$$(\ln \mu)_{mixture} = (\ln \mu)_{ideal} + \beta$$

β is the excess viscosity. It is the correction for nonideality which depends on the groups present, their concentrations, and their sizes. It can be split into two parts:

$$\beta = \beta^S + \beta^G$$

where β^S = the structural contribution

β^G = the group contribution

Ratcliff et al. (83, 85) defined the structural contribution as

$$\beta^S = \Sigma x_i \beta_i^S$$

where

$$\beta_i^S = \frac{A}{\overline{MW}} (N_i - \overline{N})^2$$

or $\beta^S = \frac{A}{\overline{MW}} \Sigma x_i (N_i - \overline{N})^2$

where A = a constant

$\overline{MW}$ = average molecular weight of the mixture $= \Sigma x_i MW_i$

$\overline{N} = \Sigma x_i N_i$

N_i = total number of groups in molecular species i

The group contribution β^G is defined as:

$$\beta^G = \Sigma x_i \beta_i^G$$

and

$$\beta_i^G = \sum_k N_{ki} (B_k - B_{ki}^*) =$$

where

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

B_k = the individual gropus making molecular species i and defined as $B_k = b_{ki} \chi_{ki}$

B_{ki}^* = is the standard state value of B_k at a group composition corresponding to pure i:

$$B_k = B_k(\chi_1, \chi_2, \ldots, \chi_k, T, P)$$

Wedlake and Ratcliff (85) assumed that at a given temperature and pressure, the B's depend only on the group composition and not on how the groups are joined into molecules. Later Wedlake (84) stated that B_k's depend on the group composition χ_k and on individual group contributions arise out of binary group interactions.

The group fraction χ_k of group type k is defined in the same way as a mole fraction, i.e.,

$$\chi_k = \frac{\sum_i x_i N_{ki}}{\sum_k \sum_i x_i N_{ki}}$$

where x_i = mole fraction of component i

N_{ki} = number of active groups of type k in component i

Wedlake's contribution to the model was his differentiation between CH_3 and CH_2. He also extended the model to the prediction of multigroup binary mixture viscosities. He differed from Ratcliff and Khan (83) by presenting the structural contribution as follows:

$$\beta^S = \frac{a_0 x_1 x_2}{\overline{MW}} \left[\ln\left(\frac{\mu_1}{\mu_2}\right)\right]^2$$

where a_0 = constant for fixed temperature and pressure

$\overline{MW}$ = average molecular weight

x_1 = mole fraction of component 1

x_2 = mole fraction of component 2

μ_1 = absolute viscosity of component 1

μ_2 = absolute viscosity of component 2

He defines B_k as:

$$B_k = \sum_i a_{kL} \chi_k \chi_L$$

where a_{kL} = constant assumed to be independent of group composition but dependent on temperature and pressure arises out of binary group interaction. It is defined as:

$$a_{kL} = a'_{kL} + \frac{a''_{kL}}{T}$$

a'_{kL}, a''_{kL} = constants

T = absolute temperature

k = active group of type k

L = active group for type L

His term for the group contribution becomes:

$$\beta^G = \sum_i x_i \sum_k N_{ki} \sum a_{kL}(\chi_k \chi_L - \chi^*_{ki} \chi^*_{Li})$$

where x_i = mole fraction of component i

N_{ki} = number of active groups of type k in component i

χ_k = group fraction of active group type k

χ_L = group fraction of active group type L

i = component i

k = active group of type k

χ^*_{ki} and χ^*_{Li} represent the standard state value of B_k at a group composition corresponding to pure molecular i.

Summary of This Work

The structural contribution was expressed as in the original modification of Ratcliff and Wedlake (85) and did not follow Wedlake modification (84), i.e.:

$$\beta^S = \frac{A}{\overline{MW}} \Sigma x_i (N_i - \overline{N})^2$$

where A = structural constant

$\overline{MW}$ = average molecular weight defined as:

$$\overline{MW} = \Sigma\, x_i\, MW_i$$

MW_i = molecular weight of component i

x_i = mole fraction of component i

N_i = total number of groups in component i

$\overline{N}$ = average number of groups defined as:

$$\overline{N} = \Sigma x_i N_i$$

"A" the structural constant need not be precise, so it was generated once from alkane-alkane mixtures and was used for all the mixtures. Generating different A's for different systems was not justified. Goswamy (86) stated that contributions are not affected significantly by structure. Table IX shows that the structural contribution has far less weight than the group contribution in the predicted viscosity.

The group contribution β^G was defined as follows:

$$\beta^G = \sum_i x_i \sum_k N_{ki}(B_k - B_{ki}^*)$$

where x_i = mole fraction of component i

N_{ki} = number of groups of type k in component i

B_k = the individual groups that make up component i, defined as:

$$B_k = \Sigma b_{ki} \frac{\sum_i x_i N_{ki}}{\sum_k \sum_i x_i N_{ki}}$$

B_{ki}^* = the value of B_k at a group composition corresponding to pure molecular i

$$B_{ki}^* = \Sigma b_{ki} \frac{\Sigma N_{ki}}{N_i}$$

b_{ki} = constants of the expanded power series of $\frac{\sum_i x_i N_{ki}}{\Sigma\Sigma x_i N_{ki}}$ and $\frac{\Sigma N_{ki}}{N_i}$ respectively

To account for temperature effects, the coefficients of the expanded power series of B_k and B_k^* were related to the absolute temperature. The final form of the liquid mixture viscosity equation is as follows:

$$\mu = \exp[\sum_i x_i \ln\mu_i + \beta^S + \beta^G]$$

or

$$\mu = \exp[\Sigma\, x_i \ln\mu_i + \frac{A}{MW} \Sigma\, x_i(N_i - \overline{N})^2 + \sum_i x_i \sum_k N_{ki}(B_k - B_{ki}^*)]$$

where

$$B_k = b_{ki} \frac{x_i B_{ki}}{\sum\sum_{ki} x_i N_{ki}}$$

$$B_{ki}^* = b_{ki} \frac{N_{ki}}{N_i}$$

and all the terms are defined as above.

CHAPTER IV

RESULTS AND DISCUSSION

The functional relationship between the coefficients of the structural contribution, or the group contribution, and temperature was established by the following procedure. The experimental viscosity data were regressed at constant mole fraction and at different temperatures using a nonlinear least-square fitting subroutine, MARQ, written by Chandler (102) to find the optimal constants. By plotting the generated constants as function of temperature, a functional behavior was established.

Temperature was included in the viscosity function by substituting the structural and the group coefficients by the functional relationship. Regressing the experimental data again with the mentioned substitution generated constants for the structural contribution and constants for each active group. To generate constants for new active groups, the experimental data of the new groups were regressed while the structural constants and the previously determined active group constants were held constant. For example, experimental viscosities of some alkane-alkane mixtures were regressed and two structural constants were generated. Constants for CH_3 and constants for CH_2 groups were generated also. When alcohol-water mixtures were introduced, their experimental viscosities were regressed while the structural constants and the CH_3, CH_2 constants were held constant and the constants for the OH group were generated.

The same procedure was followed in generating the other active groups constants. Once the constants were generated, they were used in a computer program for predicting viscosity of mixtures consisting of the same type of groups. The input data needed for the predictive program besides the constants are pure components viscosities, components mole fractions, components molecular weights, number of active groups and temperature.

The model was applied to thirty-eight mixtures covering eight groups. The mixtures were alkane-alkane, alkane-alcohol, alchol-alcohol, alcohol-water, ethanolamine-water, carboxylic acids, ketones and some other miscellaneous mixtures as ethylene glycol-water, formamide-water and formamide-diethyl formamide. The groups covered were CH_3, CH_2, CO, COOH, OH, NH_2, NH and N.

Generating structural constants for each family of mixtures was not justified and structural constants generated from alkane-alkane mixtures were used for all the families. Table I shows the active groups and their constants.

The number of data points, temperature range, absolute average deviation, maximum positive and negative deviations, and overall absolute deviation for each family are summarized in Tables II to VII. Mixtures with asterisks were predicted by using the generated constants.

The percent deviation was defined as:

$$PDEV = [(EXP - Calc)/EXP] \times 100$$

TABLE I

ACTIVE GROUPS AND THEIR CONSTANTS

Structural Constants	CH_3	CH_2	CO	COOH	OH	NH_2	NH	N
-0.9411	-4.2411	0.5646	5.7590	5.2427	5.8572	15.1062	-16.3025	65.8619
	10.5310	-1.0889	5.4169	-8.0309	-4.0657	1.7834	-111.3089	-45.4972
	-11.1663	-0.4917	-20.9713	-1.5901	-0.7103	-42.3575	-19.9408	-12117.9800

where

PDEV = point percent deviation
EXP = experimental viscosity in cp
Calc = calculated viscosity in cp

The maximum positive deviation percent was defined as the percent deviation whose value was the largest positive deviation among the total number of points regressed or predicted. The maximum negative deviation percent was defined as the percent deviation whose value was the largest negative deviation among the total number of points regressed or predicted. The absolute average deviation was defined as:

$$\mathrm{AADEV} = \Sigma \frac{|\mathrm{PDEV}|}{\mathrm{NPTS}}$$

where

AADEV = absolute average deviation
PDEV = point percent deviation
NPTS = total number of data points

The overall absolute average deviation for the regressed systems was defined as:

$$\mathrm{OAADEV} = \frac{\Sigma \mathrm{AADEV}}{\mathrm{NS}}$$

where

OAADEV = overal absolute average deviation
AADEV = absolute average deviation
NS = total number of systems regressed simultaneously

Table II shows alkane-alkane mixtures with temperature ranging between 50.0°F (10°C) and 131°F (55°C). The absolute average deviation is as low as 0.98% for n-pentadecane-n-hexane and as high as 3.04 for n-hexane-n-dodecane. The maximum deviation for any data points is 14.05% for the n-hexane-n-dodecane system. It occurs at 131°F (55°C) and at 0.935 mole fraction of n-hexane (0.065 mole fraction of n-dodecane). The overall absolute average deviation is 2.16 for all alkane-alkane data sets.

Table III shows the comparison of alkane-alcohol mixtures. Mixtures shown without asterisks are the mixtures used for generating the group constants, while those with asterisks are the mixtures predicted. Temperature for all the alkane-alcohol mixtures ranges between 50°F (10°C) and 104°F (40°C). The absolute average deviation runs between 1.17% for the predicted viscosity of ethanol-n-hexane systems and 7.04% for the predicted n-octanol-n-nonane system. Maximum positive deviation is 7.95% for n-dodecane-ethanol system. It occurs at 50°F (10°C) and 0.164 mol fraction of n-dodecane. Maximum negative deviation is 18.76% for the predicted system n-octanol-n-nonane. It occurs at 50°F (10°C) and equimolar of n-octanol and n-none.

Table IV shows the results for alcohol-water mixtures. The mixtures without asterisks are mixtures used in regression, while those with asterisks are those predicted. The temperature ranges between 32°F (0.0°C) and 212°F (100°C). The absolute average deviation is as low as 2.23% for the methanol-water mixture and as high as 6.36% for the ethanol-water mixture. The overall absolute average deviation for all systems is 3.8%. The maximum negative deviation is 30.0% for the

TABLE II

ALKANE AND ALKANE MIXTURES

Mixture	No. of Points	Temperature Range °K	Abs. Av. Dev. %	Max. + Dev. %	Max. - Dev. %	Ref.
N-Pentadecane + N-Hexane	24	283.14 - 313.15	0.98	3.36	-0.81	90
N-Hexane + N-Dodecane	33	298.15 - 328.15	3.04	14.05	-3.37	90,99
N-Pentadecane + N-Nonane	27	283.15 - 313.15	2.47	4.64	0.00	90

Overall absolute average Deviation = 2.16

TABLE III

ALKANE AND ALCOHOL MIXTURES

Mixture	No. of Points	Temperature Range °K	Abs. Av. Dev. %	Max. + Dev. %	Max. - Dev. %	Ref.
Ethanol + N-Hexane*	21	283.15 - 313.15	1.170	2.65	-2.80	90
N-Dodecane + Ethanol	22	283.15 - 313.15	3.330	7.95	-9.70	90
N-Nonane + Ethanol	21	283.15 - 313.15	3.013	0.73	-8.76	90
N-Pentanol + N-Hexane	27	283.15 - 313.15	6.170	0.00	-15.30	90
N-Dodecane + N-Pentanol*	24	283.15 - 313.15	5.920	0.00	-11.77	90
N-Octanol + N-Hexane*	21	283.15 - 313.15	5.370	0.00	-14.74	90
N-Octanol + N-Nonane*	21	283.15 - 313.15	7.040	0.00	-18.76	90
N-Pentadecane + N-Octanol	21	283.15 - 313.15	5.640	0.00	-12.39	90

Overall absolute average deviation = 4.54

TABLE IV

ALCOHOL AND WATER MIXTURES

Mixture	No. of Points	Temperature Range °K	Abs. Av. Dev. %	Max.+ Dev. %	Max.- Dev. %	Ref.
Methanol + Water	32	273.15 - 373.15	2.23	13.25	-2.22	92,96,99
Ethanol + Water	39	273.15 - 373.15	6.36	17.05	-18.93	93,96,99
Water + N-Propanol	33	273.15 - 373.15	4.07	8.09	-16.70	94,96
Iso-Propanol + Water*	121	273.15 - 373.15	4.71	15.65	-30.78	94,96
Water + N-Butanol	30	273.15 - 373.15	2.56	7.80	-9.12	95,96
Iso-Butanol + Water*	20	273.15 - 373.15	2.84	13.05	-3.85	95,96

Overall absolute average deviation 3.8%

predicted iso-propanol-water system. It occurs at 212°F (100°C) and 0.1 mole fraction of iso-propanol. The maximum positive deviation is 17.05%. It occurs in ethanol-water system at 77°F (25°C).

Table V shows results for ketone mixtures and carboxylic acid mixtures. The temperature ranges between 32°F (0.0°C) and 122°F (50°C). The absolute average deviation is as low as 7.47% for the n-butyric acid - acetone mixture and as high as 27.09% for the methyl propyl ketone - acetone mixture. The overall absolute average deviation is 9.17% for carboxylic acid mixtures, while it is 18.3% for ketone mixtures. Maximum positive deviation is 36.85% for acetic acide-water system and it occurs at 0.73 mole fraction of acetic acid at almost all the temperatures. That raises the suspicion that the data for 0.73 mole fraction - may be in error. The maximum negative deviation is 47.9%. It occurs in the methyl propyl ketone - acetone system at 0.4 mole fraction of methyl 1 propyl ketone.

Testing the experimental data for consistency shows that significant errors are in some of the systems such as acetic acid-water and methanol-acetone.

Table VI shows the results for ethanolamine-water mixtures. The temperature ranges between 100°F (37.78°C) and 450 °F (232.22°C). The absolute average deviation runs between 3.88% and 18.88% for the regressed systems. The overall absolute average deviation for the regressed systems is 11.1%. The maximum positive deviations for the aqueous monoethanolamine, diethanolamine and triethanolamine are 49.65%, 35.28% and 16.98% respectively. The maximum negative deviations are 0.0% for both aqueous monoethanolamine and diethanolamine while it is 4.77% for aqueous triethanolamine.

TABLE V

KETONES AND CARBOXYLIC ACID MIXTURES

Mixture	No. of Points	Temperature Range °K	Abs. Av. Dev. %	Max. + Dev. %	Max. - Dev. %	Ref.
N-Butyric Acid + Acetone	33	298.15 - 318.15	7.47	9.48	-17.780	99
Acetic Acid + Methyl Ethyl Ketone	33	298.15 - 318.15	10.34	14.93	-12.580	99
Acetic Acid + Methyl Propyl Ketone	33	298.15 - 318.15	8.54	9.63	-22.804	99
Acetic Acid + Acetone	44	298.15 - 323.15	4.60	9.93	-10.030	99
Acetic Acid + Water	132	288.15 - 368.15	14.90	36.85	-43.910	100
Overall absolute average deviation = 9.17%						
Methanol + Acetone	58	273.15 - 318.15	17.74	38.22	-23.010	99
Acetone + Water	68	293.15 - 323.15	17.15	1.88	-42.160	101
Methyl Ethyl Ketone + Acetone	22	293.15 - 313.15	11.23	0.00	-19.910	99
Methyl Propyl Ketone + Acetone	22	293.15 - 313.15	27.09	0.00	-47.990	99
Overall absolute averaage deviation = 18.3%						

TABLE VI

ETHANOLAMINE AND WATER MIXTURES

Mixture	No. of Points	Temperature Range °K	Abs. Av. Dev. %	Max.+ Dev. %	Max.- Dev. %	Ref.
Monoethanol Amine + Water	20	310.93 - 477.59	18.88	49.65	0.0	98
Diethanol Amine + Water	20	338.71 - 505.37	10.43	35.28	0.0	98
Triethanol Amine + Water	20	338.71 - 505.37	3.88	16.98	0.0	98

Overall absolute average deviation = 11.1%

Testing the data for consistency shows that at high temperature extrapolation took place. This extrapolation is beyond the range of the experimental data.

Table VII shows miscellaneous mixtures. The temperature ranges between 50°F (10°C) and 104°F (40°C) for alcohol-alcohol mixtures and the overall absolute average deviation is 2.32%. For formamide-diethylformamide the temperature range is 77°F (25°C) to 167°F (75°C) and the absolute average deviation is 3.02%. The maximum positive deviation is 6.64% and the maximum negative deviation is 9.97%. The absolute average deviation for aqueous formamide over a temperature range of 77°F (25°C) and 104°F (40°C) is 17.71%. The maximum positive deviation is 27% and the maximum negative deviation is 52.9%.

Testing for consistency shows that experimental data for aqueous formamide are not consistent.

Table VIII shows the structural contribution (STCN) and the group contribution (GRCN) in predicted mixture viscosity of the ethylene glycol-water system. The table shows that the structural and the group contributions (the corrections for non-ideality) account for as high as 85% of the total predicted value. The table shows that the structural contribution by itself accounts for less than 5% of the total contribution. This explains why generating the structural constants for each family of mixtures is not required.

The model was tested for low temperature range, for high temperature range and for branching. Table IX shows predicted viscosity results for the ethanol-n-heptane mixture with temperature ranging from -52°C (223.0°K) to 69.85°C (343°K). For branching Table X shows the

TABLE VII

MISCELLANEOUS MIXTURES

Mixtures	No. of Points	Temperature Range °K	Abs. Av. Dev. %	Max. + Dev. %	Max. - Dev. %	Ref.
N-Propanol + Methanol	21	283.15 - 313.15	2.74	0.00	-6.87	90
N-Octanol + Ethanol	21	283.15 - 313.15	1.90	0.00	-6.90	90
Overal absolute average deviation			2.32			
Formamide + Diethyl Formamide	48	298.15 - 348.15	3.02	6.64	-9.97	100
Formamide + Water	22	298.15 - 313.15	17.71	27.00	-52.93	99

TABLE VIII

STRUCTURAL CONTRIBUTION (STCN) AND GROUP CONTRIBUTION (GRCN) WEIGHT IN PREDICTED MIXTURE VISCOSITY (VCALC) OF ETHYLENE GLYCOL AND WATER

MFR A	TEM K	VCALC	ST CN	GR CN
0.72300	295.04	11.63134	-0.04	0.39009
0.40400	299.21	5.24221	-0.06	0.69411
0.22500	300.48	3.02537	-0.07	0.70565
0.93400	301.85	12.44241	-0.02	0.09171
0.22500	305.98	2.54819	-0.07	0.67398
0.11100	309.48	1.48981	-0.04	0.50226
0.93400	319.69	6.61067	-0.02	0.07958
0.11100	322.76	1.08511	-0.04	0.45482
0.40400	329.48	2.11629	-0.05	0.54941
0.22500	332.76	1.28376	-0.06	0.55316
0.93400	339.49	3.76969	-0.02	0.06970
0.40400	344.21	1.51258	-0.05	0.50014
0.72300	345.98	2.42026	-0.03	0.26840
0.22500	356.82	0.80969	-0.05	0.47873
0.11100	360.54	0.54871	-0.03	0.36038
0.93400	364.77	2.14135	-0.01	0.06093
0.22500	369.21	0.66538	-0.05	0.44922
0.40400	371.93	0.91157	-0.04	0.43230
0.22500	376.98	0.59505	-0.05	0.43313
0.72300	396.48	0.98200	-0.02	0.21497
0.22500	399.76	0.44741	-0.04	0.39476
0.93400	402.73	1.13449	-0.01	0.05310
0.40400	404.37	0.58434	-0.04	0.38140
0.11100	417.87	0.28340	-0.02	0.28325
0.22500	421.93	0.35584	-0.04	0.36734
0.93400	433.89	0.76569	-0.01	0.04978
0.22500	435.93	0.31404	-0.04	0.35392
0.72300	447.76	0.54370	-0.02	0.19267
0.40400	451.37	0.36806	-0.03	0.34140
0.93400	462.41	0.57285	-0.01	0.04836
0.22500	463.32	0.25470	-0.04	0.33442
0.22500	470.93	0.24209	-0.03	0.33031
0.11100	473.54	0.18807	-0.02	0.24667
0.40400	474.04	0.31028	-0.03	0.33143
0.72300	500.54	0.35792	-0.02	0.18733
0.93400	502.08	0.40834	-0.01	0.04814

TABLE IX

PREDICTION OF ETHANOL AND N-HEPTANE MIXTURE VISCOSITY AT LOW TEMPERATURE

VEXPR	VCALC	MFR A	TEM K	PDEV
1.73200	2.59839	0.35210	223.00	-50.02250
3.75100	3.55008	0.59170	223.00	5.35645
6.40100	4.30982	0.76540	223.00	32.66953
6.88500	5.51145	0.89690	223.00	19.94984
1.21100	1.10131	0.35210	243.00	9.05759
1.69000	1.52052	0.59170	243.00	10.02869
3.23200	2.13353	0.76540	243.00	33.98744
3.68800	2.90310	0.89690	243.00	21.28262
0.78100	0.76913	0.35210	263.00	1.52033
1.17400	0.97911	0.59170	263.00	16.60050
1.68900	1.34646	0.76540	263.00	20.28083
2.15100	1.77923	0.89690	263.00	17.28366
0.55100	0.57252	0.35210	283.00	-3.90578
0.80300	0.68496	0.59170	284.00	14.69969
1.01200	0.92370	0.76540	283.00	8.72500
1.29000	1.18562	0.89690	283.00	8.09176
0.43000	0.44039	0.35210	303.00	-2.41538
0.56600	0.49570	0.59170	303.00	12.42071
0.69800	0.65234	0.76540	303.00	6.54197
1.86300	0.80903	0.89690	303.00	56.57389
0.33700	0.34971	0.35210	323.00	-3.77290
0.41700	0.37262	0.59170	323.00	10.64249
0.50000	0.47674	0.76540	323.00	4.65174
0.60600	0.57004	0.89690	323.00	5.93396
0.26800	0.28518	0.35210	343.00	-6.41153
0.31800	0.28896	0.59170	343.00	9.13184
0.37100	0.35871	0.76540	343.00	3.31375
0.44100	0.41293	0.89690	343.00	6.36532

AVE. ABSOLUTE PERCENT DEVIATION= 12.33035

TABLE X

PREDICTION OF ISO-BUTANOL AND WATER MIXTURE VISCOSITY

VEXPR	VCALC	MFR A	TEM K	PDEV
8.31700	8.31700	1.00000	273.15	0.00000
8.53300	8.62583	0.57900	273.15	-1.08790
2.65000	2.55260	0.01500	273.15	3.67565
1.75250	1.75250	0.00000	273.15	0.00000
4.03600	4.03600	1.00000	293.15	0.00000
3.80700	3.66018	0.57900	293.15	3.85663
1.32400	1.35999	0.01500	293.15	-2.71791
1.00150	1.00150	0.00000	293.15	0.00000
1.62600	1.62600	1.00000	323.15	0.00000
1.51700	1.37422	0.57900	323.15	9.41221
0.65900	0.68731	0.01500	323.15	-4.29646
0.54410	0.54410	0.00000	323.15	0.00000
0.78700	0.78700	1.00000	353.15	0.00000
0.76500	0.66525	0.57900	353.15	13.03981
0.40600	0.42242	0.01500	353.15	-4.04311
0.35090	0.35090	0.00000	353.15	-0.00000
0.52900	0.52900	1.00000	373.15	0.00000
0.51000	0.45494	0.57900	373.15	10.79706
0.31700	0.32920	0.01500	373.15	-3.84953
0.28000	0.28000	0.00000	373.15	-0.00000

AVE. ABSOLUTE PERCENT DEVIATION= 2.83881 prediction of mixture viscosity for the iso-butanol-water system over a temperature range of 0°C (273.15 °K) to 100°C (373.15°K).

There is no existing predictive technique that addresses itself to liquid mixture viscosity over a wide range of temperature, so experimental viscosity data were used for comparison. Wedlake (84) covers a range of temperature between 10°C (283.15°K) to 40°C (313.15°K). Table XI shows a comparison between this work and his in that range.

Generating reliable constants in this study lies on one major factor, reliable and consistent experimental data. In choosing such data when different sets are available the author used consistency tests developed by Fluid Properties Research Inc. at Oklahoma State University and his judgement supported by private communications (87, 106). When no options were present the consistency tests were conducted and the data were used. Samples of the data are presented in Figures 1-12.

Figure 1 shows predicted and experimental viscosities for the n-decane-n-heptane mixture as a function of temperature over a wide range of concentration. Deviation in this set of mixtures i.e., alkane-alkane mixtures occurs at low temperatures. Alkane-alkane mixtures do not exhibit maximum or minimum when viscosity is plotted as a function of mole fraction and Figure 2 shows that.

Figures 3 and 4 show predicted and experimental viscosities for the n-octanol-n-nonane mixture as a function of temperature and mole fraction. The maximum positive deviation occurs at low temperature (50°F or 10°C) and at approximately 0.6 mol fraction of n-octanol (0.4 of the alkane).

TABLE XI

VISCOSITY OF ETHANOL AND N-HEXANE MIXTURE AS PREDICTED BY THIS WORK AND WEDLAKE'S WORK

Mole Fraction "A"	Exp - Vis. cp	Predicted vis Using This Work		Predicted vis Using Wedlake (85)	
		cp	% Dev	cp	% Dev
0.1636	0.3664	0.3766	-2.780	0.3720	1.53
0.3329	0.4333	0.4379	-1.060	0.4297	0.16
0.4988	0.5460	0.5316	2.640	0.5292	3.08
0.6629	0.7094	0.6914	2.530	0.6974	1.69
0.8379	0.9794	0.9784	0.102	1.0055	-2.67
0.1636	0.3103	0.3182	-2.540	0.3140	-1.20
0.3329	0.3576	0.3625	-1.360	0.3550	0.73
0.4988	0.4380	0.4299	1.840	0.4262	2.69
0.6629	0.5561	0.5441	2.600	0.5460	1.82
0.8379	0.7517	0.7476	0.550	0.7639	-1.62
0.1636	0.2656	0.2725	-2.590	0.2680	-0.90
0.3329	0.2992	0.3049	-1.910	0.2971	0.70
0.4988	0.3565	0.3541	0.670	0.3484	2.27
0.6628	0.4426	0.4370	1.270	0.4345	1.83
0.8379	0.5860	0.5834	0.440	0.5912	-0.89
Absolute average deviation			1.66		1.59

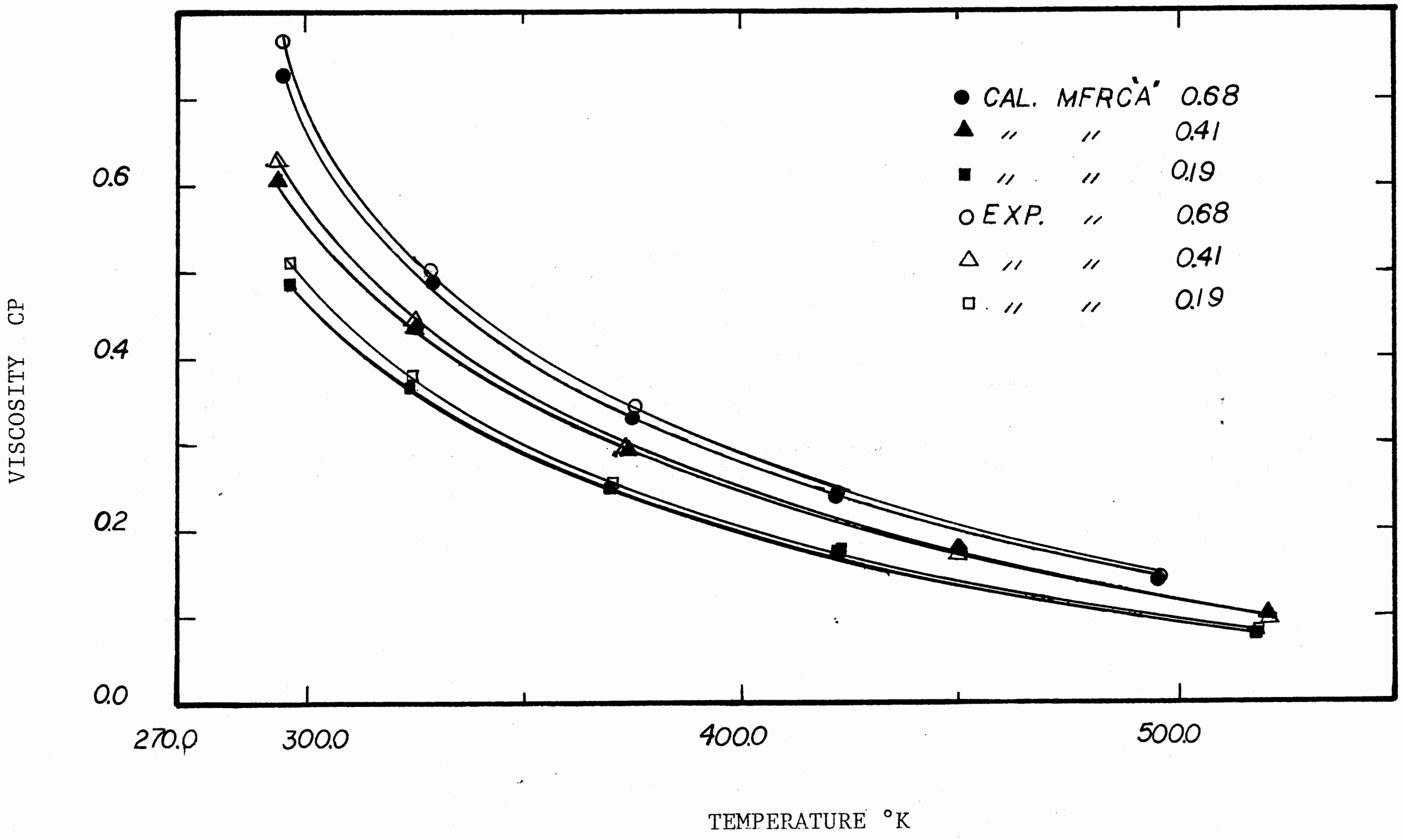


Figure 1. N-Decane (A) and N-Heptane (B) Mixture (vis-Temp)

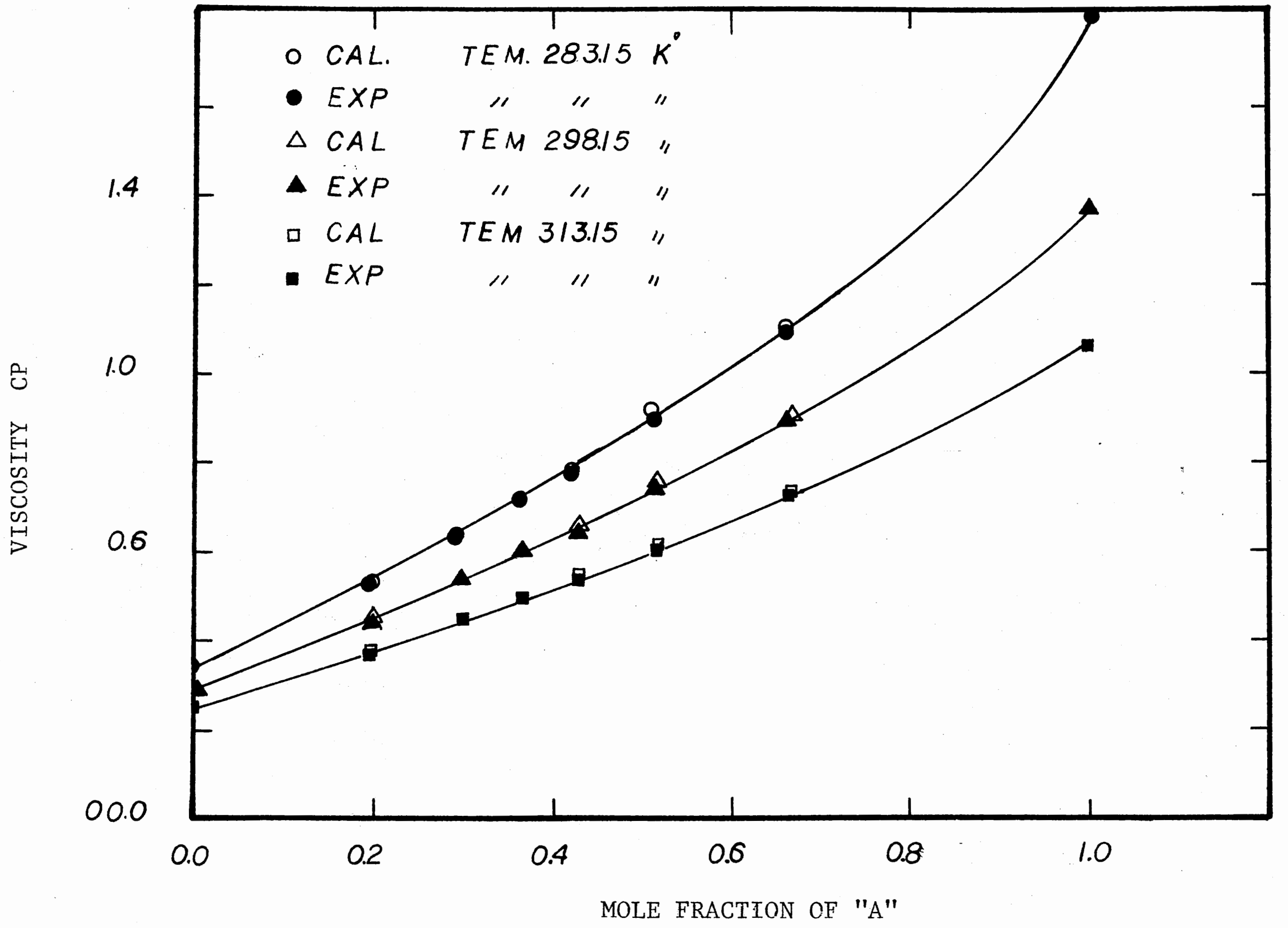


Figure 2. N-Dodecane (A) and N-Hexane (B) Mixture (vis-MFR "A")

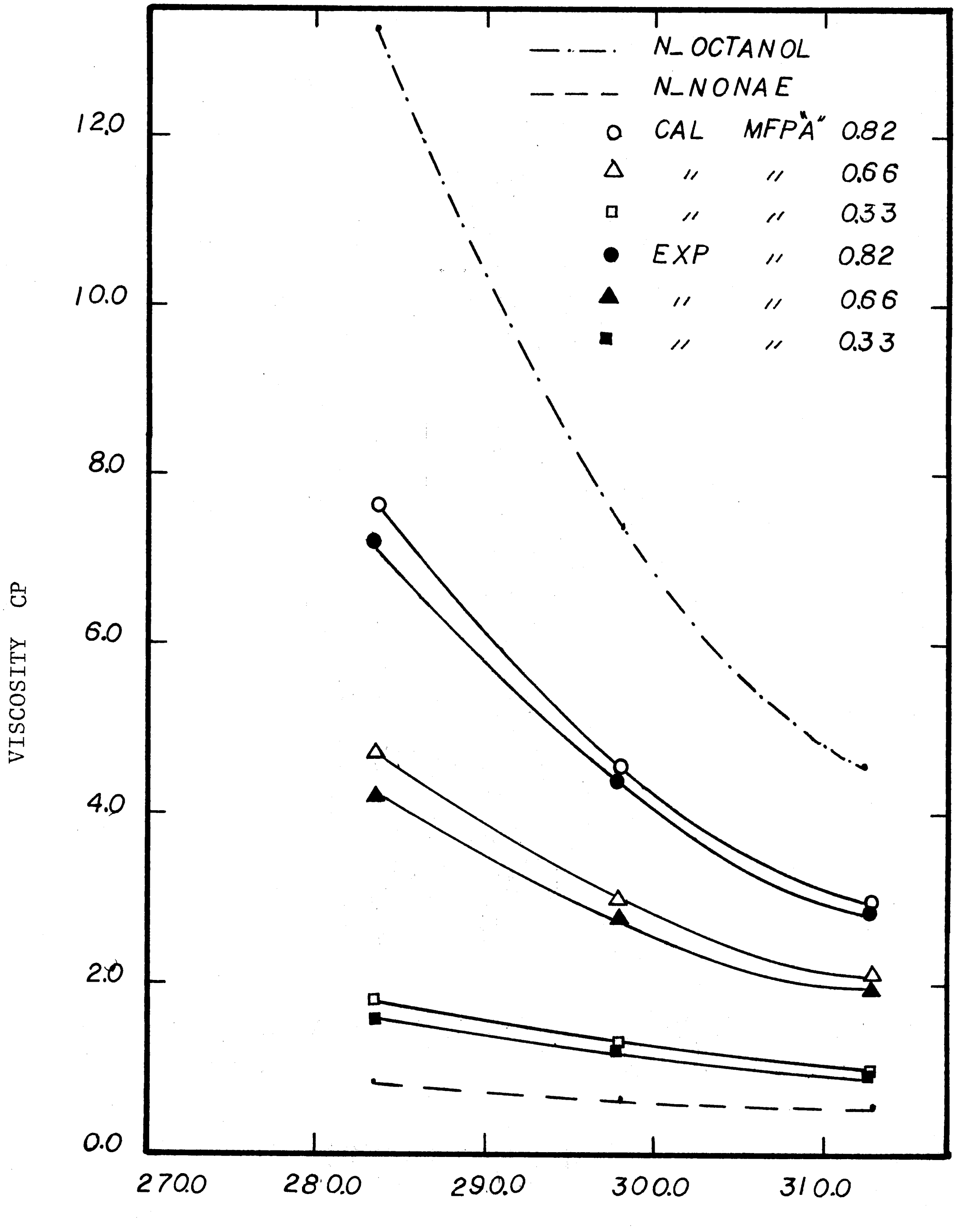


Figure 3. N-Octanol (A) and N-Nonane (B) Mixture (vis-Temp)

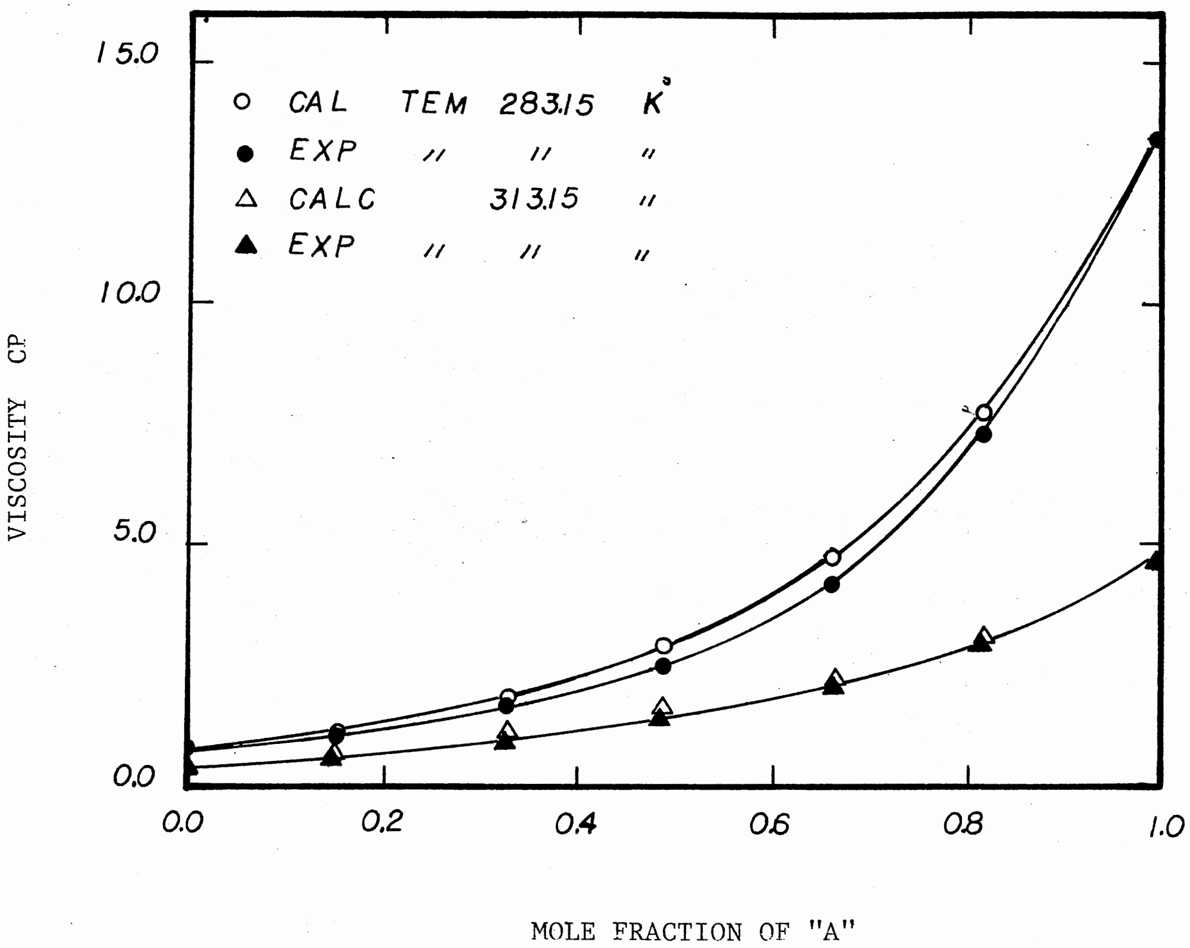


Figure 4. N-Octanol (A) and N-Nonane (B) Mixture (vis-MFR "A")

Figures 5 and 6 show the predicted and the experimental viscosities for the n-propanol-n-methanol mixture as a function of temperature and mole fraction. The maximum positive deviation occurs at low temperature (50°F or 10°C) and equimolar fraction of the two components.

Figures 7 and 8 show the predicted and experimental viscosities for the iso-propanol-water mixture as a function of temperature and mole fraction. The maximum positive deviation at 32°F (0.0°C) and at equal mole fractions of the two components. This type of mixture exhibits a maximum at low temperatures then this maximum levels off at high temperatures.

Figures 9 and 10 show the predicted and the experimental viscosities for the acetic acid-water mixture as a function of temperature and mole fraction. The viscosity goes through a maximum with composition. The maximum positive deviation occurs at 59°F (15°C) and approximately 0.2 mol fraction acetic acid. The maximum negative deviation occurs at 59°F (16°C) and approximately 0.8 mol fraction of acetic acid.

Testing the data for consistency shows that the 15°C data points are not good.

Figures 11 and 12 show the predicted and the experimental viscosities for the triethanolamine-water mixture as a function of temperature and mole fraction. The curves show maximum and minimum. Again, as in the previous systems, the deviation is shown to occur at low temperature. Here it is shown to occur at approximately 340°F (66.85°C) and 0.22 mole fraction of triethanolamine.

In summary maximum positive or negative deviations occur at extreme conditions; either at low temperature and/or concentrations or at high temperature and/or concentrations. When polar components are involved

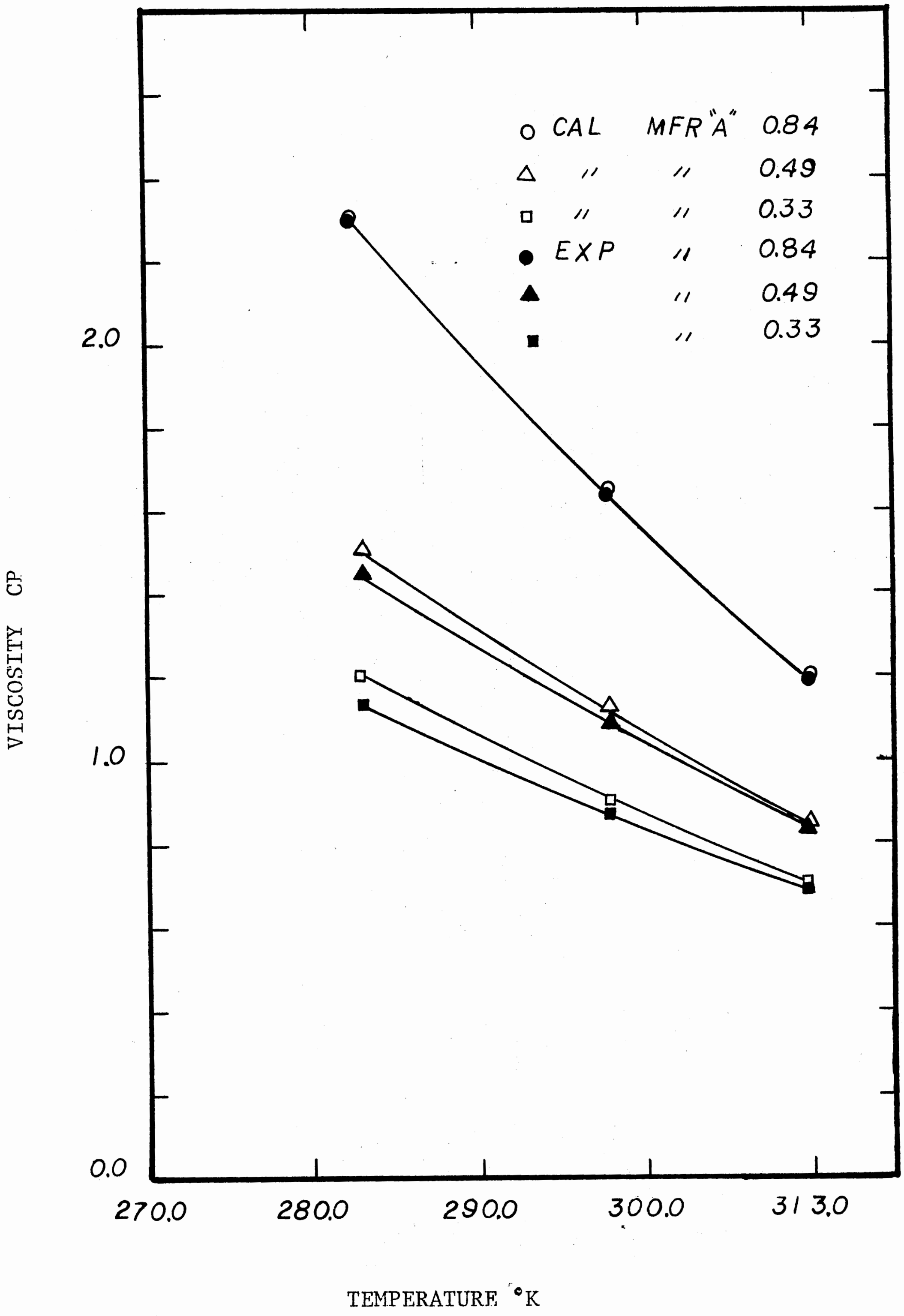


Figure 5. N-Propanol (A) and Methanol (B) Mixture (vis-Temp)

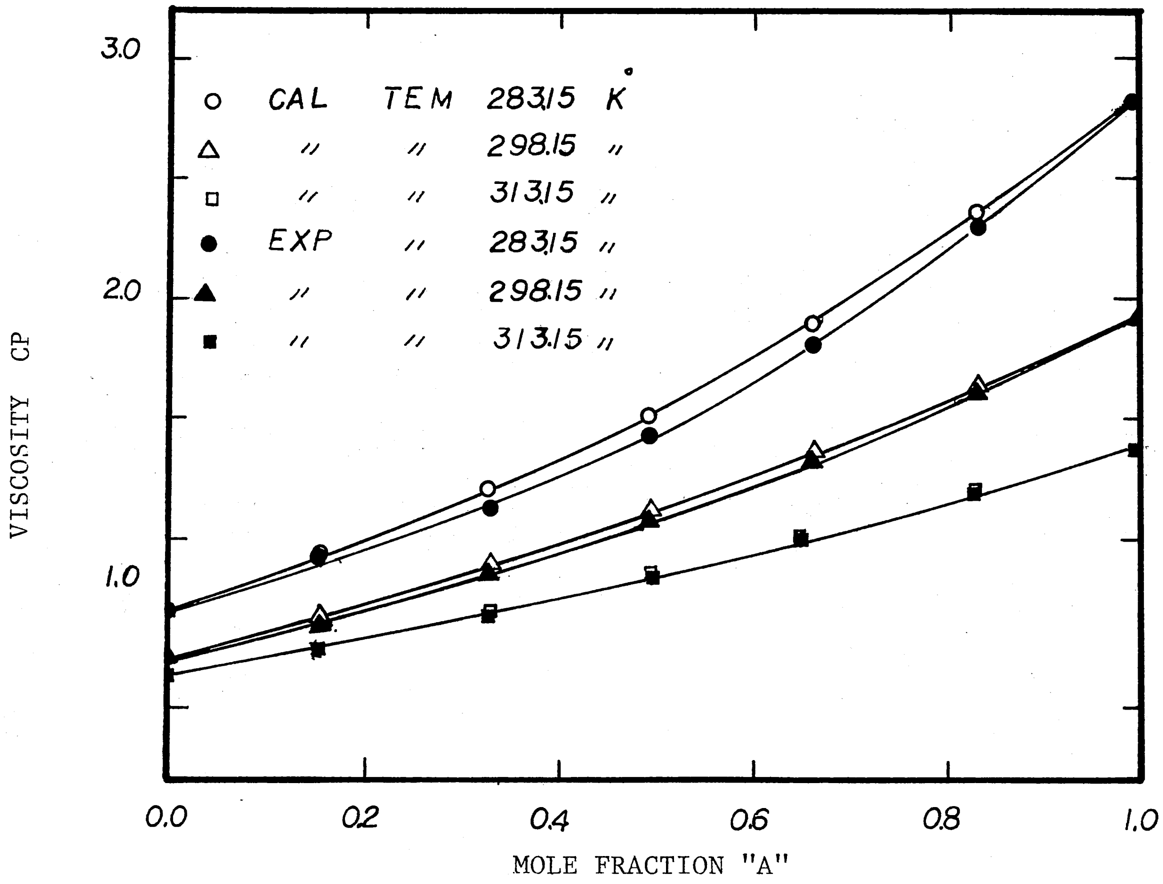


Figure 6. N-Propanol (A) and Methanol (B) Mixture (vis-MFR "A")

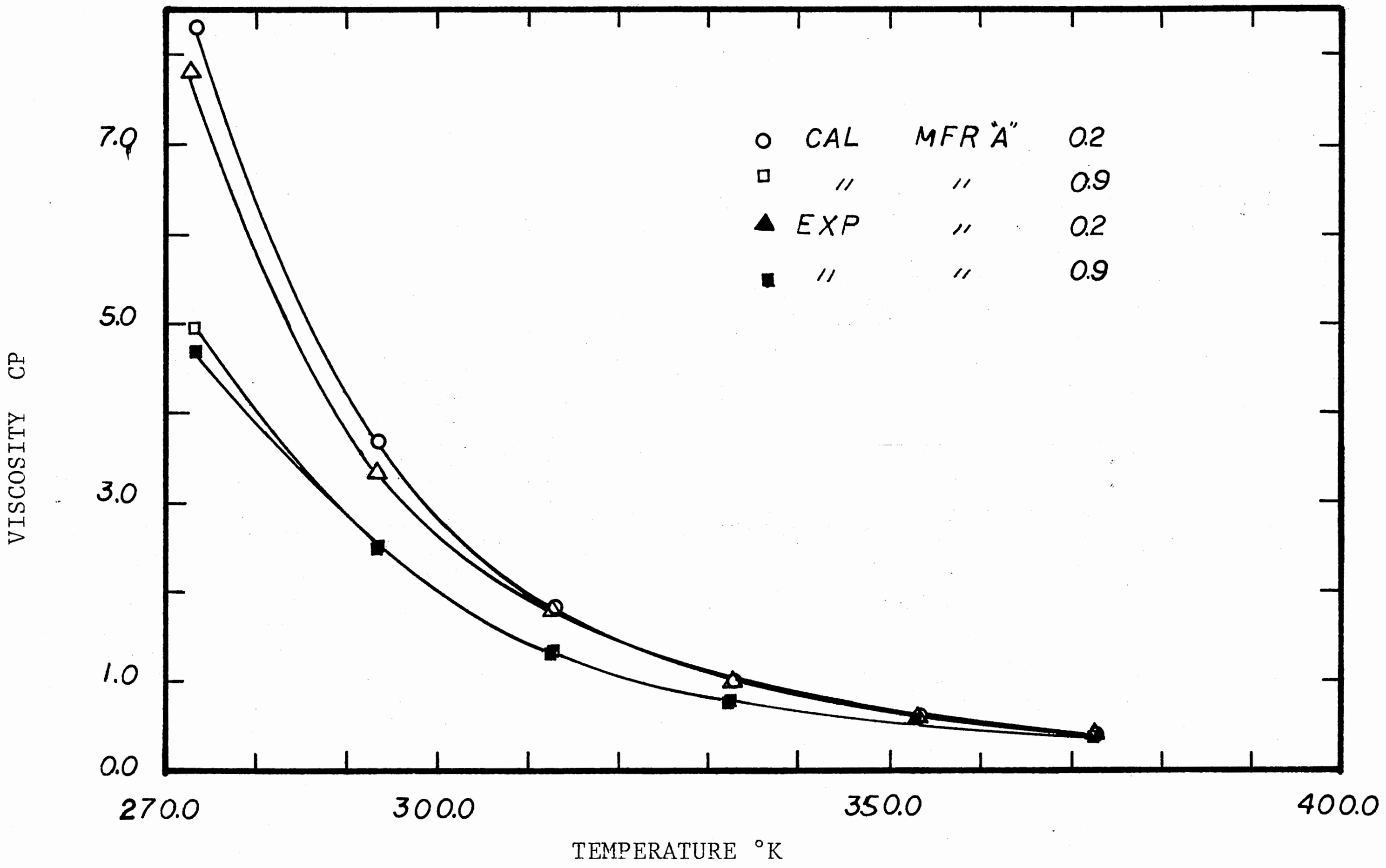


Figure 7. Iso-Propanol (A) and Water (B) Mixture (vis-Temp)

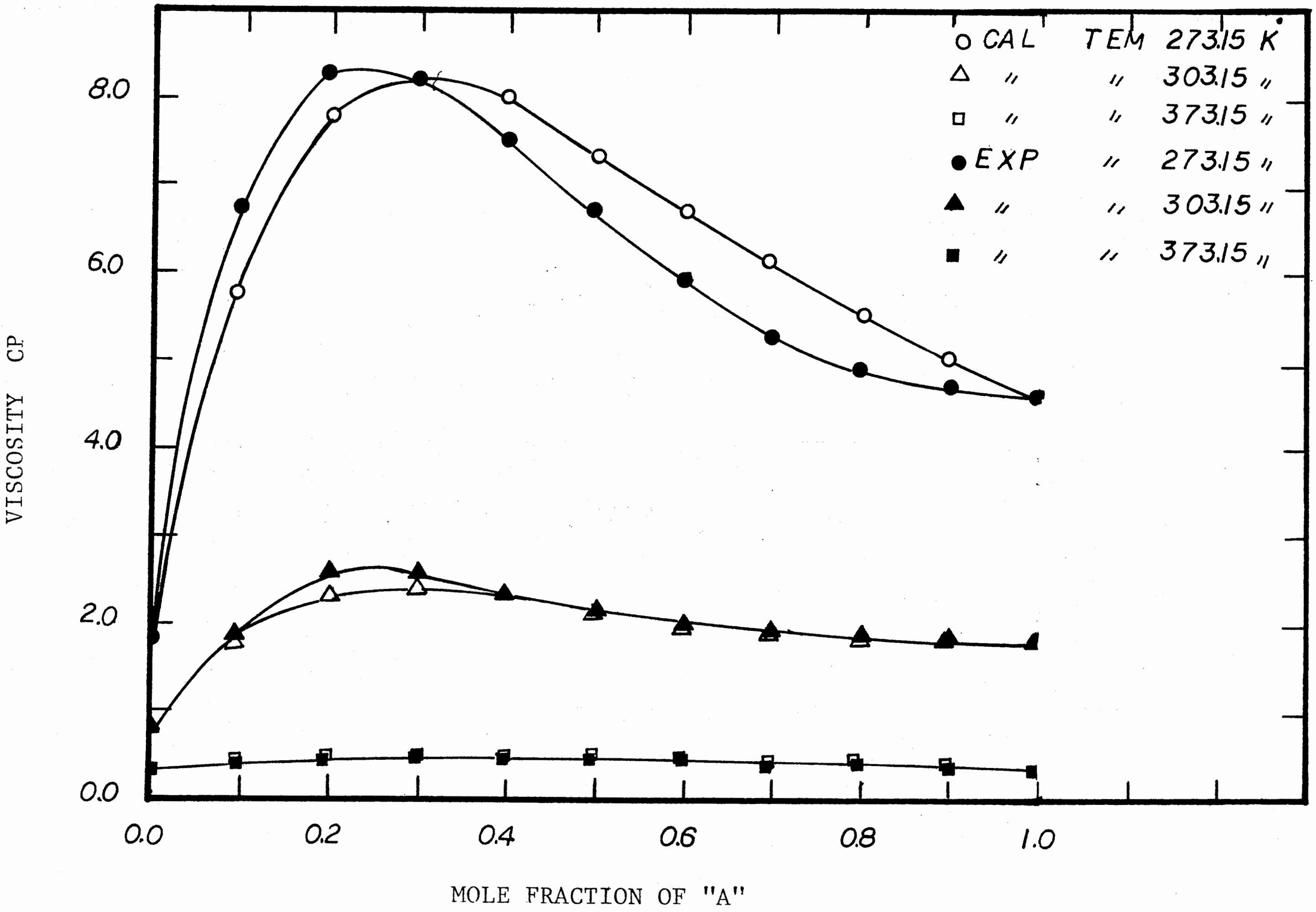


Figure 8. Iso-Propanol (A) and Water (B) Mixture (vis-MFR "A")

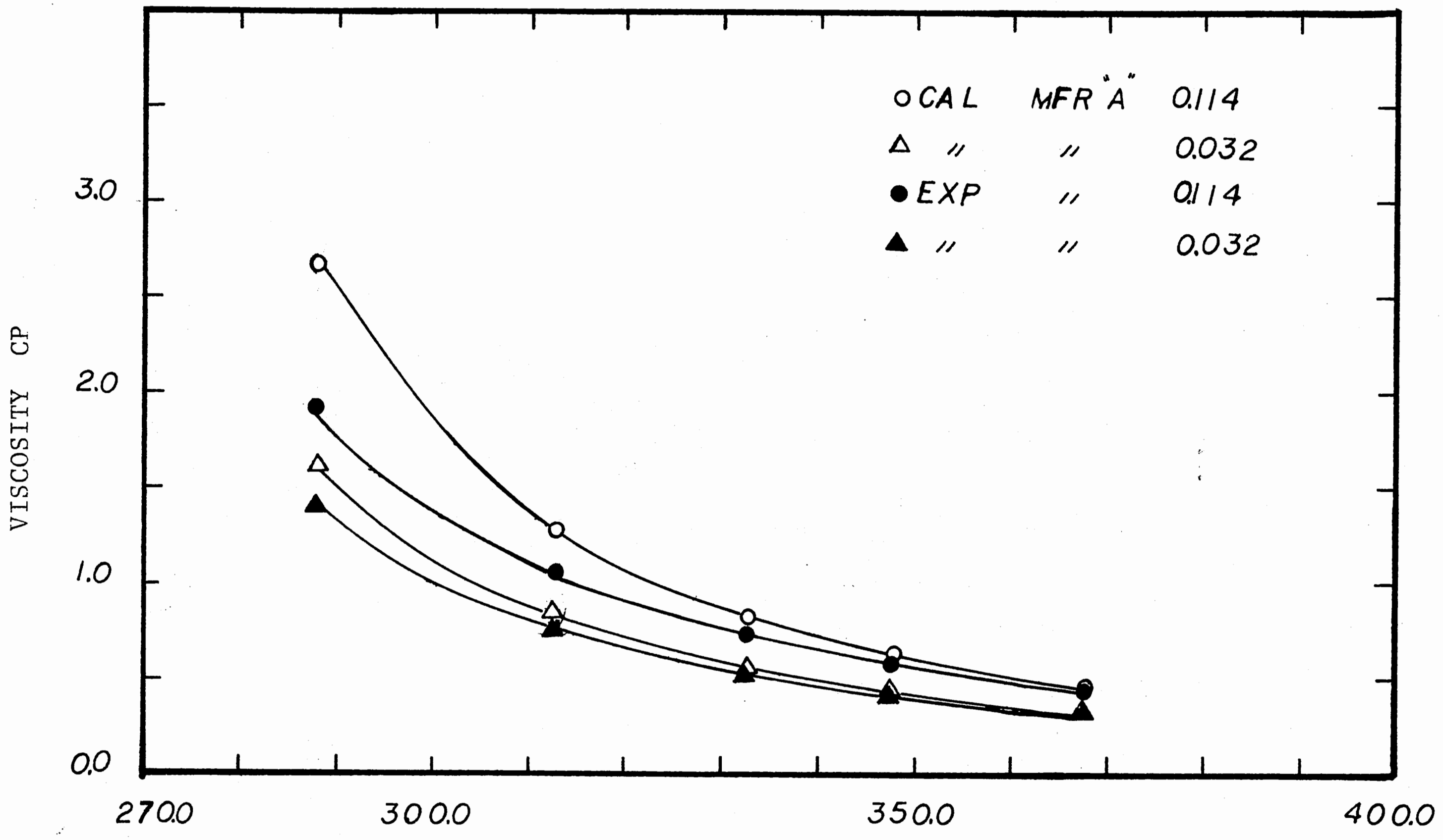


Figure 9. Acetic Acid (A) and Water (B) Mixture (vis-Temp)

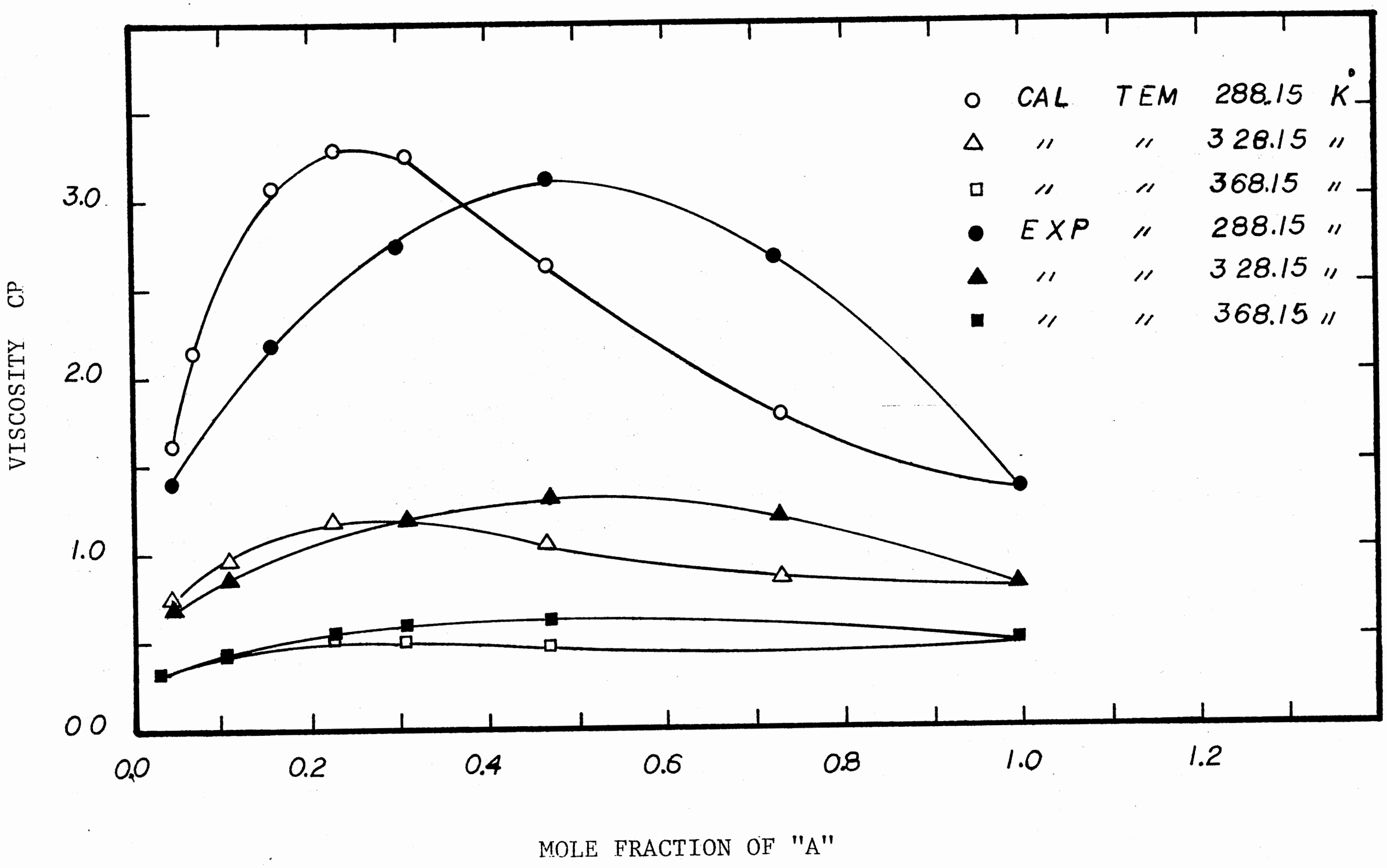


Figure 10. Acetic Acid (A) and Water (B) Mixture (vis-MFR "A")

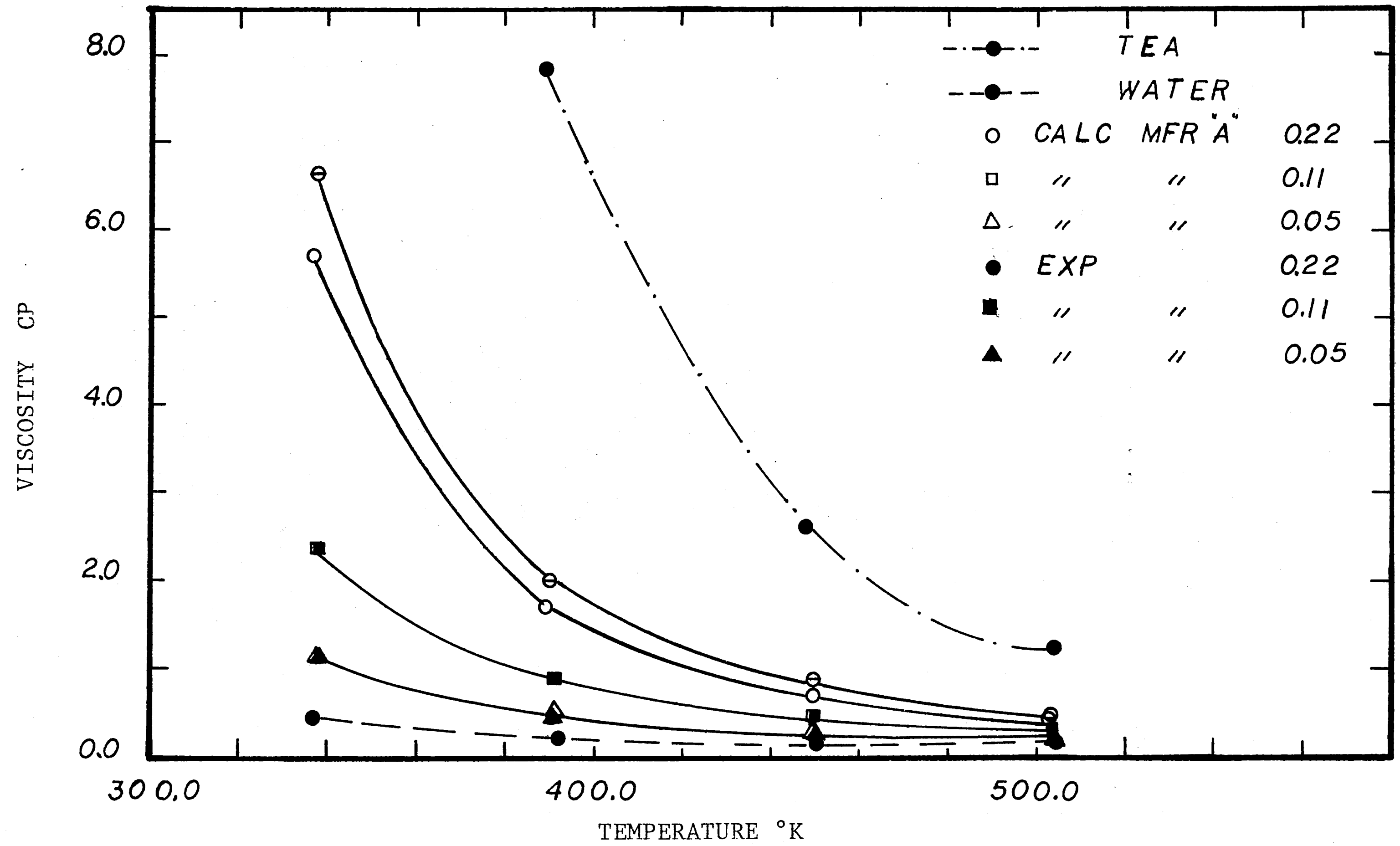
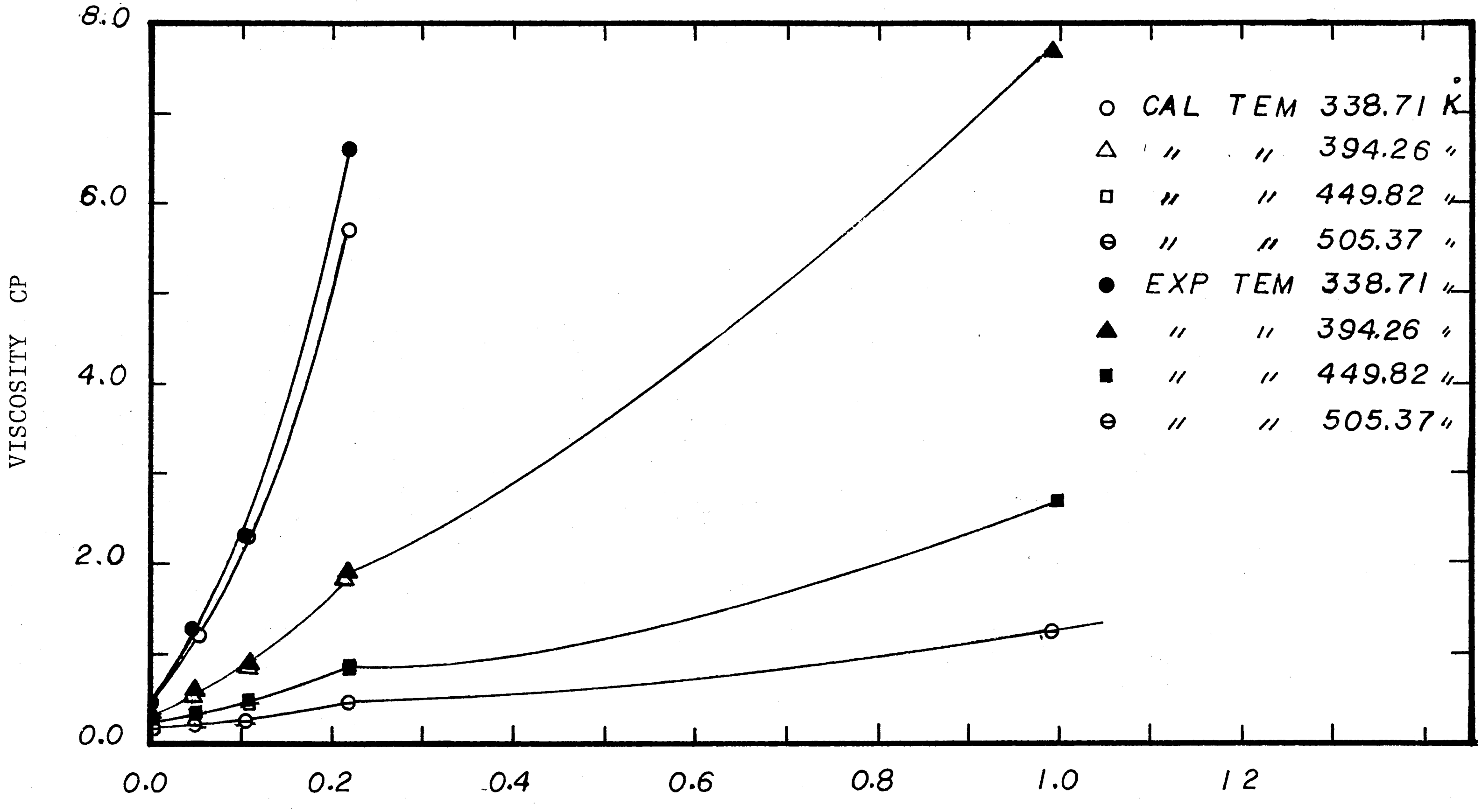


Figure 11. Triethanol Amine (A) and Water (B) Mixture (vis-Temp)



MOLE FRACTION OF "A"

Figure 12 Triethanol Amine (A) and Water (B) Mixture (vis-MFR "A") maximum positive or negative deviations occur at extreme temperatures and equimolar concentrations.

The absolute average and overall absolute average deviation for alkane-alkane, alkane-alcohol, alcohol-alcohol, alcohol-water, ethylene glyco-water, and triethanolamine-water were below 4%. Carboxylic acids, mono- and diethanolamine-water and ketone mixtures were higher. Some of them were as high as 18%. Consistency tests show that errors took place in carboxylic acid mixtures, aqueous mono- and diethanolamine and ketone-ketone mixtures data. The unavailability of other data options for choosing from in the last families of mixtures and inconsistency were the reasons for such high deviations.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. The Ratcliff-Khan Group Solution Model for predicting mixture viscosity at room temperature, which was modified by Goswamy, extended to cover temperatures to the critical.

2. The new model is capable of handling multicomponent, multigroup mixtures of straight and branched chains, polar and non-polar components over a wide range of concentration and temperature.

3. The structural contribution and the group contribution coefficients of each active group are related to the temperature by an exponential form.

4. Constants of eight active groups were generated. These groups are CH_3, CH_2, COOH, CO, OH, NH_2, NH and N.

5. The new model is capable of predicting mixture viscosity of all liquid mixtures consisting of the above mentioned active groups. Its interpolation and extrapolation predictive power is very satisfactory.

6. The most noticable deviations in predicted viscosity for mixtures that do not form maxima or minima occur at extreme conditions of concentration and or temperature, i.e., at high or low concentration. While for mixtures that form maximas or minimas most deviations in predicted viscosity occur at equimolar quantities.

Recommendations

For further investigation and improvement of the work the following recommendations are made:

1. Consistent experimental data covering wide range of temperature are required for generating the constants.

2. The liquid mixtures used for generating the constants need to be representative mixtures covering the branched as well as the straight chains, the polar as well as the non-polar and the large as well as the small components.

3. Constants for cyclic, aromatic, sulfur containing and halogen containing groups following the same procedure are needed.

4. The group contribution model is powerful. It should be utilized for the prediction of other physical and thermodynamic properties.

BIBLIOGRAPHY

1. Brush, S. G., *Chem. Rev.*, *62*, 513 (1962).

2. Touloukian, Y. S., S. C. Saxena and P. Hestermans, *Thermophysical Properties of Matter Volume 11: Viscosity*, IFI, Plenum, New York (1975).

3. Scatchard, G., *Chem. Rev.*, *8*, 321 (1931).

4. Hildebrand, J. H., J. M. Prausnitz, and R. L. Scott, *Regular and Related Solutions*, Van Nostrand Reinhold Co., New York (1970).

5. Barker, J. A., *J. Chem. Phys.*, *20*, 1526 (1952).

6. Rowlinson, J. S., *Trans. Foraday Soc.*, *50*, 647 (1954).

7. Leland, T. W., and P. S. Chappelear, *Ind. Eng. Chem.*, *60*, 7, 15 (1968).

8. Gubbins, K. E., *A.I.Ch.E. J.*, *19*, 684 (1973).

9. Lucassen-Reynders, E. H., *J. Coll. Inter. Sci.*, *41*, 156 (1972).

10. Lucassen-Reynders, E. H., *J. Coll. Inter. Sci.*, *42*, 554 (1973).

11. Lucassen-Reynders, E. H., *Prog. Surf. Mem. Sci.*, *10*, 253 (1976).

12. Nielsen, L. E., *Predicting the Properties of Mixtures: Mixture Rules in Science and Engineering*, New York: Marcel Dekker, Inc., (1978).

13. Doolittle, A. K., *Newtonian Flow in Polymer Chemistry*, In Alexander J. (Ed.). Colloid Chemistry, pp. 149-173, New York: Reinhold (1950).

14. Arrhenius, S., *Z. Phys. Chem.*, *1*, 285 (1887).

15. Findlay, Y. A., *Z. Phys. Chem.*, *69*, 203 (1901).

16. Bingham, E. C., *Amer. Chem. J.*, *35*, 3, 195 (1906).

17. Drucker, K. and Kassel, R., Z. Phys. Chem., 76, 367 (1911).

18. Lee, C. H., Phil. Mag., 1, 1, 128 (1901).

19. Kendall, J. and K. P. Monroe, J. Amer. Chem. Soc., 42, 1776 (1920).

20. Lautie, R., Bull. Soc. Chim. Fr., 5, 353 (1946).

21. Irving, J. B., "Viscosities of Binary Liquid Mixtures: A Survey of Mixture Equations," National Engineering Laboratory, Report No. 630, Department of Industry, U. K., February (1977).

22. Van der Wyke, A. J., Nature, 138, 845 (1936).

23. Dolezalek, F., Z. Phys. Chem., 83, 40 (1913).

24. Mato, F. and J. L. Hernandez, An. Fis. Quim., 63B, 13 (1967).

25. Mato, F. and J. L. Hernandez, An. Fis. Quim., 65, 9 (1969).

26. Sachanov, A. and N. Rjachowsky, Z. Phys. Chem., 86, 529 (1914).

27. Grunberg L., Nature, London, 164, 799 (1944)

28. Hind, R. K., E. McLaughlin and A. R. Ubbelohde, Trans. Farraday Soc., 56, 328 (1960).

29. Bearman, R. J. and P. F. Jones, J. Chem. Phys., 33, 5, 1432 (1960).

30. Chakrabertty, S. K. and P. B. Ganguly, Proc. Nat. Acad. Sci. India, 7, 4, 205 (1937).

31. Spells, K. E., Trans. Faraday Soc., 32, 530 (1936).

32. Srinivasan, M. K., J. Indian Chem. Soc., 16, 305 (1939).

33. Bhagwat, W. V. and K. Mandloi, J. Indian Chem. Soc., 23, 349 (1946).

34. Fried, V., E. Hala and J. Pick, Collection Czechoslov. Chem. Comm., 24, 400 (1959).

35. Chacravarti, A. S., Curr. Sci., 16, 1, 23 (1947).

36. Bachinskii, A. I., Z. Phys. Chem., 84, 643 (1913).

37. Meyer, J. and B. Mylius, Physik Chemie, 95, 349 (1920).

38. Macleod, D. B., Trans. Faraday Soc., 30, 482 (1934).

39. Gugel, B. M., J. Phys. Chem., (Moscow), 11, 105 (1938).

40. Luchinskii, G. P., Academy of Sciences of the U.S.S.R., 1, 4 (1941).

41. Kottler, F., J. Phys. Chem., 47, 3, 277 (1943).

42. Doolittle, A. K.,"Newtonian Flow in Polymer Chemistry,"In Alexander, J. (Ed.). Colloid Chemistry, pp. 149-173, New York: Reinhold, (1950).

43. Doolittle, A. K., J. Applied Phys., 22, 12, 1471 (1951).

44. Cohen, M. H. and Turnbull, D., J. Chem. Phys., 31, 1164 (1959).

45. Buchanskii, A. I., J. Phys. Chem. (Moscow), 11, 597 (1938).

46. Wilson, O. G., Nat. Petrol. News, 21, 21, 87 (1929).

47. Wright, W. A., J. of Materials, 4, 1, 19 (1969).

48. Nederbragt, G. W., J. Inst. Petrol., 38, 240 (1952).

49. Reed, T. M. and T. E. Taylor, J. Phys. Chem., 63, 58 (1959).

50. Glasstone, S., K. J. Laidler and H. Eyring, The Theory of Rate Process, pp. 514-516, New York: McGraw-Hill, (1941).

51. McAllister, R. A., A.I.Ch.E. J., 6, 3, 427 (1960).

52. Reid, R. C., J. M. Prausnitz and T. K. Sherwood, The Properties of Gases and Liquids, 3rd Ed., pp. 457-463, New York: McGraw-Hill, (1977).

53. Katti, P. K. and M. M. Chaudhri, J. Chem. Eng. Data, 9, 1, 142 (1964).

54. Cronauer, D. C., R. R. Rothfus and R. I. Kermode, J. Chem. Eng. Data, 10, 2, 131 (1965).

55. Auslander, G., Br. Chem. Eng., 10, 3, 196 (1965).

56. Heric, E. L. and J. G. Brewer, J. Chem. Eng. Data, 12, 4, 547 (1967).

57. Heric, E. L. and J. G. Brewer, J. Chem. Eng. Data, 14, 1, 55 (1969).

58. Krishnan, M. R. V. and G. S. Laddha, Ind. & Eng. Chem. Fund., 7, 2, 324 (1968).

59. Saraiya, N. K. and J. Winnick, J. Chem. Phys., 49, 1447 (1968).

60. Macedo, P. B. and T. A. Litovitz, J. Chem. Phys., 42, 245 (1965).

61. Goldhammer, D. A., Z. Phys. Chem., 71, 577 (1910).

62. Samu B. and F. W. Lima, Chem. Abstr., 46, 8444 (1952).

63. Souders, M., J. Amer. Chem. Soc., 60, 154 (1938).

64. Ishikawa, T., Bull. Chem. Soc. Japan, 4, 5 (1929).

65. Cragoe, C. S., "Changes of the Viscosity of Liquids with Temperature, Pressure and Composition," Proc. First World Petr. Cong., London: Vol. 11, pp. 529-541 (1933).

66. Lederer, E. L., Nature, 139, 27 (1937).

67. Blok, H., "Viscosity-Temperature-Pressure Relationships, Their Correlation and Significance for Lubrication," Proc. Third World Petr. Cong., The Hague: Sec. VII, pp. 304-319 (1951).

68. Andrade, E. N. Dac, Phil. Mag., 17, 112, 497 (1934).

69. Tuomikoski, P., Suomen Kem., 15, 13, 19 (1942).

70. Reogiers, M. and L. Roegiers, Chem. Abstr., 42, 3234 (1948).

71. Tamura, M. and M. Kurata, Bull. Chem. Soc. Japan, 25, 1, 32 (1952).

72. Fried, V., E. Hala and J. Pick, Coll. Czech. Chem. Comm., 24, 400 (1959).

73. Roelands, C. J. A., "Correlational Aspects of the Temperature-Pressure Relationship of Lubricating Oils," Doctoral Thesis, Delft: Technological University of Delft, (1968).

74. Cullinan, H. T., Ind. & Eng. Chem. Fund., 7, 1, 177 (1968).

75. Cokelet, G. R., F. J. Hollander and J. H. Smith, J. Chem. Eng. Data, 14, 4, 470 (1969).

76. Mikhail, S. Z. and W. R. Kimel, J. Chem. Eng. Data, 6, 4, 53 (1961).

77. Langmier, I., Third Colloid Symposium Monograph, Chemical Catalog Comp., New York, (1925).

78. Flory, P. J., J. Chem. Phys., 10, 1, 51 (1942).

79. Huggins, M. L., J. Phys. Chem., 46, 1, 151 (1942).

80. Bronsted, J. N. and J. Koeford, K. Danske. Videnske. Selsk. Skr., Mat. Fys. Medd., 22, 17, 1 (1946).

81. Griest, E. M., W. Webb and R. W. Schiessler, J. Chem. Phys., 29, 4, 711 (1958).

82. Dixon, J. A., J. Chem. Phys., 4, 4, 289 (1959).

83. Ratcliff, G. A. and M. A. Khan, Canadian J. Chem. Eng., 49, 125 (1971).

84. Wedlake, G. D., "The Viscosity of Newtonian Hydrocarbon Liquid Mixtures; Determination by Capillary Viscometry Methods and Prediction by a Group Solution Model," Doctoral Thesis, Canada: McGill University, (1978).

85. Wedlake, G. D., and G. A. Ratcliff, Canadian J. Chem. Eng., 51, 511 (1973).

86. Goswamy, V., "A Group Solution Approach for the Prediction of Liquid Mixture Viscosity," M.S. Report, Stillwater: Oklahoma State University (1981).

87. Maddox, R. N., Private Communications.

88. Revue Roumaine de Chemie, 20, 1, 55 (1975).

89. Aleskerov, M. A., A. A. Mamadeov and Sh. Kh. Khalilov, Izvestiya Vysshikh Uchebnykh Zavedenii, Neft i Gaz, 22, 4, 58 (1979).

90. Wedlake, G. D., "The Viscosity of Newtonian Hydrocarbon Liquid Mixtures: Determination by Capillary Viscometry Methods and Prediction by Group Solution Model," Ph.D. Dissertation, Ottawa: McGill University (1978).

91. Shikhaliev, Ya. A., A. A. Mamedov and M. A. Aleskerov, Russian J. Phys. Chem., 48, 7, 1002 (1974).

92. Westmeier, S., Chem. Tech. (Leipzig), 28, 6, 350 (1976).

93. Bingham, E. C., J. E. Hatfield and R. F. Jackson, Bur. Stand. J. Res. Sci., Paper 298 (1917).

94. Westmeier, S., Chemische Technik, 28, 8, 480 (1976).

95. Westmeier, S., Chemische Technik, 30, 7, 354 (1978).

96. Weber, W., Rheol. Acta., 14, 1012 (1975).

97. Mikhail, S. Z. and W. R. Kimel, J. Chem. and Eng. Data, 8, 3, 323 (1963).

98. The Dow Chemical Company, Gas Conditioning Fact Book, The Dow Chemical Company, Midland, Michigan (1962).

99. Kubota, H., S. Tsuda and M. Murata, The Rev. Phys. Chem. Japan, 49, 2, 59 (1979).

100. Landolt, H. H. and R. Bornstein, Zahlenwerte und Fundtion aus Physik, Chemie, Astronomie, Geophysik und Technik, Band 11, Teil 5 New York: Springer-Verlog (1969).

101. Howard K. S., and R. A. McAllister, *A.I.Ch.E. J.*, *4*, 3, 362 (1958).

102. Chandler, J. P., MARQ 2.6, A.N.S.I. Standard Fortran, Dept. of Computing and Information Sciences, Oklahoma State University, Stillwater, Oklahoma, January (1979).

103. Coursey, B. M., and E. L. Heric, *Canadian J. Chem.*, *49*, 2631 (1971).

104. Guggenheim, E. A., *Proc. Roy. Soc. (London)*, *A183*, 203 (1944).

105. Guggenheim, E. A., *Proc. Roy. Soc. (London)*, *A183*, 213 (1944).

106. Erbar, R. C., Private Communications.

2

VITA

Suleiman Yousef Diab

Candidate for the Degree of

Doctor of Philosophy

Thesis: PREDICTION OF LIQUID MIXTURES VISCOSITY OVER A WIDE RANGE OF TEMPERATURE USING GROUP CONTRIBUTION METHOD

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Annaba, Palestine, December 5, 1943, the son of Mr. and Mrs. Yousef Diab. Married to Rijaya H. Badwan, August 6, 1965. Have two sons; Labeed, born December 16, 1969 and Basher, born November 16, 1974.

Education: Graduated from Al-Hashimieh Secondary School, Biereh, West Bank, in June 1960; from Teacher's Training Center, Ramallah, West Bank in June 1962; received Bachelor of Science degree in Chemical Engineering from Texas A & M University, College Station, Texas in December 1973; received Master of Science degree in Chemical Engineering from Oklahoma State University, Stillwater, Oklahoma in May 1980; completed requirements for the Doctor of Philosophy Degree in Chemical Engineering at Oklahoma State University, Stillwater, Oklahoma, in December, 1982.

Professional Experience: Science teacher with UNARWA in Jordan from 1962 to 1964; Teacher with the Ministry of Education of Kuwait from 1964 to 1970; Process Chemical Engineer with Kuwait Asphalt Emulsion Company from 1974 to 1976; Deputy Director of the Industrial section of Dar El-Khaleedg, Kuwait from 1976 to 1978; Teaching Assistant at the School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma from 1978 to 1980; Research Assistant at the Algae Center at Oklahoma State University, Stillwater, Oklahoma from 1979 to 1980; Research Assistant at the Fluid Properties Research, Inc., Oklahoma State University, Stillwater, Oklahoma from 1980 to present.

Membership in Scholarly or Professional Societies: Member, Omega Chi Epsilon (national Chemical Engineering honor society); Member, American Institute of Chemical Engineers; Associate Member, Kuwait Society of Engineers; Member, National Society of Professional Engineers.