PREDICTION OF LIQUID-MIXTURE HEAT CAPACITY BY GROUP CONTRIBUTION METHOD

By

CHEIN-HSIUN TU

Bachelor of Science
Tatung Institute of Technology
Taiwan, Republic of China
1974

Master of Science
Washington State University
Pullman, Washington
1981

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, 1985

PREDICTION OF LIQUID-MIXTURE HEAT CAPACITY

BY GROUP CONTRIBUTION METHOD

Thesis Approved:

R. N. Maddox
Thesis Adviser

Fayl L. McLaughlin

Arland H. Johannes

Robert H. Heidersbach, Jr.

Billy L. Haynes

Norman N. Durham
Dean of Graduate College

PREFACE

A group-contribution method is presented for the prediction of heat capacities of nonelectrolyte liquid mixtures. This method combines Kehiaian's group-surface interaction concept with the model for heat capacity which is based on an extension of Guggenheim-Barker's rigid pseudolattice model of liquid mixtures. The resulting model is capable of predicting heat capacity of multicomponent mixtures of polar and nonpolar molecules over a wide range of temperature and concentration.

Using the predictive constants obtained from data reductions, the heat capacities of a large number binary mixtures can be predicted. This is demonstrated for thirty eight binary mixtures containing water, hydrocarbons, and n-alcohols over the temperature range 178 to 383 K. The results show that the proposed method is powerful and its application to systems other than those considered in this study is recommended.

I am particularly indebted to my adviser, Dr. Robert N. Maddox, for his intelligent guidance and continuing encouragement throughout the course of this study. Appreciation is also extended to the other committee members, Dr. Anthony L. Hines, Dr. Gilbert J. Mains, Dr. Faye C. McQuiston, Dr. Robert H. Heidersbach, Jr., and Dr. Arland H. Johannes for

their advisement and interest.

The assistance provided by all the faculty, staff, and graduate students of School of Chemical Engineering is acknowledged. The help of Dr. J. P. Chandler in the use of Marquart's subroutine is highly appreciated. Thanks are also due to the University Computer Center of Oklahoma State University for the facility and computer time offered.

I would also like to express my appreciation to my parents, Chiao-Yun and Chen-Mien Tu, my brothers, and my sisters for their constant support and encouragement during the long way of my graduate study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

A	constant in Eq. 2-45
AAPD	average absolute percent deviation
AD	average deviation, defined by Eq. 3-9
A_{CH_4}	molecular surface area of methane
A_s	group surface area of type s
A_{mn}	predictive constants in Eq. 3-8
A_n	constants in Eq. 2-37
a_0, a_j	constants in Eqs. 2-46 and 2-47
a_1	constant in Eq. 2-11
a_2	constant in Eq. 2-13
a_3	constant in Eq. 2-13
a	structural constant, defined by Eq. 2-29
B	constant in Eq. 2-45
B_k	contributions of group k in the solution
$B_k^{(r)}$	contributions of group k in the standard state
B_n	constants in Eq. 2-38
b_0	constant in Eq. 2-9
b_1	constant in Eq. 2-11
b_2	constant in Eq. 2-13
b_j	constants in Eq. 2-48
Calc.	calculated heat capacity
C_n	constants in Eq. 2-38
C_p	molar heat capacity

C_p^E	molar excess heat capacity, defined by Eq. 2-8
C_p^{E*}	molar excess heat capacity in the random-mixing approximation
C_{pi}^o	molar heat capacity of pure component i
C_{pi}	molar heat capacity of component i in a mixture
C_{pij}	parameter, defined by Eq. 3-14
C_{pij}^*	random-mixing parameter, defined by Eq. 3-7
C_p^{ID}	ideal-mixture heat capacity, defined by Eq. 3-12
ΔC_p^{ID}	change of molar heat capacity upon mixing in the ideal state
C_p^M	molar heat capacity of a mixture
ΔC_p	change of molar heat capacity upon mixing
C_{pst}	molar interchange heat capacities
C_{pst}^*	molar interchange heat capacities in the random-mixing approximation
c_0	constant in Eq. 2-10
c_1	constant in Eq. 2-12
c_2	constant in Eq. 2-14
c_j	constants in Eqs. 2-48 and 2-49
D_{st}	molar interchage energy, defined by Eq. 2-31
D_{st}'	differentiation of D_{st} with respect to temperature
d_j	constants in Eqs. 2-48 and 2-49
Exp.	experimental heat capacity
exp	exponential
F	a function
f_{si}	group surface fraction of type s on molecule i
f_s	group surface fraction of type s in a mixture
g	molar Gibbs free energy
g^E	molar excess Gibbs energy, defined by Eq. 2-6

Δg^{ID}	change of molar Gibbs energy upon mixing in the ideal state
g^{M}	molar Gibbs energy of a mixture
Δg	change of molar Gibbs energy upon mixing
g_{st}	molar interchange free Gibbs energies
h	molar enthalpy
h^{E}	molar excess enthalpy, defined by Eq. 2-7
h^{E*}	molar excess enthalpy in the random-mixing approximation
h^{*}_{ij}	random-mixing parameter, defined by Eq. 3-2
Δh^{ID}	change of molar enthalpy upon mixing in the ideal state
h^{M}	molar enthalpy of a mixture
Δh	change of molar enthalpy upon mixing
h_{st}	molar interchange enthalpies
h^{*}_{st}	molar interchange enthalpies in the random-mixing approximation
h'_{st}	differentiation of h_{st} with respect to temperature
IDMXEQ	ideal-mixture equation, defined by Eq. 3-12
ln	natural logarithm
K_1, K_2	proportionality constants in Eqs. 2-20 and 2-21
MXPPD	maximum positive percent deviation
MXNPD	maximum negative percent deviation
NC	number of carbon atoms in n-alcohol molecules
N_i	total number of groups on molecule i
N_{ki}	number of groups of type k on molecule i
NPTS	total number of data points
NSYS	number of systems
$\bar{N}$	average number of total groups in a mixture
$\bar{n}$	total number of group surfaces in a mixture

OAAPD	overall average absolute percent deviation
p	pressure
PD	percent deviation
|PD|	absolute value of percent deviation
q_i	total group surface area on molecule i
q_s	relative group surface area of type s
R	gas constant
R_i	surface area fraction of molecule i in a mixture
S_2	surface area of the solvent molecule
s	group surface of type s
T	temperature
T_r	reduced temperature
t	group surface of type t
u^E	molar energy change upon mixing
Δu^v	energy of vaporization
v_i	molar volume of component i
v^M	molar volume of a mixture
w	acentric factor
wh	acentric factor for a mixture, defined by Eq. 2-40
X_s, X_t	unknown parameters in Eqs. 2-30 and 2-33
X_k	group fraction of type k, defined by Eq. 2-28
x_i	mole fraction of component i in a mixture
Y_G	group contribution
Y_{Gi}	group contribution of molecule i
Y_S	structural contribution
Y_{Si}	structural contribution of molecule i
Z	coordination number
Z_{st}	weighting function, defined by Eq. 3-10

Greek Symbols

ϕ_i	volume fraction of component i
λ	a function of ϕ_2
β_i	solubility parameter of component i
Σ	summation
α_i	thermal expansion coefficient of component i
γ	Activity coefficient

Subscripts

i	component in a mixture
k	group type k
mn	index numbers for predictive constants, A_{mn}
n,j	constant index numbers
s	group surface of type s
t	group surface of type t
st	group-surface pair (s,t)

Superscripts

E	for excess properties
ID	ideal state
M	for mixture properties
o	for pure component
*	random-mixing approximation
(r)	standard state
(r1)	reference fluid 1
(r2)	reference fluid 2

CHAPTER I

INTRODUCTION

The heat capacities of liquids and liquid mixtures have wide applications in many fields of chemical engineering. In general, heat capacity data provide valuable information for heat-transfer calculations in the design and operation of chemical processes. On a theoretical basis, heat capacity data represent a potential source of information on the nature of intermolecular forces and thus, describe the ways in which the forces determine the structure and macroscopic properties of matter.

A number of estimation methods for the heat capacities of pure liquids have been presented (1). However, very few specific correlations are proposed for liquid mixtures. The development of the theoretical foundation of liquid-mixture heat capacity is still in the primitive stage. At present, no theory can be reduced to a simple function to allow for the calculation of heat capacities of liquid mixtures with reasonable effort. Thus, experimental data and reliable predictive techniques for the heat capacities of liquid mixtures are not only welcomed, but a necessity in the field of chemical thermodynamics.

Due to the paucity of experimental data on the heat capacities of liquid mixtures, one must often estimate this

property. In this work, a group-contribution technique will be proposed for the calculation of heat capacity data. The selection of a group-contribution technique lies on the fact that thousands of multicomponent mixtures exist in the chemical industries; however, the number of functional groups that constitute those mixtures is no more than 50 (2). The objective of this work is to develop a general method based on the contributions of the functional groups to predict the heat capacities of liquid mixtures. This method should be able to predict liquid-mixture heat capacity over a wide range of temperatures and concentrations and capable of handling multiple groups and polar or nonpolar molecules.

The basic work involved in this method is to extend Kehiaian's group-surface interaction technique (3) in which a random-mixing approximation was proposed for excess enthalpy based on Guggenheim's rigid pseudo-lattice model (4). The random-mixing approximation model proposed by Kehiaian was in its original form and was not applied for prediction of the heat capacities of liquid mixtures. In this work, Kehiaian's model is extended to the expression of the excess heat capacity of a multicomponent system. Based on experimental excess heat capacity data, an empirical function which includes temperature and the difference of the mole fractions of components is proposed for the molar interchange heat capacities in the working equation to generate predictive constants. Thus, the proposed model is further modified by using a weighting function, which is expressed in terms of the number of carbon atoms around the

functional group -OH, to account for nonrandomness due to the presence of the polar molecules of normal alcohols.

In this method, no physical properties other than the group surface areas and the pure component heat capacities are required for prediction of the heat capacities of liquid mixtures. The proposed model was tested for polar and non-polar mixtures containing water, hydrocarbons, and normal alcohols.

CHAPTER II

LITERATURE REVIEW

Thermodynamics of Liquid Mixtures

In studying the effect of mixing two or more substances, it is useful to separate the mixing effects by by comparing the properties of the mixture (denoted by superscript M) to those of the pure components (denoted by superscript o) at the same temperature and pressure. The change of a thermodynamic property upon mixing at constant pressure and temperature is called the thermodynamic function of mixing. Thus, for a binary system we have:

$$\Delta g = g^M(p,T,x) - x_1\, g_1^o(p,T) - x_2\, g_2^o(p,T) \qquad (2\text{-}1)$$

$$\Delta h = h^M - x_1\, h_1^o - x_2\, h_2^o \qquad (2\text{-}2)$$

$$\Delta C_p = C_p^M - x_1\, C_{p1}^o - x_2\, C_{p2}^o \qquad (2\text{-}3)$$

where g, h, and C_p stand for molar Gibbs free energy, molar enthalpy, and molar heat capacity, respectively. The relationships among the three can be expressed as:

$$\Delta h = -T^2\, d(\Delta g/T)/dT \qquad (2\text{-}4)$$

$$\Delta C_p = -T\, d^2(\Delta g)/dT^2 = d(\Delta h)/dT \qquad (2\text{-}5)$$

The thermodynamics of nonideal liquid mixtures can

also be discussed by the thermodynamic excess function (denoted by superscript E), which is the difference between the thermodynamic function for an actual system (denoted by superscript M) and that corresponding to an ideal solution (denoted by superscript ID) at the same temperature, pressure, and composition. An ideal solution is to be expected only when the molecular interaction, mass, and size are sufficiently similar. In an ideal solution, all the thermodynamic functions of mixing are zero except for those containing an entropy term. The thermodynamic excess functions are closely related to experimental measurements. For a binary system, the thermodynamic excess functions can be written as:

$$g^E = \Delta g - \Delta g^{ID} = R\,T\,(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (2\text{-}6)$$

$$h^E = \Delta h - \Delta h^{ID} = \Delta h = -T^2 d(g^E/T)/dT \qquad (2\text{-}7)$$

$$C_p^E = \Delta C_p - \Delta C_p^{ID} = \Delta C_p = d(h^E)/dT \qquad (2\text{-}8)$$

Equations 2-6 to 2-8 indicate that any of the excess functions may be calculated from the temperature variation of the other excess functions. The calculation of the excess functions from a specific excess function require accurate numerical differentiation or integration of a large amount of experimental data collected over a wide range of temperatures. Calorimetric data are often used to establish temperature dependency of the excess functions. The information that can be obtained from excess heat capacity is illustrated by the following examples:

Example 1: For constant composition, if C_p^E is zero, it follows that

$$h^E = b_0 \tag{2-9}$$

$$g^E = b_0 + c_0 T \tag{2-10}$$

where b_0 and c_0 are constants and can be obtained by the use of experimental data.

Example 2: For constant composition, if C_p^E is a constant and has a value of a_1, it follows that

$$h^E = a_1 T + b_1 \tag{2-11}$$

$$g^E = b_1 + c_1 T - a_1 T \ln(T) \tag{2-12}$$

where b_1 and c_1 are constants and can be obtained by the use of experimental data.

Example 3: For constant composition, if C_p^E is expressed as a linear function, $C_p^E = a_2 + a_3 T$, it follows that

$$h^E = a_2 T + a_3/2 T^2 + b_2 \tag{2-13}$$

$$g^E = b_2 + c_2 T - a_3/2 T^2 - a_2 T \ln(T) \tag{2-14}$$

where a_2, a_3, b_2 and c_2 are constants and can be obtained by the use of experimental data.

The degree of complexity of the temperature functions considered in the above examples depends upon the types of the intermolecular interactions in the solution. In nonelectrolyte solutions, several types of intermolecular forces are expected (5):

1. Induction forces between a permanent dipole (or quadrupole) and an induced dipole.

2. Forces of attraction (London dispersion forces) and repulsion between nonpolar molecules.

3. Specific (chemical) forces leading to association and complex formation such as hydrogen bonding.

The type and strength of the interactions control the shape and magnitude of the excess functions for the liquid system considered. The liquid is an intermediate between the crystalline and gaseous state. It is possible to establish a qualitative relationship between the intermolecular forces and the the excess functions using a simple liquid model. In general, there are two types of approaches to a theory of liquids. The first approach considers liquids to be gas-like; a liquid is pictured as a dense and highly non-ideal gas whose properties can be described by some equation of state. An equation-of-state description of pure liquids can readily be extended to liquid mixtures by using an adequate mixing rule. The other approach considers a liquid to be solid-like and in a quasi-crystalline state in which the molecules are pictured as occupying points on a lattice. Theories of liquids or liquid mixtures based on this simplified picture are called lattice theories (6). In the lattice theory of solutions, the force of attraction and the difference in size or shape between unlike molecules are considered to be the main factors that lead to the deviations from ideal behavior in liquid solutions.

For imperfect solutions, it is useful to distinguish

two limiting cases from the other types of imperfect solutions:

1. Regular solutions. For regular solutions, the molecules have approximately the same size and shape so that the interactions among the molecules do not alter significantly the arrangements of the molecules in the solution. These solutions are characterized by negligible excess entropy of mixing provided that there is no volume change upon mixing.

2. Athermal solutions. For athermal solutions, the molecules differ markedly in shape and size so that the interactions among the molecules greatly change the arrangement of the molecules in the solution. This causes deviations from ideality even though the heat of mixing is practically zero. The excess heat capacity is consequently negligible.

The imperfect solutions with large heats of mixing are considerably more complex and less predictable. Typical cases are the solutions containing hydrogen bonds. Roughly speaking, in the hydrogen bond a single hydrogen atom appears to be bonded to two distinct atoms. The energy of the hydrogen bond is large when compared to the intermolecular energies. For this reason the heat of mixing of solutions involving the formation or the destruction of hydrogen bonds may be about 2-10 kilocalories per mole (5). The molecules in solutions containing hydrogen bonds can be classified into the following two groups:

1. Free molecules (or monomolecules) whose vibrations

are not altered by the hydrogen bonds of neighboring molecules.

2. Associated complex molecules whose state of vibration has been altered by neighboring molecules.

Associated complexes are frequently formed among molecules containing atoms with considerable charges near the surface, such as the molecules containing -OH group. Experimental observations (7,8,9) indicate that these associated solutions exhibit large deviations from ideal behavior. Therefore, it seems to be reasonable to attribute a major part of the nonideality to the interactions leading to the formation of the associated complexes. At higher temperatures, the associated complexes linked by the hydrogen bond will dissociate and thus, increase the concentration of monomers (10).

The positive excess heat is mainly a measure of the number of hydogen bonds (or other local electrostatic interactions) that are broken during the formation of the mixture (11). For example, this excess heat is small in the alcohol-inert mixtures which are rich in alcohol. This is because the addition of a small amount of an inert diluent can break only few hydrogen bonds and most of the diluent is probably accomodated interstitially in a matrix of bonded alcohol molecules. However, the heat is larger in the mixtures which are lean in alcohol (except at extremely low alcohol concentration) because the addition of a small amount of alcohol to a large amount of a nonpolar liquid must break all the hydrogen bonds in the mixture. The

introduction of π-electron molecules, such as benzene to alcohols, causes an increase in excess heat (12). This behavior is attributed to a more favorable energy of interaction between a hydroxyl group and the π-electrons of an aromatic molecule than with the less polarizable electrons of a saturated hydrocarbon molecule (11). Such interaction, although not as strong as a conventional hydrogen bond, is less strict in the geometrical requirements that lead to breaking of more hydroxyl bonds.

Equations For Excess Heat Capacity

Various correlations for liquid phase thermodynamic excess functions ranging from complex statistical thermodynamic treatments to simple empirical methods have been proposed. Much of this information has been published in books by Prigogine (10), Rowlinson (11), and Barker (13) which summarize previous work and compare correlation methods with the available experimental data. However, correlations that were developed particularly for excess heat capacities of liquid mixtures are essentially nonexistent. In general, the only techniques which show some degree of success for prediction of excess heat capacities were the modified version of other excess functions. These modified excess functions can be classified into the following three categories:

1. Regular and irregular solution models for systems with small deviations from ideal behavior. In these systems, all the contributions were lumped into the parameters such as solubility parameter or interaction coef-

ficient.

2. Group contribution models which divided molecules into basic units or groups and tried to estimate the contribution of each group to the excess function.

3. Empirical methods attempting to correlate solution behavior in terms of a specific physical property or other characteristics.

A common feature of all these correlations is that they try to conceal the complexity of actual interactions in terms of empirical parameters due to the inability to mathematically solve the equations that represent these interactions.

Regular-Irregular Solution Models

The regular solution theory proposed by Hildebrand (14) has been used extensively as an initial approach to many areas of solution thermodynamics. The regular solution theory was developed based on random mixing of molecules that limits its rigorous application to systems which exhibit small deviations from ideality. The regular solution theory was modified by Maron (15), Maron et al. (16), and Rose (17) to include nonrandomness resulting from different molecular interaction forces and was called "the irregular solution theory". This irregular solution theory is less restricted and ensures improved results for more complex solutions.

In regular solution theory, Hildebrand assumed that the molecular forces of attraction were due primarily to London dispersion forces. The molar energy of mixing (u^E) of a

binary liquid mixture is then:

$$u^E = (x_1 v_1 + x_2 v_2)\{(\Delta u_1^V/v_1)^{\frac{1}{2}} - (\Delta u_2^V/v_2)^{\frac{1}{2}}\}^2 \phi_1 \phi_2 \quad (2\text{-}15)$$

Equation 2-15 was developed based on the additional assumptions that the excess volume was zero at constant pressure and the potential energy of liquid was almost identical to the energy of vaporization (Δu^V). Rewriting Eq. 2-15 in terms of the solubility parameter (β) gives:

$$u^E = v^M \phi_1 \phi_2 (\beta_1 - \beta_2)^2 \quad (2\text{-}16)$$

where ϕ_i is the volume fraction of components i; v^M is the molar volume of the mixture. Elimination of excess entropy and excess volume at constant pressure results in:

$$u^E = g^E = h^E = v^M \phi_1 \phi_2 \ (\beta_1 - \beta_2)^2 \quad (2\text{-}17)$$

The excess heat capacity is related to the temperature dependence of the heat of mixing and can be written as:

$$C_p^E = d(h^E)/dT$$

$$= 2 v^M \phi_1 \phi_2 (\beta_1 - \beta_2)(d\beta_1/dT - d\beta_2/dT) \quad (2\text{-}18)$$

Substituting the temperature-dependent solubility parameter, $d(\ln \beta_i/dT) = -1.25 \alpha_i$, derived by Hildebrand into Eq. 2-18 gives

$$C_p^E = -2.5 v^M \phi_1 \phi_2 (\beta_1 - \beta_2)(\alpha_1 \beta_1 - \alpha_2 \beta_2) \quad (2\text{-}19)$$

where α_i is the thermal expansion coefficient of pure component i.

Rose (17) proposed a correlation for prediction of heat of mixing based on the Flory-Huggins theory (15,16) of irregular solutions. His heat of mixing equation for a binary mixture can be written as:

$$h^E = -K_1 R T^2 S_2 \phi_1 \phi_2 \lambda / v_1 \qquad (2\text{-}20)$$

where

K_1 = a proportionality constant
S_2 = surface area of the solvent molecule
λ = a function of ϕ_2 and can be represented by a series expansion on ϕ_2
v_1 = molar volume of component 1

For mixtures of a homologous series of solute in a solvent composed of spherical shaped molecules, the surface of the solvent molecule was represented by Rose as $S_2 \approx (v_2)^{2/3}$. Equation 2-20 becomes:

$$h^E = -K_2 R T^2 \lambda (v_2)^{2/3} \phi_1 \phi_2 / v_1 \qquad (2\text{-}21)$$

An equation for the excess heat capacity can be obtained by differentiating Eq. 2-21 with respect to temperature:

$$C_p^E = -K_2 R T (2\lambda + T\, d\lambda/dT)(v_2)^{2/3} \phi_1 \phi_2 / v_1 \qquad (2\text{-}22)$$

The parameter λ in Eq. 2-22 may be obtained by using a non-linear least-squares data reduction scheme.

The regular solution model was developed primarily for binary nonpolar mixtures when the intermolecular interaction is due to London dispersion forces. The most questionable

assumption involved in this theory, according to Prausnitz (5), is geometric-mean rule for the cohesive energy density of the unlike molecule interaction. The irregular solution model was developed for more complex binary solutions by introducing a semiempirical interaction coefficient, λ. This interaction coefficient, λ, was an unspecified function of composition, temperature, and size of the solvent molecules. Thus, experimental data was required to evaluate this function before any prediction could be made from this model.

Group Contribution Models

The group contribution concept was first proposed by Langmuir (18). He stated that in a liquid solution of polymer molecules, the important factor in predicting the thermodynamic properties is the interactions of functional groups comprising the molecules rather than the interactions of molecules themselves. Significant progress in this direction has been made and many group contribution models have been developed. In general, the models for solution thermodynamics can be classified into two categories: one is the group solution models, which uses the group (or local) composition concept and assumes the properties of solution can be determined from the interactions among the individual functional groups in the solution; the other is group surface models, which characterizes the functional groups comprising the molecules in terms of different types of surfaces and considers the interactions among these group

surfaces to contribute to the properties of the solution.

Group solution models have been used for the predictions of activity coefficients, heat of mixing, and liquid-mixture viscosity (19,20,21,22). Generally speaking, these models assume the nonideal behavior in solution is attributed to the interactions of molecular groups and the overall skeleton of the molecules. These effects are assumed to be additive. Thus

$$Y = Y_S + Y_G \tag{2-23}$$

$$Y_S = \sum_i x_i Y_{Si} \tag{2-24}$$

$$Y_G = \sum_i x_i Y_{Gi} \tag{2-25}$$

The contribution from interactions among molecular groups, Y_{Gi}, is assumed to be the summation of the differences between the individual contributions of functional group k, B_k, and the individual contributions in the conventional standard state environment, $B_k^{(r)}$. Thus, the group contribution, Y_{Gi}, for component i containing group k can be written as:

$$Y_{Gi} = \sum_k N_{ki} (B_k - B_{ki}^{(r)}) \tag{2-26}$$

where N_{ki} is the number of groups of type k in component i. The standard state value $B_{ki}^{(r)}$ is usually taken as the value of B_k at a group composition corresponding to pure component i. The individual group contributions (B_k) in any solution containing groups of a given kind is assumed to be a function of group compositions, temperature, and pressure and

can be expressed as:

$$B_k = F(\bar{X}_1, \ldots, \bar{X}_k, T, p) \qquad (2\text{-}27)$$

where $\bar{X}_k$ is the group fraction of type k evaluated by

$$\bar{X}_k = \sum_i x_i N_{ki} \Big/ \sum_k \sum_i x_i N_{ki} \qquad (2\text{-}28)$$

The function B_k must be evaluated from experimental data for excess heat capacity.

The structural contribution Y_{Si} can be expressed as:

$$Y_{Si} = a \sum_i x_i (N_i - \bar{N})^2 \qquad (2\text{-}29)$$

where

a = a structural constant

N_i = number of groups in component i

$\bar{N}$ = average number of groups in the mixture, defined by $\sum_i N_i x_i$

In general, the structural contribution is much smaller than the group contribution and need not be known with high accuracy.

Kehiaian (23) presented a general theory for excess Gibbs free energy and excess enthalpy in terms of group surface for several basic classes of organic mixtures based on the Guggenheim-Barker quasi-lattice model (4,24,25). The general theory accounts for different types of contacts between two given elements of surfaces on a molecule. For example, a normal alcohol is considered to have two types of group surfaces-hydroxyl and aliphatic (CH_3- or -CH_2-). The

theory requires a knowledge of the number and the types of surfaces on each molecule and energies for all possible interactions of these surfaces. Therefore, the molar excess enthalpy (h^E) of surface contacts (s,t) in the real mixtures was derived to be:

$$h^E = (\sum_i q_i x_i)/2 \sum_s \sum_t (X_s X_t - \sum_i R_i X_{si} X_{ti}) D_{st} h_{st} \qquad (2\text{-}30)$$

where

$$D_{st} = \exp\{-g_{st} / Z R T\} \qquad (2\text{-}31)$$

g_{st} = molar interchange Gibbs free energies

h_{st} = molar interchange enthalpies

Z = coordination number

q_i = surface area on molecule i

R_i = surface fraction of component i in the mixture, and is defined by $q_i\ x_i\ /\ \sum_i q_i\ x_i$

x_i = mole fraction of component i in the mixture

The parameters X_s in Eq. 2-30 must be obtained by solving the following equations simultaneously

$$X_s(X_s + \sum_t X_t\ D_{st}) = \sum_i f_{si}\ R_i$$

$$= f_s \qquad (s,t = a,b,\ldots,\bar{n}) \qquad (2\text{-}32)$$

where

s,t = group surface types in the mixture

f_{si} = surface fraction of type s on molecule i, and is defined by $q_{si}\ /\ q_i$

f_s = surface fraction of type s in the mixture

q_{si} = group surface area of type s on molecule i

$\bar{n}$ = total number of group surfaces in the mixture

An expression for molar excess heat capacity (C_p^E) can be obtained by differentiating Eq. 2-30 with respect to temperature

$$C_p^E = (\sum_i q_i x_i)/2 \sum_s \sum_t (X_s X_t - \sum_i R_i X_{si} X_{ti}) C_{pst} \qquad (2\text{-}33)$$

$$C_{pst} = D_{st}\, h'_{st} + h_{st}\, D'_{st} \qquad (2\text{-}34)$$

where

$$h'_{st} = d(h_{st})/dT \qquad (2\text{-}35)$$

$$D'_{st} = d(D_{st})/dT \qquad (2\text{-}36)$$

Group solution models were based on group (or local) composition concept. The apparent inconsistencies between the local-composition models and the theoretical basis that led to the developments of the models had been discussed by several authors (26,27,28,29). As demonstrated by Fischer (26), for the energy interactions considered in the model, the local-composition concept failed, and the physical basis of all equations based on this concept seemed to be doubtful. McDermott et al. (27) and Flemr (28) also indicated that the parameters in the local-composition models could not represent group contributions to the property. This is because the local group fractions were not consistent with the overall composition of the mixture. The quasi-chemical pseudo-lattice models were developed from Guggenheim's

regular solution theory. As indicated by Fischer (26), Guggenheim's regular solution theory gave qualitatively correct prediction on excess Gibbs free energy. In addition, Kehiaian's group-contribution theory was recommended by Fischer (26) for further theoretical development. However, as indicated by Kehiaian (23), neither his model nor probably any other existing models were able to correlate excess heat capacities.

Empirical Correlations

The preceding semitheoretical models attempt to characterize the excess properties through an understanding of the physical parameters influencing these properties. A simpler approach involves attributing the excess properties to a specific concentration or other property dependent parameters, which can be used to evaluate these excess properties for a particular mixture.

Scatchard (30) proposed that the excess heat capacity of a binary mixture was concentration dependent at constant temperature and could be fitted by a power series:

$$C_p^E = x_1 x_2 \sum_n A_n (x_1 - x_2)^n \qquad (2\text{-}37)$$

This function satisfies the obvious requirement that C_p^E be zero for both pure components and can also be fitted to the experimental data by choosing higher order terms. Several modifications (31,32,33,34) have been proposed but none of them had significant advantage over the model presented by Scatchard. Equation 2-37 can be extended to include the

temperature dependency of the excess heat capacities as:

$$C_p^E = x_1\, x_2 \sum_n (B_n + C_n/T)(x_1 - x_2)^n \qquad (2\text{-}38)$$

Teja (35) proposed a general corresponding state principle (GCSP) for thermodynamic and transport properties. According to his GCSP, a reduced property of any pure fluid can be obtained from the known properties of two reference fluids (denoted by superscripts r1 and r2) at the same temperature and pressure. An expression for the dimensionless residual heat capacity can be written as

$$\{(C_p - C_p^o)/R\} = \{(C_p - C_p^o)/R\}^{(r1)} +$$
$$\{(w - w^{(r1)})/(w^{(r2)} - w^{(r1)})\}\{(C_p - C_p^o)/R\}^{(r2)} -$$
$$\{(w - w^{(r1)})/(w^{(r2)} - w^{(r1)})\}\{(C_p - C_p^o)/R\}^{(r1)} \qquad (2\text{-}39)$$

where C_p^o is the heat capacity of pure componenet and w is the acentric factor. Equation 2-39 may be extended to mixtures using a mole-fraction average for the acentric factor, wh, defined by:

$$wh = x_1\, w_1 + x_2\, w_2 \qquad (2\text{-}40)$$

When two pure components of a binary mixture are used as the reference fluids, Eq. 2-39 can be reduced to the following form through the use of Eq. 2-40

$$\{(C_p^M - C_p^{ID})/R\} = x_1\{(C_{p1} - C_{p1}^o)/R\} +$$
$$x_2\{(C_{p2} - C_{p2}^o)/R\} \qquad (2\text{-}41)$$

The ideal-state heat capacity of the mixture (C_p^{ID}) in Eq. 2-41 can be obtained from pure component heat capacities using the following mixing rule:

$$C_p^{ID} = x_1 C_{p1}^o + x_2 C_{p2}^o \qquad (2\text{-}42)$$

Combining Eqs. 2-41 and 2-42 leads to:

$$C_p^M = x_1 C_{p1} + x_2 C_{p2} \qquad (2\text{-}43)$$

Since pressure has little effect on the heat capacities of liquids, Eq. 2-43 can be written as:

$$C_p^M(T_r) = x_1 C_{p1}(T_r) + x_2 C_{p2}(T_r) \qquad (2\text{-}44)$$

where T_r is the reduced temperature. The heat capacities of pure-component reference fluids were correlated by Teja (35) by the following relationship:

$$\ln(C_p/R) = A - B/T \qquad (2\text{-}45)$$

Constants A and B for various components may be obtained from fitting Eqs. 2-44 and 2-45 to the experimental heat capacity data. As indicated by Teja (35), this method worked well for nonpolar mixtures but was found to deviate from experimental data for aqueous solutions.

As can be seen from this survey, there is no general equation that can be used to predict the heat capacities for different liquid mixtures. However, it seems that the group contribution approach has the potential to become a general applicable technique for various systems and is fundamentally adapted to predicting mixture heat capacities for sys-

tems of appropriate classes of molecules. However, systematic experimental data are required to generate predictive group constants.

Heat Capacity and Heat of Mixing Data

Heat Capacity Data

Many researchers have studied the heat capacities of liquid mixtures; however, only few systematic observations have been conducted on a particular class of molecules. The majority of the data in the literature is of little use due to the fact that they are either the duplicate of previous work, incomplete data, or inconsistent data. Some good compilations of heat capacity data for liquid mixtures have been pulished (36,37). A four volume set on the properties of binary mixtures was completed by Timmermans (36). Organic mixtures in which one compound contains a hydroxyl group are the subject of volume II (36). A six volume set on the thermophysical properties research literature retrieval guide was completed by Chaney et al. (37). Properties of mixtures and solutions can be found in volume 6 (37).

Several studies have been conducted on straight chain hydrocarbons. Culter and Morrison (38) studied the mixtures of methane and propane covering the concentration range 0.05-0.9 mole fraction of methane and the temperature range 90-110 K. Rodriguez and Patterson (39) measured the heat capacities over the entire composition range for the

following normal alkane mixtures: 1) hexane-hexadecane, octane-tetradecane, octane-hexadecane, and nonane-hexadecane at 293.15, 313.15, and 328.15 K; 2) hexane-octane, -nonane, and -tetradecane at 293.15 and 313.15 K; 3) hexane-dodecane and nonane-dodecane at 293.15 and 328.15 K; 4) octane-dodecane and dodecane-hexadecane at 313.15 and 328.15 K. The excess heat capacities were all negative, generally decreasing in magnitude with increasing temperature. The maximum contribution of excess heat capacity to the total heat capacity was found to be 1.1 % for the systems under consideration. The mixtures of two n-alkanes are almost ideal.

Few systematic studies have been conducted on mixtures of normal paraffin hydrocarbons with other solvents. Bhattacharyya and Patterson (40) studied the systems of octane, decane, and dodecane with cyclohexane over the entire composition range at 283.15, 298.15, and 328.15 K and hexadecane with cyclohexane from 293.15-328.15 K. Their data indicated that C_p^E values were negative and decreased in magnitude with increasing temperature. Mixtures of hexane, octane, decane, and hexadecane with benzene were investigated by Rodriguez and Patterson (41). The results were similar to those reported by Bhattacharyya and Patterson for n-alkane-cyclohexane systems.

Heat capacities for mixtures containing normal alcohols and normal alkanes were studied by several investigators. Klesper (42) and Brown (43) measured heat capacities of n-heptane-ethanol mixtures over the entire composition range at temperatures ranging from 205.55 to 343.15 K. Rećko (44)

studied the excess heat capacity of n-propyl alcohol-n-heptane and n-propyl alcohol-n-hexadecane mixtures. Specific heats were determined for five different concentrations of the above-mentioned two systems over the temperature range 298.15-313.15 K. The excess heat capacity curve for nonpolar mixtures is generally symmetrical with respect to the composition. The n-propyl alcohol-n-heptane system had its C_p^E maximum shifted toward low concentrations of alcohols due to association effect. The C_p^E in the mixture of n-propyl alcohol-n-hexadecane was almost symmetrical over the entire composition range. This is due to the compensation of the effects of the association and the molecular size. Kalinowska et al. (45) investigated mixtures of 1-propanol-n-hexane and 1-propanol-n-heptane over the entire composition range at temperatures ranging from 185 to 300 K. Kalinowska and Wóycicki (46) studied 1-hexanol-n-hexane mixtures over the temperature range 232-300 K. Molar heat capacities of 1-hexanol-n-hexane were higher than those of 1-propanol-n-hexane or 1-propanol-n-heptane and increased with increasing temperature. C_p^E values were negative at low temperatures and increased with increasing temperature to positive values.

Extensive investigations of the temperature dependency of excess heat capacities for ethanol-methylcyclohexane and ethanol-toluene systems were conducted by Hwa and Ziegler (47). The data were taken for five different ethanol-methylcyclohexane mixtures over the temperature range 208.15-308.15 K and seven ethanol-toluene mixtures ranging

from 178.15-308.15 K. The uncertainty in heat capacity was reported to be less than 0.2 %. The uncertainty in excess heat capacity was estimated to be 0.258 J/mol/K. The excess heat capacity of these systems increases with increasing temperature. This indicates that the heat effect due to the hydrogen bonds is larger at higher temperature, except in the dilute alcohol concentrations of the ethanol-toluene system where the effect of π-electron-hydroxyl bond formation is dominant. Temperature-dependent excess heat capacities in ethanol-toluene mixtures over the temperature range 298.15-347.37 K were also studied by Pedersen et al. (48). Their data agreed well with those from Hwa and Ziegler. Recko (12) studied the excess heat capacities of the n-propyl alcohol-benzene and n-propyl alcohol-cyclohexane systems. Heat capacities were determined over the temperature range 298.15-313.15 K for five mixtures with various concentrations. The results agreed with the assumption of the existence of an interaction between π-electrons of the aromatic molecules and the -OH group of alcohol molecules. The π-electrons of the solvent are the main factor that causes an increase in heat of mixing. Klesper (42) also measured ethanol-cyclohexane mixtures for four concentrations at temperatures ranging from 293.15-343.15 K.

Solutions of normal alcohols and water were studied by Benson et al. (49,50). Heat capacities were determined for aqueous methanol, ethanol, and 1-propanol at 288.15 K, 298.15 K, and 308.15 K. For the methanol and ethanol systems, excess heat capacities increased with increasing temp-

erature for all compositions. This behavior reflects an increasing net disruption of hydrogen bonds with increasing temperature. Excess heat capacities for aqueous 1-propanol also increased with increasing temperature except at high mole fractions of water.

Heat of Mixing Data

Several good compilations on heat of mixing data have been published. Rowlinson (13) devoted two chapters of his book to the discussion of experimental data available on various binary systems. A handbook of heats of mixing has recently completed by Christensen et al. (51). This book consists of tables which summarize the published literature data through 1980. Quantities of such data can also be found in Kehiaian (52). The heat of mixing data obtained from these references were useful and provided consistent excess heat capacity data for this study.

Heats of mixing for mixtures of n-hexane-methanol were measured by Savini et al. (53). The data were taken for the entire composition range from 298.15-323.15 K. Ragaini et al. (54) investigated mixtures of 1-pentanol and n-heptane over the temperature range 288.15-303.15 K. Featherstone and Dikinson (55) studied the 1-octanol-n-decane system over the temperature range 293.15-313.15 K. The heat of mixing data measured in these studies were all positive and increased with increasing temperature. The molar excess enthalpy of mixtures of water and ethanol was investigated at 323.15, 331.15, 343.15, 363.15, and 383.15 K by Larkin

(56). The heat of mixing of this system increased with increasing temperature. This agreed well with the fact that the number of hydrogen bonds that were broken in the mixture increased with increasing temperature.

Mrazek and Van Ness (57) examined the effect of temperature on heat of mixing for the normal alcohols methanol, ethanol, propanol, butanol, and pentanol in benzene, toluene, and ethylbenzene at 298.15, 308.15, and 318.15 K. The heat of mixing of these systems increased with increasing temperature. Normal alcohol-cyclohexane systems were studied extensively by Veselý et al. (58). Data for mixtures of 1-propanol-cyclohexane and 1-butanol-cyclohexane were taken over the entire composition range at 298.15, 303.15, 313.15, 318.15, and 323.15 K.

To obtain molar excess heat capacity data, the molar excess enthalpy (h^E) of each system was correlated with the following equation for a binary mixture:

$$h^E = x(1 - x)(a_0 + \sum_j a_j \, x^{j-\frac{1}{2}}) \qquad j = 1,2,3,5 \qquad (2\text{-}46)$$

The molar excess heat capacity (C_p^E) was obtained by differentiating Eq. (2-46) with respect to temperature

$$C_p^E = x(1-x)\{da_0/dT+\sum_j da_j/dT \; x^{j-\frac{1}{2}}\} \quad j = 1,2,3,5 \qquad (2\text{-}47)$$

where a_0 and a_j are functions of temperature and were expressed as quadratic equations:

$$a_j = b_j + c_j \, T + d_j \, T^2 \qquad j = 0,1,2,3,5 \qquad (2\text{-}48)$$

$$d(a_j)/dT = c_j + 2 \, d_j \, T \qquad j = 0,1,2,3,5 \qquad (2\text{-}49)$$

Since the value of excess heat capacity was obtained by differentiation of the heat of mixing data with respect to temperature, a loss of accuracy would be expected. These excess heat capacities are shown in Appendix A.

CHAPTER III

PROPOSED PREDICTION METHOD

Theoretical Background

The method presented in this chapter is based on the well-known group-contribution concept which has been applied successfully for estimating a wide variety of pure-component properties, such as liquid densities, heat capacities, and critical constants. The basic principle involved in the group-contribution method is that there are thousands of compounds of interest; however, the number of functional groups that constitute those compounds is much smaller. Therefore, if we assume a physical property of a fluid is the sum of all the contributions made by the groups present in the molecule, we can obtain a possible method to correlate the properties of a very large number of fluids in terms of a much smaller number of parameters which characterize the contributions of individual groups.

Extension of the group-contribution idea to mixtures is attractive because the large number of multicomponent liquid mixtures exist in chemical industries contains no more than fifty functional groups (2). The group contribution model proposed for calculating the heat capacities of liquid mixtures in this study is based on Kehiaian's group surface

theory. The basic concept of the group surface model is that a solution is considered as a mixture of the individual groups which are characterized by different types of surfaces in the solution. This scheme assumes that the thermodynamic excess properties are determined by the interactions between these group surfaces, and these contributions depend in some way upon the numbers and types of structural groupings which constitute the solution. It further assumes that the group contributions depend only on the group environment and are independent of the way that the groups are connected. Consequently, once the group contributions are established using experimental data, the excess functions of additional mixtures with the same groupings can also be estimated. Any group-contribution method is essentially an approximation technique because the contribution of a given group in one molecule is not necessarily the same as that in another molecule.

Proposed Model

As indicated in the preceding chapter, the Guggenheim-Barker-Kehiaian (GBK) theory is based on a quasi-chemical pseudo-lattice model. In addition, it considers interactions in terms of group surfaces. This theory was studied carefully and was found to give qualitatively correct predictions on excess Gibbs free energies (26). However, the thermodynamic excess functions derived from the GBK theory are complicated so that these excess functions must be simplified and/or modified in order to be used conveniently.

The proposed model begins with GBK's simplest approach, which is the random-mixing (or zeroth) approximation, for liquid mixtures of nonpolar molecules. In the random-mixing approximation, the molar excess enthalpy can be obtained from Eq. 2-30 when Z approaches infinity. In this case the molar excess enthalpy (h^{E*}) of a multicomponent mixture is given by:

$$h^{E*} = 0.5 \left(\sum_i q_i x_i\right) \sum_i \sum_j R_i R_j h^*_{ij} \qquad (3\text{-}1)$$

$$h^*_{ij} = -0.5 \sum_s \sum_t (f_{si} - f_{tj})(f_{ti} - f_{tj}) h^*_{st} \qquad (3\text{-}2)$$

where h^*_{st} is the molar interchange enthalpy of the surface contact (s,t) in the random-mixing approximation. The surface fraction of molecule i in the mixture is:

$$R_i = q_i x_i / \sum_i q_i x_i \qquad (3\text{-}3)$$

The group surface fraction of type s in molecule i is defined by:

$$f_{si} = q_{si} / q_i \qquad (3\text{-}4)$$

$$q_i = \sum_s q_{si} \qquad (3\text{-}5)$$

The geometrical parameter "relative molecular surface" (q_i) of molecule i is calculated by adding appropriate group increments (q_{si}) by Bondi's method (59).

Equations 3-1 and 3-2 can be extended to the molar excess heat capacity (C_p^{E*}) of a multicomponent mixture in the random-mixing approximation in the following form:

$$C_p^{E*} = 0.5 \left(\sum_i q_i x_i\right) \sum_i \sum_j R_i R_j C^*_{pij} \qquad (3\text{-}6)$$

$$C^*_{pij} = -0.5 \sum_s \sum_t (f_{si} - f_{sj})(f_{ti} - f_{tj}) C^*_{pst} \qquad (3\text{-}7)$$

where C^*_{pst} is the molar interchange heat capacity of surface contact (s,t) in the random-mixing approximation and must be obtained from experimental data on mixtures.

In order to generate predictive group constants for group contributions, a general form which can be used to describe the behavior of the interchange parameter (C^*_{pst}) in Eq. 3-7 must be developed. The interchange parameter (C^*_{pst}) is assumed to be temperature and concentration dependent. After that, the experimental excess heat capacities for the nonpolar mixtures of n-alkane-cyclohexane and n-alkane-benzene were used to calculate the parameter (C^*_{pst}) at various temperatures and concentrations using Eqs. 3-6 and 3-7. The molar interchange parameter (C^*_{pst}) was found to be dependent on both concentration and temperature. The values of C^*_{pst} for the n-hexadecane-cyclohexane mixtures at different concentrations and temperatures were plotted in Figures 1 and 2. From the results shown in those two Figures, it is obvious that a simple polynomial function can be employed to represent the shape of each curve in the Figures.

For the sake of simplicity, a second-order polynomial, which is a function of temperature and the difference of the mole fractions of the components, was used to represent C^*_{pst}

$$C^*_{pst} = \sum_m \sum_n A_{mn} T^m (x_i - x_j)^n \qquad m,n = 0,1,2 \qquad (3\text{-}8)$$

The coefficient, A_{mn}, depends on the type of group surface

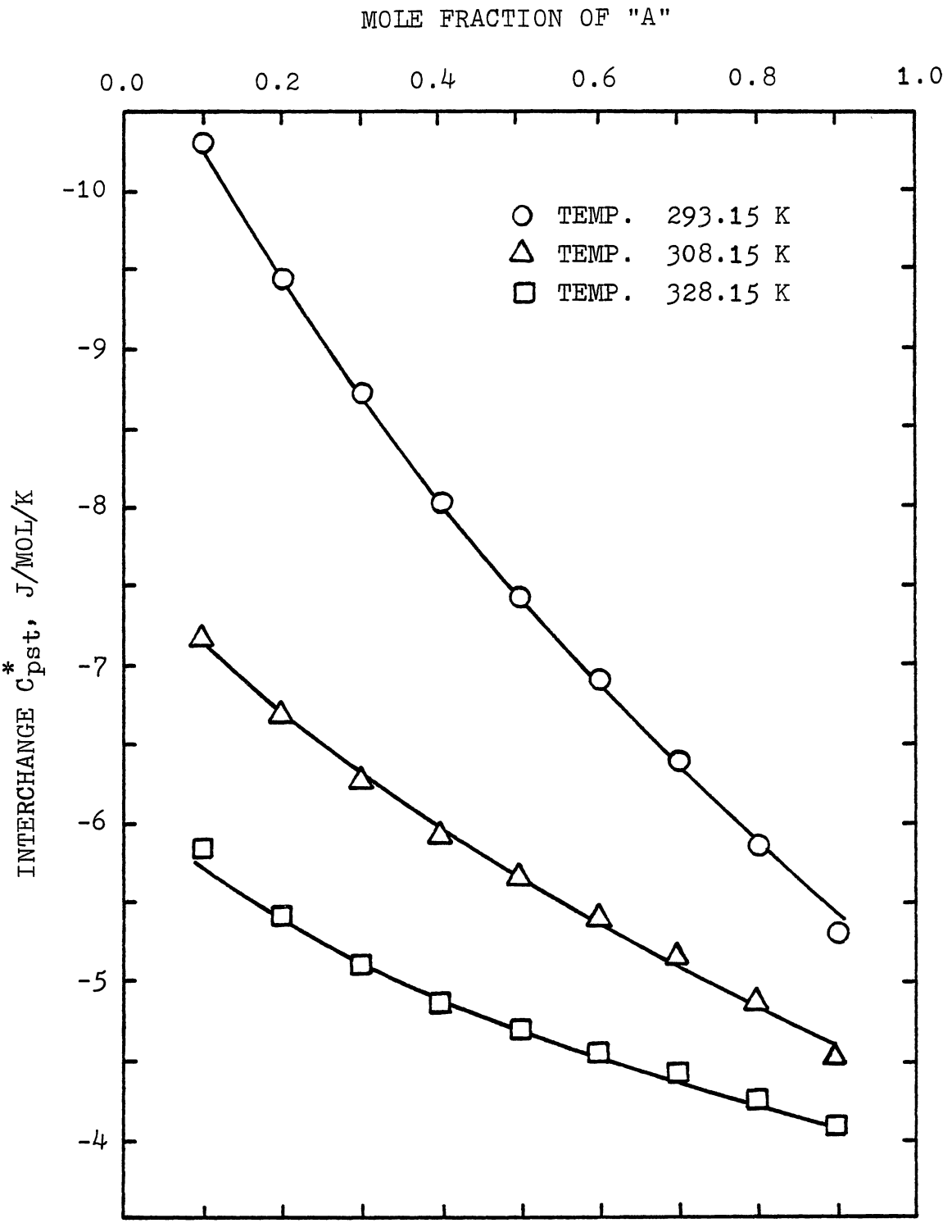

Figure 1. Composition Dependence of C^*_{pst} for the Cyclohexane(A)-N-Hexadecane(B) Mixtures

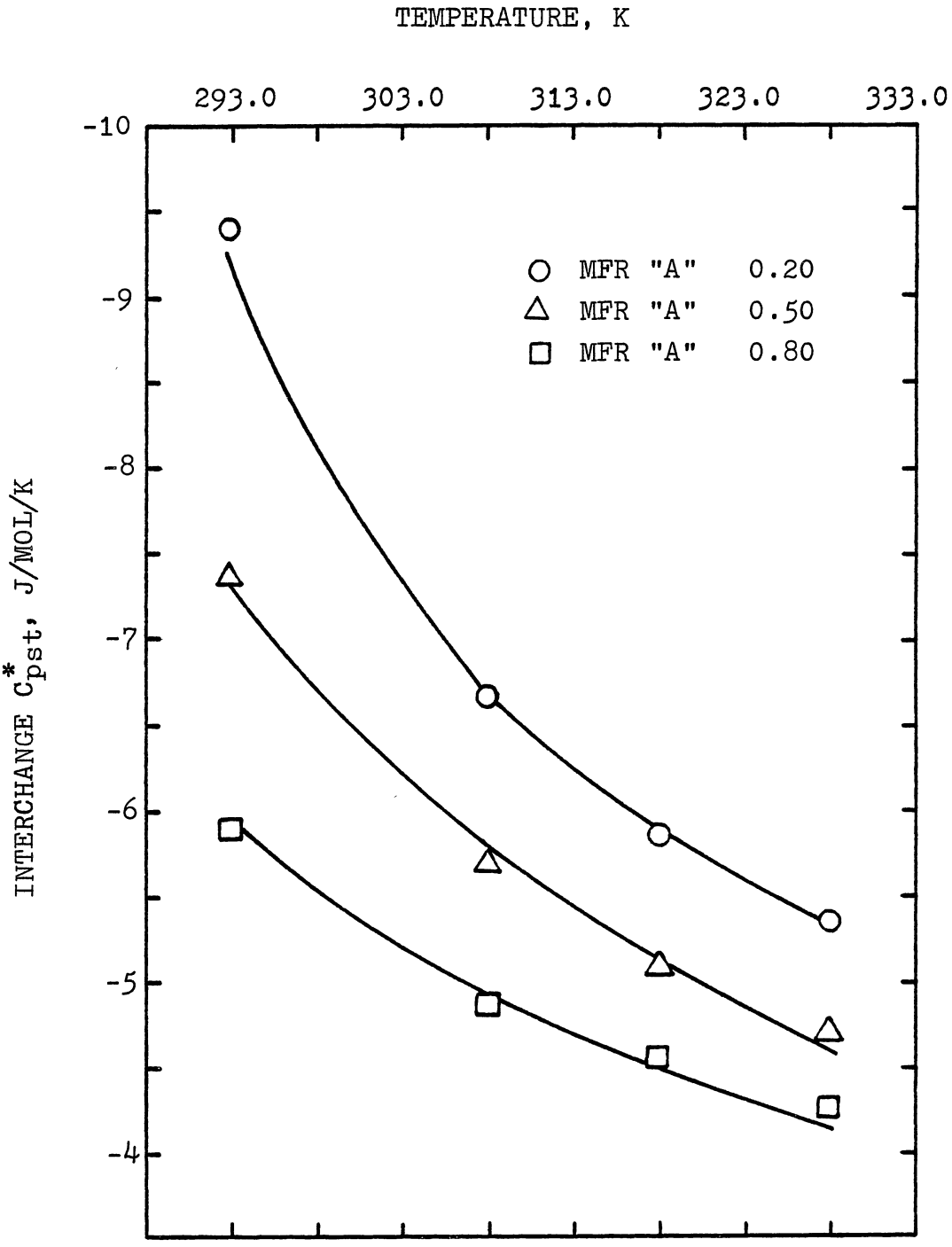

Figure 2. Temperature Dependence of C^*_{pst} for the Cyclohexane(A)-N-Hexadecane(B) Mixtures

interaction present. Equations 3-6 to 3-8 represent a generalized group surface model, which is based on the group contribution approach, for the excess heat capacity of nonpolar mixtures.

In polar mixtures, with orientational dependent group interaction, the shape of the excess function is distorted with respect to the result of the random-mixing approximation. The fact that a group contribution method can not be applied to polar molecules is not crucial in practice. The classical quasi-chemical treatment uses a single parameter, which is the coordination number Z, to account for nonrandomness. The random-mixing equations were obtained for Z approaching infinity. In the classical model the entire interchange energy of any contact was assumed to generate nonrandomness to the extent expressed by the coordination number Z. Generally, Z was assumed to be the same for all the surface contacts because no explicit relationship could be found for Z with the interchange energy. However, as indicated by Kehiaian (60), a physically more realistic approach should have its own coordination number for each nonrandmness contact.

At this point, the task remaining is to generate proper correction factors based on the coordination number for the random-mixing interchange heat capacities (C^{*}_{pst}) in Eq. 3-7 to account for nonrandomness. When this random-mixing model shown by Eqs. 3-6 to 3-8 was applied to correlate the experimental excess heat capacity data for the normal alcohols methanol, ethanol, propanol, pentanol, and octanol in the

normal alkanes hexane, heptane, and decane, the average correlation deviations from the experimental data exhibited a trend which was related to the number of carbon atoms (NC) in the n-alcohol molecules. For mole fractions of n-alcohol between 0.02-0.81 and at a temperature of about 300.0 K, the average deviations varied from a positive value of 3.95 J/mol/K for the methanol-hexane system to a negative value of -5.47 J/mol/K for the 1-octanol-decane system. This trend is shown in Figure 3. Similar trends in average deviations were found for mixtures of benzene (or alkylbenzenes), cyclohexane (or alkylcyclohexanes), and water with n-alcohols. The average deviation (AD) is defined as:

$$AD = \{\Sigma \text{ (Calc. - Exp.)}\} \text{ / NPTS} \qquad (3\text{-}9)$$

where Calc. is the calculated value and Exp. is the experimental value. From these results, a weighting function, in terms of NC, can be obtained to correct the deviations due to the nonrandomness effect. This nonrandomness effect is primarily caused by the presence of the polar compound which contains a hydroxyl group. For mixtures containing hydrocarbons, water, and n-alcohols, the correction factors were obtained from the following weighting function (Z_{st}):

$$\begin{aligned} Z_{st} &= NC^{0.8} && \text{for n-alcohols in hydrocarbons} \\ &= NC^{1.1} && \text{for n-alcohols in water} \\ &= 1 && \text{for nonpolar mixtures} \end{aligned} \qquad (3\text{-}10)$$

The function Z_{st} depends upon each pair of surface contacts (s,t) present in the mixture.

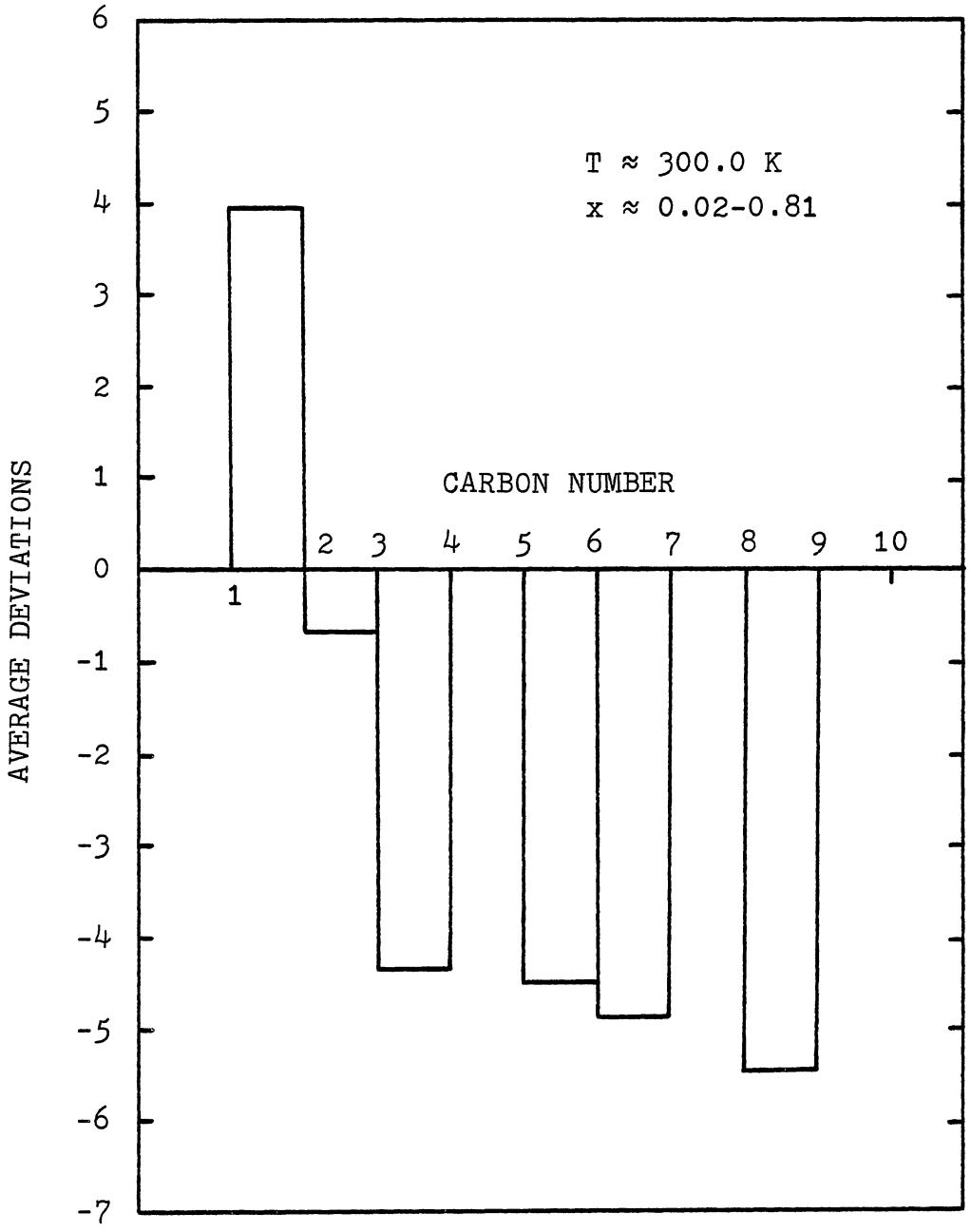

Figure 3. Variations of Average Deviations in Heat Capacities with Carbon Number of N-Alcohols for N-Alkane-N-Alcohol Mixtures

The model proposed for the prediction of the molar heat capacities of liquid mixtures can be summarized as:

$$C_p^M = C_p^{ID} + C_p^E \tag{3-11}$$

The ideal-mixture heat capacity (C_p^{ID}) in Eq. 3-11 can be calculated by using the following mixing rule

$$C_p^{ID} = \sum_i x_i \, C_{pi}^o \tag{3-12}$$

where C_{pi}^o is the heat capacity of pure component i. The molar excess heat capacity (C_p^E) can be written as:

$$C_p^E = 0.5 \left(\sum_i q_i \, x_i\right) \sum_i \sum_j R_i \, R_j \, C_{pij} \tag{3-13}$$

$$C_{pij} = -0.5 \sum_s \sum_t (f_{si} - f_{sj})(f_{ti} - f_{tj}) Z_{st} C_{pst}^* \tag{3-14}$$

$$\begin{aligned} Z_{st} &= NC^{0.8} && \text{for n-alcohols in hydrocarbons} \\ &= NC^{1.1} && \text{for n-alcohols in water} \\ &= 1 && \text{for nonpolar mixtures} \end{aligned} \tag{3-10}$$

$$C_{pst}^* = \sum_m \sum_n A_{mn} \, T^m \, (x_i - x_j)^n \qquad m,n = 0,1,2 \tag{3-8}$$

where the coefficient, A_{mn}, is the predictive group constant in this method.

CHAPTER IV

RESULTS AND DISCUSSION

Estimation of Interaction Parameters

In the model developed in Chapter III, each type of molecule i is characterized by the following geometrical parameters: the molecular surface (q_i); the relative group surface increments (q_{si}); the group surface fraction of type s (f_{si}). To evaluate these geometrical parameters, the method adopted was the one proposed by Bondi (59,61). In this method each atom is considered to be spherical and the surface area (A_s) of a given group s, which is composed of various atoms, is calculated on the basis of the geometry of bonded atoms with inter-penetrating surfaces. The fraction of surface left for a possible contact is calculated from the covalent radii and Van der Waals radii (61,62). The data for the geometrical parameter, i.e., the relative group surface of type s on molcule i (q_{si}) are given in Appendix B. The surface area of molecule i (q_i) was calculated additively by using the corresponding group surfaces (q_{si}). The group surface fraction of type s on molecule i (f_{si}) was evaluated from Eq. 3-4.

The following abbreviations for the types of contact surfaces will be used throughout this work for convenience:

CH_2 - aliphatic (CH_3- or -CH_2-),

ACH_2 - alicyclic (-CH_2-) as in cyclohexane or alkylcyclohexanes,

ACH - aromatic (=CH-) as in benzene or alkylbenzenes,

OH - hydroxyl (-OH) bound to -CH_3 or -CH_2- in normal alcohols,

H_2O - water.

The data base contains consistent literature data for 38 mixtures that cover six pairs of binary surface contacts. The systems that were used for testing the applicability of the proposed model include n-alcohol-n-alkane, n-alkane-cyclohexane (or alkylcyclohexane), n-alcohol-cyclohexane (or alkylcyclohexane), n-alkane-benzene (or alkylbenzene), n-alcohol-benzene (or alkylbenzene), and n-alcohol-water. The six pairs of surface contacts involved in these systems are aliphatic/hydroxyl (CH_2,OH), aliphatic/aromatic (CH_2,ACH), aliphatic/alicyclic (CH_2,ACH_2), aromatic/hydroxyl (ACH,OH), alicyclic/hydroxyl (ACH_2,OH), and water/hydroxyl (H_2O,OH).

For each class of mixture, the heat capacity must be studied in a systematic way with respect to the interactions of a given functional group. Each individual pair of functional groups (s,t) is characterized by the molar interchange heat capacity (C^*_{pst}) which includes nine predictive constants, A_{mn}, as shown in Eq. 3-8. To obtain these active constants, A_{mn}, the nonlinear least-squares program, MARQ, written by Chandler (63) was used to adjust the constants to fit the model to the experimental excess heat capacity data. To generate new constants, A_{mn}, for a new pair of groups,

the experimental data for the pair of groups were regressed while the previously generated constants, A_{mn}, for the other pairs of groups were held constant. For example, if experimental heat capacities of n-alkane-n-alcohol mixturs were regressed, the constants, A_{mn}, for the group pair (CH_2,OH) were generated. If experimental heat capacities of n-alkane-benzene mixtures were regressed, the constants, A_{mn}, for the group pair (CH_2,ACH) were generated. Now, for n-alcohol-benzene (or alkylbenzene) mixtures, their experimental heat capacity data were regressed while the previously generated constants, A_{mn}, of (CH_2,OH) and constants, A_{mn}, of (CH_2,ACH) were held constant, and the new constants, A_{mn}, for the group pair (ACH,OH) were generated.

The predictive constants, A_{mn}, for the six pairs of groups are given in Table I. The heat capacities for the multicomponent liquid mixtures composed of the above-mentioned binary surface contacts can be predicted using the data given in Table I, the geometrical parameters, and the pure-component heat capacities.

Computed Results and Comparison

In this work, the proposed method was applied to 8 n-alkane-n-alcohol mixtures, 3 n-alcohol-water mixtures, 8 n-alcohol-benzene (or alkylbenzene) mixtures, 4 n-alcohol-cyclohexane (or alkylcyclohexane) mixtures, 10 n-alkane-benzene (or alkylbenzene) mixtures, and 5 n-alkane-cyclohexane (or alkylcyclohexane) mixtures. The deviations of the heat capacities between the computed results and the experimental

TABLE I

THE CONSTANTS, A_{mn}, IN EQ. 3-8 FOR THE PAIRS OF INTERACTION GROUPS

(CH_2,ACH)	(CH_2,ACH_2)	(CH_2,OH)	(ACH,OH)	(ACH_2,OH)	(H_2O,OH)
8809.469	227.8827	1206.111	-6406.859	-96.35534	70.42308
-57.90071	-1.522927	-10.56080	40.22299	-1.860623	-2.028844
0.095043	0.002501	0.023013	-0.061351	0.008603	0.007348
8336.475	-33.28000	48.68275	-6638.886	-456.6640	295.0808
-54.81836	0.220200	1.446264	44.62264	4.510664	-0.080793
0.090081	-0.000363	-0.007129	-0.076638	-0.011658	-0.003598
16527.76	-17.11535	-1253.131	-14455.67	1632.968	-1506.821
-108.6963	0.117525	10.58173	97.03291	-9.143418	11.48762
0.178628	-0.000202	-0.020144	-0.161706	0.013429	-0.020234

data were summarized in Tables II through VII. The number of data points, temperature range, average absolute percent deviations, and overall average absolute percent deviation for each type of mixture are also presented. For the purpose of examining the validity of the proposed model, the heat capacities of the mixtures with asterisks were predicted by using the pre-determined group constants, A_{mn}, as shown in Table I. As can be seen from Tables II through VII, the results obtained from both correlation and prediction schemes were equally good.

The percent deviation (PD) is defined as

$$PD = \{(Calc. - Exp.) / Exp.\}100 \qquad (4\text{-}1)$$

where Calc. is the calculated value and Exp. is the experimental value. The average absolute percent deviation (AAPD) is defined as:

$$AAPD = \Sigma\ |PD| / NPTS \qquad (4\text{-}2)$$

NPTS is the number of data points of each system. The maximum positive percent deviation (MXPPD) is the largest positive percent deviation among NPTS PD's. The maximum negative percent deviation (MXNPD) is the largest negative percent deviation among NPTS PD's. The overall average absolute percent deviation (OAAPD) is defined as:

$$OAAPD = \Sigma\ AAPD / NSYS \qquad (4\text{-}3)$$

where NSYS is the number of systems in each type of mixture.

Table II shows the n-alkane-n-alcohol mixtures used to

generate constants, A_{mn}, for the group pair (CH_2,OH) listed in Table I. The heat capacities for the mixtures with asterisks were those predicted by using the constants, A_{mn}, generated from the mixtures without asterisks. For cases in which the temperature of the n-alkane-n-alcohol mixtures ranges from 181 to 343 K, the overall average absolute percent deviation from the experimental heat capacity data is 0.93 %.

Table III shows the results for n-alkane-benzene (or alkylbenzene) mixtures. Mixtures without asterisks are those used to generate the constants, A_{mn}, for the group pair (CH_2,ACH); those with asterisks are the ones used for predictions. Temperature for all systems ranged from 298.1 to 310.7 K. The overall average absolute percent deviation from the experimental heat capacity data is 0.17 %.

Table IV shows the comparison of the results for different n-alcohol-benzene (or alkylbenzene) mixtures. In these mixtures, there are three pairs of surface contacts: aliphatic/hydroxyl (CH_2,OH), aliphatic/aromatic (CH_2,ACH), and aromatic/hydroxyl (ACH,OH). To generate constants, A_{mn}, for the new group pair (ACH,OH), the mixtures without asterisks were used for regression, while the previously determined constants, A_{mn}, for (CH_2,OH) and (CH_2,ACH) were held constant. The heat capacities of the mixtures with asterisks were those predicted from the constants, A_{mn}, for the three group pairs. The temperature for all the mixtures considered ranged from 178.1 to 347.4 K. The average absolute percent deviation from the experimental heat capacity

TABLE II

RESULTS OF LIQUID HEAT CAPACITY CORRELATION AND PREDICTION FOR N-ALCOHOL-N-ALKANE MIXTURES

Mixtures	NPTS	Temp. Range,K	MXPPD	MXNPD	AAPD	Ref.
Methanol-Hexane	69	307-323	1.61	-2.83	1.04	TA1
Ethanol-Heptane	54	254-343	1.40	-2.02	0.77	42,43
1-Propanol-Hexane	126	181-304	0.67	-2.99	0.97	45
1-pentanol-Heptane	31	293-303	0.84	-2.71	1.00	TA2
1-Hexanol-Hexane	69	232-302	1.06	-2.46	0.72	46
1-Octanol-Decane	92	293-313	1.57	-2.67	0.94	TA3
1-Propanol-Heptane*	117	201-303	0.52	-1.89	0.62	45
1-Propanol-Hexadecane*	15	303-313	0.77	-3.77	1.36	44

OAAPD = 0.93 %

1. * not included in regression.
2. NPTS stands for the number of data ponits.
3. MXPPD is the maximum positive percent deviation.
4. MXNPD is the maximum negative percent deviation.
5. AAPD stands for the average absolute percent deviation.
6. OAAPD is the overall average absolute percent deviation.
7. TA1-TA3 represents Table XI to Table XIII in Appendix A.

TABLE III

RESULTS OF LIQUID HEAT CAPACITY CORRELATION AND PREDICTION FOR N-ALKANE-BENZENE (OR ALKYLBENZENE) MIXTURES

Mixtures	NPTS	Temp. Range,K	MXPPD	MXNPD	AAPD	Ref.
Heptane-Benzene	15	298.1	0.31	-0.05	0.04	52
Hexane-Benzene	9	310.7	0.00	-0.27	0.19	41
Octane-Benzene	9	310.7	0.00	-0.22	0.14	41
Dodecane-Benzene	9	310.7	0.17	-0.04	0.12	41
Hexadecane-Benzene	9	310.7	0.76	-0.00	0.51	41
Tetradecane-Toluene*	5	298.1	0.46	-0.00	0.37	52
Heptane-Ethyl-benzene*	8	298.1	0.09	-0.00	0.04	52
Heptane-Propyl-benzene*	6	298.1	0.08	-0.01	0.04	52
Heptane-Butyl-benzene*	5	298.1	0.16	-0.00	0.13	52
Benzene-Propyl-benzene*	5	298.1	0.12	-0.00	0.09	52

OAAPD = 0.17 %

* not included in regression.

TABLE IV

RESULTS OF LIQUID HEAT CAPACITY CORRELATION AND PREDICTION FOR N-ALCOHOL-BENZENE (OR ALKYLBENZENE) MIXTURES

Mixtures	NPTS	Temp. Range,K	MXPPD	MXNPD	AAPD	Ref.
Methanol-Benzene	27	298-318	1.18	-1.41	0.73	TA4
Ethanol-Benzene	30	298-318	1.49	-1.74	0.86	TA5
Ethanol-Toluene	129	178-347	1.96	-1.60	0.64	47,48
1-Propanol-Benzene	20	298-313	0.47	-3.26	1.10	12
1-Pentanol-Benzene	30	298-318	2.01	-0.64	0.99	TA6
1-Propanol-Toluene*	30	298-318	1.25	-2.22	0.96	TA7
1-Butanol-Ethyl-benzene*	30	298-318	0.47	-2.51	0.88	TA8
1-Pentanol-Ethyl-benzene*	30	298-318	1.05	-1.22	0.64	TA9

OAAPD = 0.85 %

1. * not included in regression.

2. TA4-TA9 represents Table XIV to Table XIX in Appendix A.

data is 0.64 % for the ethanol-toluene system and 1.10 % for the 1-propanol-benzene system. The maximum percent deviation is 3.26 % for the 1-propanol-benzene mixture. The overall average absolute percent deviation from the experimental heat capacity data is 0.85 %.

Table V shows the results for n-alkane-cyclohexane (or alkylcylohexane) mixtures. The mixtures without asterisks are those used in regressive analysis to generate constants, A_{mn}, for the group pair (CH_2,ACH), while the mixtures with asterisks are the ones used for prediction. The temperature ranged from 293.2 K to 328.2 K. The overall average absolute percent deviation from the experimental heat capacities of all mixtures is 0.35 %.

Table VI shows the comparison of the results for the n-alcohol-cyclohexane (or alkylcyclohexane) mixtures. This class of mixture contains three pairs of surface contacts: aliphatic/hydroxyl (CH_2,OH), aliphatic/alicyclic (CH_2,ACH_2), and alicyclic/hydroxyl (ACH_2,OH). New constants, A_{mn}, for the binary contacts (ACH_2,OH) were generated from the mixtures without asterisks, while the previously determined constants, A_{mn}, for (CH_2,OH) and (CH_2,ACH_2) were held constant. The heat capacities of the mixtures with asterisks were those predicted from the constants, A_{mn}, of the above three group pairs. The temperature in the systems considered ranged from 268.1 to 343.1 K. The maximum percent deviation from the experimental heat capacity data is 2.64 % for the 1-butanol-cyclohexane mixture. The overall average absolute percent deviation is 0.60 %.

TABLE V

RESULTS OF LIQUID HEAT CAPACITY CORRELATION AND PREDICTION FOR N-ALkANE-CYCLOHEXANE (OR ALKYLCYCLOHEXANE) MIXTURES

Mixtures	NPTS	Temp. Range,K	MXPPD	MXNPD	AAPD	Ref.
Octane-Cyclohexane	27	283-328	0.79	-0.07	0.24	40
Dodecane-Cyclo hexane	27	283-328	0.10	-0.58	0.24	40
Hexadecane-Cyclo-hexane	45	293-328	1.28	-0.00	0.57	40
Hexane-Cyclohexane*	12	298	0.00	-0.87	0.56	52
Decane-Cyclohexane*	27	283-328	0.27	-0.28	0.15	40
		OAAPD = 0.35 %				

* not included in regression.

TABLE VI

RESULTS OF LIQUID HEAT CAPACITY CORRELATION AND PREDICTION FOR N-ALCOHOL-CYCLOHEXANE (OR ALKYLCYCLOHEXANE) MIXTURES

Mixtures	NPTS	Temp. Range,K	MXPPD	MXNPD	AAPD	Ref.
Ethanol-Cyclohexane	44	293-343	1.10	-2.27	0.73	42
1-Propanol-Cyclo-hexane	139	298-323	0.86	-1.80	0.55	TA10
1-Butanol-Cyclo-hexane	138	298-323	1.96	-2.64	0.53	TA11
Ethanol-Methyl-Cyclohexane*	45	266-308	0.82	-2.25	0.59	47
		OAAPD = 0.60 %				

1. * not included in regression.

2. TA10 and TA11 are Table XX and Table XXI in Appendix A.

Table VII shows the results for the mixtures that are composed of n-alcohol and water. There are three pairs of surface contacts in these mixtures: aliphatic/hydroxyl (CH_2,OH), aliphatic/water (CH_2,H_2O), and water/hydroxyl (H_2O,OH). The new constants, A_{mn}, for the group pair (H_2O,OH) were generated from water-ethanol mixtures, while the previously determined constants, A_{mn}, for the group pair (CH_2,OH) were held constant. The contribution from the interactions of the group pair (CH_2,H_2O) to the mixture heat capacities was assumed to be negligible. This assumption seems to be reasonable because the mutual solubilities of water and n-alkanes are very small. The mixtures with asterisks are those used for prediction. The temperature of the systems under consideration ranged from 288.1 to 383.1 K. The maximum percent deviation is 7.66 % for the 1-propanol-water mixture. The overall average absolute percent deviation is 0.99 %.

Table VIII gives a summary for the number of data points used, the temperature range, and the overall average absolute percent deviation (OAAPD) for each class of mixture studied. The smallest OAAPD is 0.17 %, which was obtained for the n-alkane-benzene (or alkylbenzene) system, and the largest OAAPD is 0.99 %, which was obtained for the n-alcohol-water system.

The equation for an ideal mixture defined by Eq. 3-12 was used for the purpose of comparison because there was no general technique available for the calculation of liquid mixture heat capacity over a wide range of temperature and

TABLE VII

RESULTS OF LIQUID HEAT CAPACITY CORRELATION AND PREDICTION FOR N-ALCOHOL-WATER MIXTURES

Mixtures	NPTS	Temp. Range,K	MXPPD	MXNPD	AAPD	Ref.
Ethanol-Water	217	288-383	1.77	-2.44	0.56	49,50 56,64
Methanol-Water*	69	288-308	3.13	-0.36	0.83	49,50
1-Propanol-Water*	69	288-308	7.66	-0.90	1.59	49,50
		OAAPD = 0.99 %				

* not included in regression.

TABLE VIII

SUMMARY FOR ALL THE SYSTEMS STUDIED

Systems	NPTS	Temperature Range,K	OAAPD
n-Alkanes-n-Alcohols	573	181.0-343.1	0.95
n-Alcohols-Water	355	288.1-383.1	0.99
n-Alcohols-Benzene#	326	178.1-347.4	0.85
n-Alcohols-Cyclohexane*	366	268.1-343.1	0.60
n-Alkanes-Benzene#	80	298.1-310.7	0.17
n-Alkanes-Cyclohexane*	138	283.1-328.1	0.35

1. # includes alkylbenzenes.
2. * includes alkylcyclohexanes.
3. NPTS stands for the number of data ponits.
4. OAAPD is the overall average absolute percent deviation.

composition. Table IX shows the comparison of the heat capacities predicted from the proposed method with those calculated from the ideal-mixture equation for the polar mixtures containing normal alcohols. The comparison of the results predicted from the proposed method with those calculated from the ideal-mixture equation for the nonpolar mixtures is presented in Table X. As can be seen from these tables, the proposed method has significant advantage over the ideal-mixture equation in calculating the heat capacities for the polar liquid mixtures. Even for the nonpolar mixtures, which can be treated as ideal mixtures due to the fact that the excess heat capacities are very small with respect to total heat capacities, the proposed method still gives better results. Sample plots of predicted results for ethanol-methylcyclohexane, water-1-propanol, and water-methanol mixtures are presented in Figures 4 to 6. An illustrative prediction using the proposed method is shown in Appendix B.

TABLE IX

COMPARISON OF HEAT CAPACITIES PREDICTED FROM THIS WORK WITH THOSE CALCULATED FROM IDEAL MIXTURE EQUATION DEFINED BY EQ. 3-12 FOR POLAR MIXTURES

Mixtures	NPTS	Temp. Range,K	IDMXEQ (AAPD)	This Work (AAPD)
1-Propanol-Heptane	117	201-303	2.219	0.620
1-Propanol-Hexadecane	15	303-313	4.700	1.357
Methanol-Water	69	288-308	4.580	0.834
1-Propanol-Water	69	288-308	7.766	1.594
1-Propanol-Toluene	30	298-318	7.140	0.962
1-Butanol-Ethyl-benzene	30	298-318	6.489	0.880
1-Pentanol-Ethyl-benzene	30	298-318	5.661	0.637
Ethanol-Methyl-cyclohexane	45	266-308	4.309	0.599
OAAPD =			5.358	0.935

1. NPTS stands for the number of data ponits.
2. IDMXEQ is the ideal mixture equation.
3. AAPD stands for the average absolute percent deviation.
4. OAAPD is the overall average absolute percent deviation.

TABLE X

COMPARISON OF HEAT CAPACITIES PREDICTED FROM THIS WORK WITH THOSE CALCULATED FROM IDEAL MIXTURE EQUATION DEFINED BY EQ. 3-12 FOR NONPOLAR MIXTURES

Mixtures	NPTS	Temp. Range,K	IDMXEQ (AAPD)	This Work (AAPD)
Tetradecane-Toluene	5	298	1.120	0.367
Heptane-Ethylbenzene	8	298	0.658	0.045
Heptane-Propylbenzene	6	298	0.493	0.044
Heptane-Butylbenzene	5	298	0.507	0.129
Benzene-Propylbenzene	5	298	0.437	0.089
Hexane-Cyclohexane	12	298	0.536	0.562
Decane-Cyclohexane	27	283-328	0.935	0.152
OAAPD =			0.669	0.198

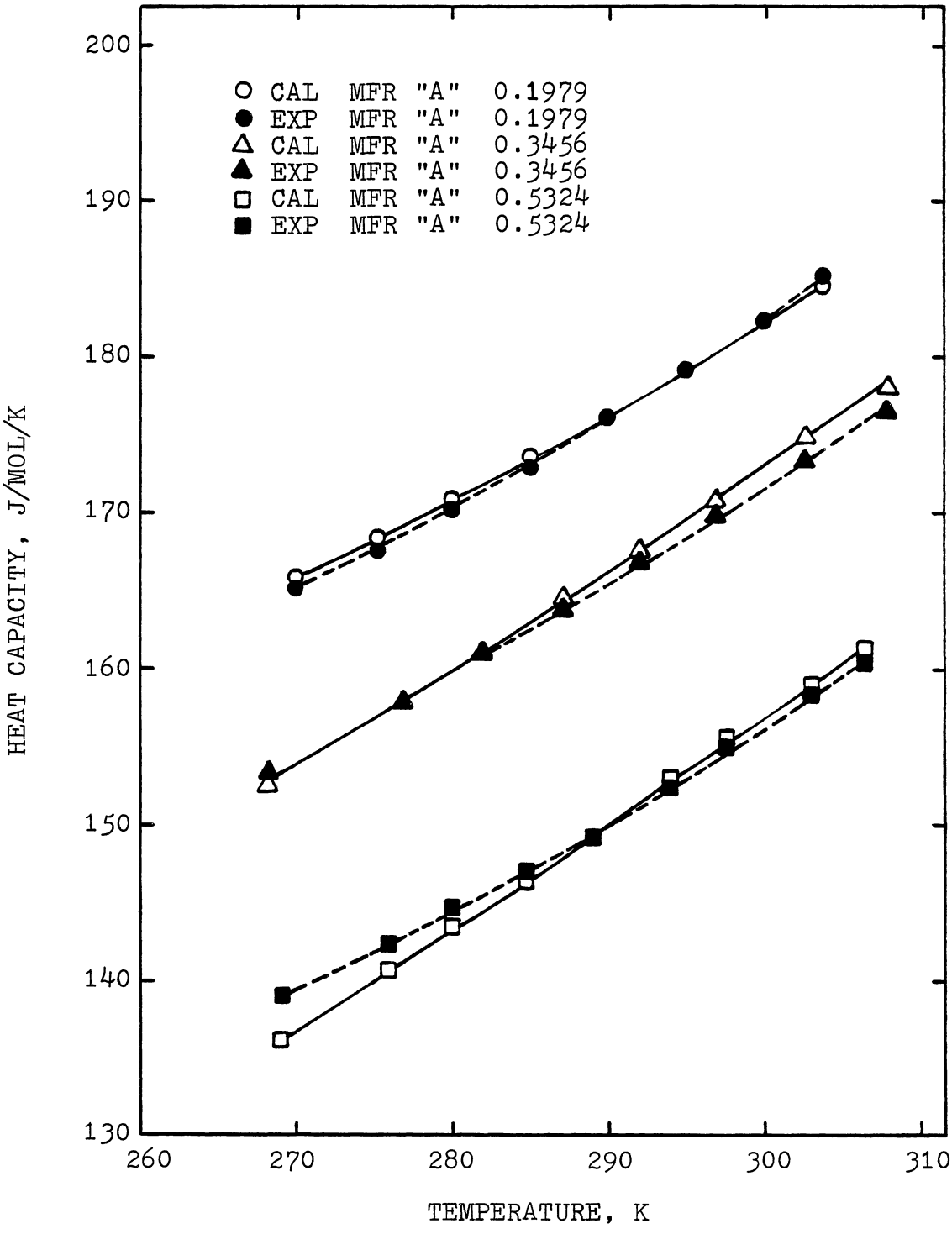

Figure 4. Ethanol (A) and Methylcyclohexane (B) Mixtures

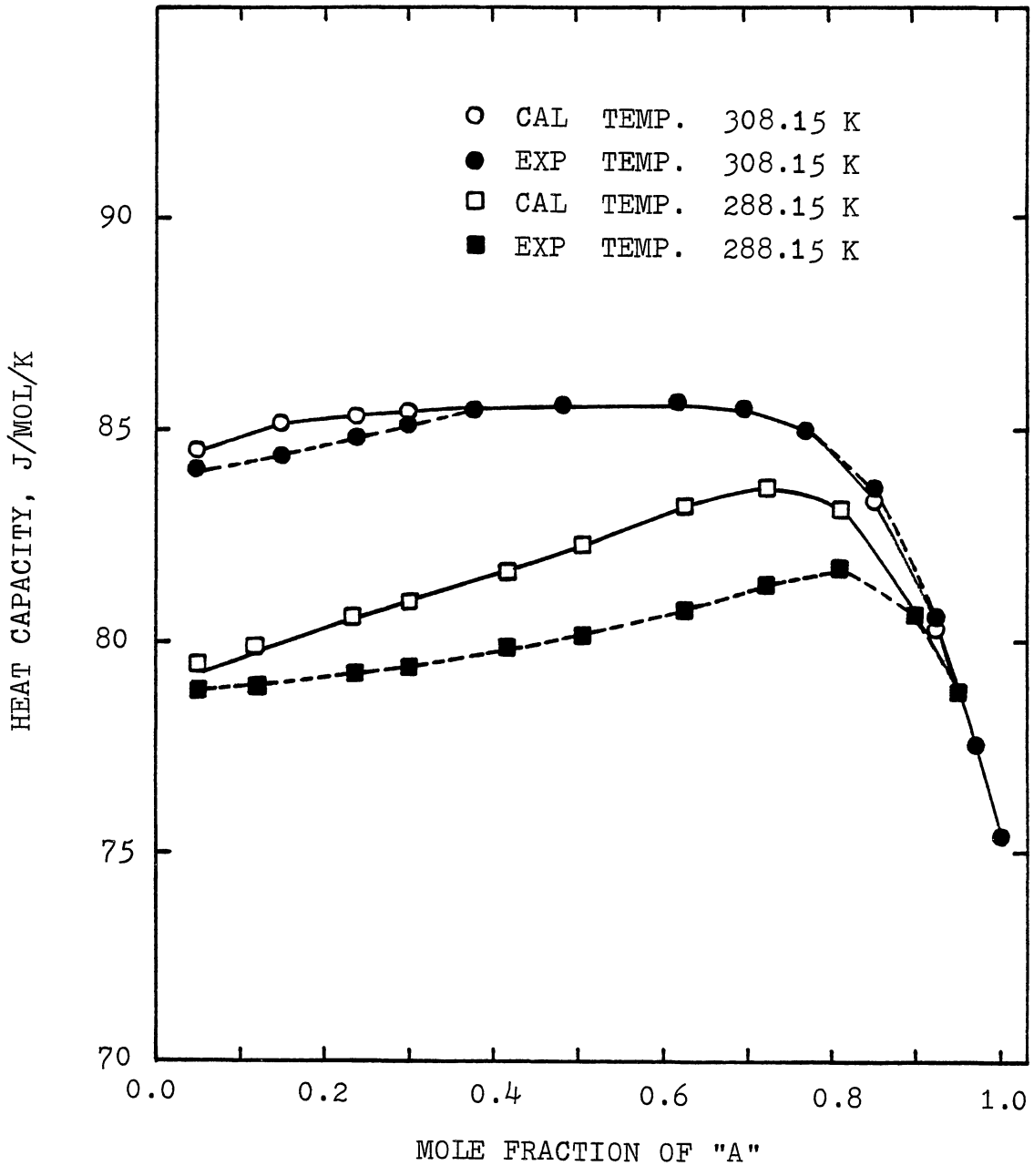

Figure 5. Water (A) and Methanol (B) Mixtures

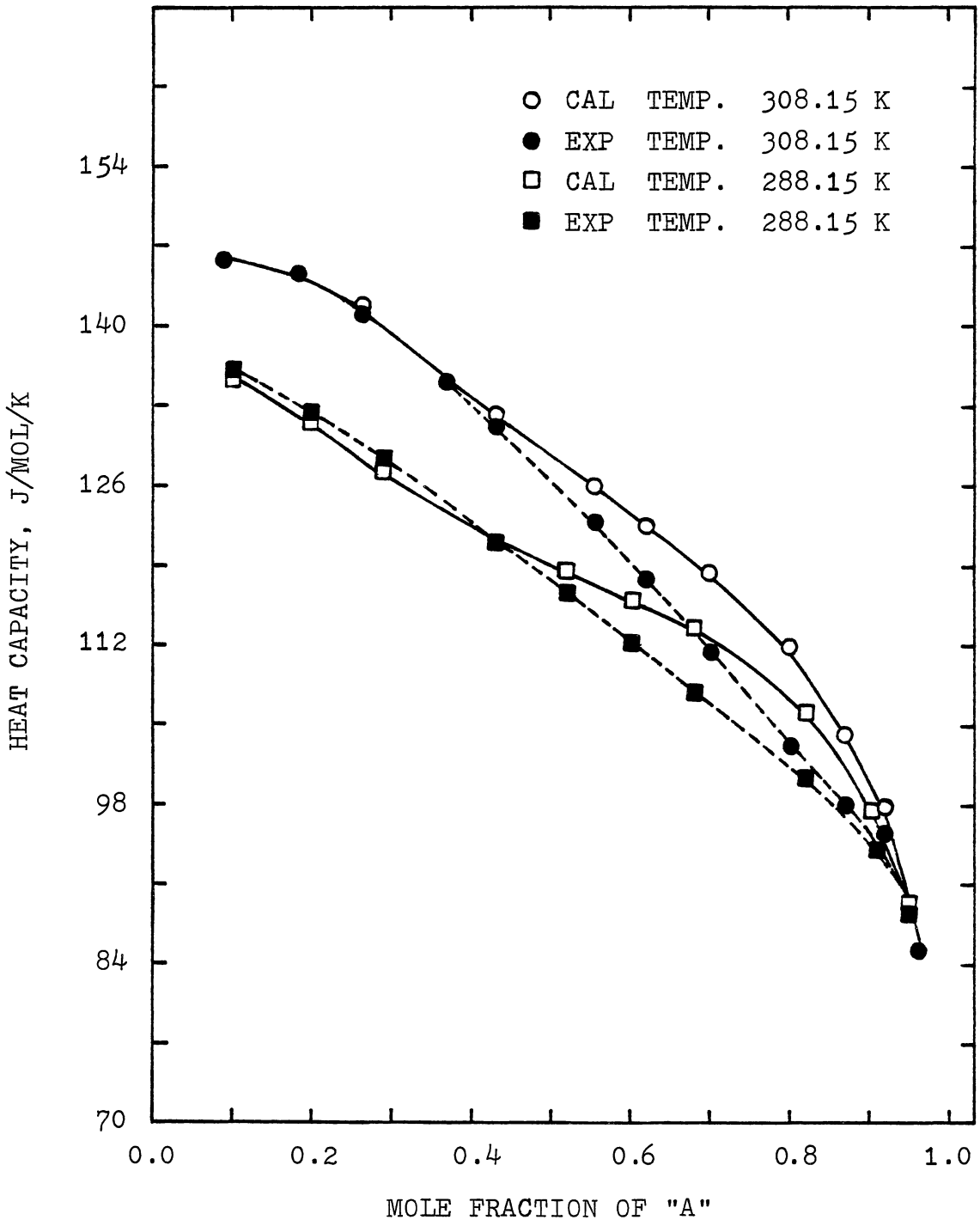

Figure 6. Water (A) and 1-Propanol (B) Mixtures

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The following conclusions can be drawn from the results of this work:

1. The Kehiaian excess-enthalpy equation, which is based on the Guggenheim-Barker quasi-chemical pseudo-lattice model and the random-mixing technique, has been extended successfully to predict heat capacities of organic liquid mixtures by applying a group contribution method.

2. A second order polynomial, which is expressed in terms of temperature and the difference of mole fractions of components, is proposed for the calculation of the interchange heat capacities (C^*_{pst}) in the working equation. The coefficients of C^*_{pst} become the predictive constants for the group contribution method.

3. A weighting function, which is expressed in terms of the number of carbon atoms in normal alcohols, can effectively account for the nonrandomness effect on the excess heat capacities of the polar mixtures containing normal alcohols.

4. The proposed model is capable of handling multicomponent, multigroup mixtures of polar and nonpolar molecules

over a wide range of temperature and concentration.

5. The predictive constants for six binary group surface contacts were generated. These group pairs are (CH_2,OH), (CH_2,ACH), (ACH,OH), (CH_2,ACH_2), (ACH_2,OH), and (H_2O,OH). The proposed model is able to predict the heat capacities for liquid mixtures of these pairs of surface contacts.

6. The proposed method has been tested for binary polar and nonpolar liquid mixtures containing water, hydrocarbons, and n-alcohols. It shows a remarkable improvement over the ideal-mixture equation defined by Eq. 3-12 in predicting the heat capacities for liquid mixtures.

Recommendations

For further investigation the following recommendations are made:

1. Apply the proposed method to mixtures containing other functional groups than those considered in this work.

2. Extend the current study to other multicomponent systems than binary systems.

3. The group contribution approach is promising and should be adopted for prediction of other physical and thermodynamic properties than heat capacity.

BIBLIOGRAPHY

(1) Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, The Properties of Gases and Liquids, McGraw-Hill Book Co., N.Y. (1977).

(2) Fredenslund, A., R. L. Johns, and J. M. Prausnitz, AIChE J., 21(6), 1086 (1975).

(3) Kehiaian, H. V., J. P. E. Grolier, and G. C. Benson, J. chem. Phys., 75, 1032 (1978).

(4) Guggenheim, E. A., Mixtures, Oxford University press, London, 270 (1952).

(5) Prausnitz, J. M., Molecular Thermodynamics of Fluid-phase Equilibria, Prentice-Hall, Englewood Cliffs, New Jersey (1969).

(6) Prigogine, I., R. Defay, and D. H. Everett, Chemical Thermodynamics, pp. 386-388, Longmans, Green and Co LTD, London, Great Britain (1954).

(7) Fortier, J. L. and C. B. George, J. Chem. Thermodynamics, 8(5), 411 (1976).

(8) Kalinowska, J., S. J. Jedlińska, and W. Wóycicki, J. chem. Thermodynamics, 13, 357 (1981).

(9) Brown, I., W. Fock, and F. Smith, Aust. J. Chem., 17, 1106 (1964).

(10) Prigogine, I., The Molecular Theory of Solutions, pp. 305-308, Interscience Publishers, Inc., N.Y. (1957).

(11) Rowlinson, J. S., Liquids and liquid Mixtures, Academic Press Inc., N.Y., 2nd Ed. (1959).

(12) Rećko, W. M., Bull. Acad. Polon. Sci., Sér. Sci. Chim., 16(10), 549 (1968).

(13) Barker, T. A., Lattice Theories of the Liquid State, MacMillan Co., N.Y. (1963).

(14) Hildebrand, J. H. and R. L. Scott, The solubilities of Nonelctrolytes, Dover Publications, N.Y., 3rd Ed. (1964).

(15) Maron, S. H., J. Polymer Sci., 38, 329 (1959).

(16) Maron, S. H., M. M. Wang, and N. J. Nakajima, J. Polymer Sci., 46, 333 (1960).

(17) Rose, V. C., Jr., "Binary Heats of Mixing for Straight Chain Alcohols and Hydrocarbons in Various Solvents", Ph.D. Thesis, University of Missouri (1965).

(18) Langmuir, I., Third Colloid Symposium Monograph, The Chemical Catalog Company, Inc., N.Y. (1925).

(19) Wilson, G. M. and C. H. Deal, Ind. Eng. Chem. Fundamentals, 1(1), 20 (1962).

(20) Ratcliff, G. M. and K. C. Chao, Can. J. Chem. Eng., 49, 120 (1971).

(21) Ratcliff, G. A. and M. A. Khan, Can. J. Chem. Eng., 49, 125 (1973).

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

(23) Kehiaian, H. V., J. Chim. Phys., 75, 1531 (1978).

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

(25) Barker, J. A., J. Chem. Phys., 20, 794 (1952).

(26) Fischer, J., Fluid Phase Equil., 1, 33 (1978).

(27) McDermott, C. and N. Ashton, Fluid Phase Equil., 2, 91 (1978).

(28) Flemr, V., Coll. Czech. Chem. Commun., 41, 3347 (1976).

(29) Panayiotou, C. and J. H. Vera, Can. J. Chem. Eng., 59, 501 (1981).

(30) Scatchard, G., Chem. Rev., 44, 7 (1949).

(31) Basmadjian, D. and B. C. Y. Lu, Can. J. Chem. Eng., 41, 177 (1963).

(32) Otterstedt, J. E. A. and R. W. Missen, Can. J. Chem. Eng., 40, 12 (1962).

(33) Schnaible, H. W., H. C. Van Ness, and J. M. Smith, AIChE J., 3, 147 (1957).

(34) Wilson, G. M., J. Am. Chem. Soc., 86, 127 (1964).

(35) Teja, A. S., J. Chem. Eng. Data, 28(1), 83 (1983).

(36) Timmermans, J., "Phsico-Chemical Constants of Binary Systems in Concentrated Solutions, (Two organic compounds at least one a hydroxyl derivative)", Interscience Publisher, N.Y., Vol. 2 (1955).

(37) Chaney, J. F., V. Ramdas, C. R. Rodriguez, and W. H. Wu, "Thermophysical Properties Research Literature Retrieval Guide 1900-1980 Vol. 6 Mixtures and Solutions", IFI/Plenum Data Company, N.Y. (1982).

(38) Culter, A. J. B. and J. A. Morrison, Trans. Faraday Soc., 61, 429 (1965).

(39) Rodriguez, A. T and D. Patterson, J. Chem. Soc., Faraday Trans. 2, 78, 491 (1982).

(40) Bhattacharyya, S. N. and D. Patterson, J. Phys. Chem., 83(23), 2979 (1979).

(41) Rodriguez, A. T. and D. Patterson, J. Chem. Soc., Faraday Trans. 2, 78, 917 (1982).

(42) Klesper, I., Z. Phys. Chem., 51(1/2), 1 (1966).

(43) Brown, G. N., "Temperature dependence of Excess Thermodynamic Properties of ethanol+n-heptane and 2-propanol+n-heptane Solutions", Ph.D. Thesis, Georgia Institute of Technology (1970).

(44) Rećko, W. M., Bull. Acad. Polon. Sci., Sér. Sci. Chim., 16(10), 553 (1968).

(45) Kalinowska, B., J. Jedlińska, J. Stecki, and W. Wóycicki, J. Chem. Thermodynamics, 13, 357 (1981).

(46) Kalinowska, B. and Wóycicki, J. Chem. Thermodynamics, 16. 609 (1984).

(47) Hwa, S. C. P. and W. T. Ziegler, J. Phys. Chem., 70(8), 2572 (1966).

(48) Pedersen, M. J., W. B. Kay, and H. C. Hershey, J. Chem. Thermodynamics, 7, 1107 (1975).

(49) Benson, G. C. and P. J. D'Arcy, J. Chem. Eng. Data, 27(4), 439 (1982).

(50) Benson, G. C., P. J. D'Arcy, and O. Kiyohara, J. Solution Chem., 9(12), 931 (1980).

(51) Christensen, J. J., R. W. Hanks, and R. M. Izatt,

Handbook of Heat of Mixing, John Wiley&Son, N.Y. (1982).

(52) Kehiaian, H. V., editor-in-chief, "International Data Series, Selected Data Mixtures, Series A", Texas A&M University, College Station, Texas (1983).

(53) Savini, C. G., D. R. Winterhalter, and H. C. Van Ness, J. Chem. Eng. Data, 10(2), 171 (1965).

(54) Ragaini, R. S. and S. Carrá, Lincei-Rend. Sc. fis. mat. e nat., 45, 540 (1968).

(55) Featherstone, J. D. B. and N. A. Dickinson, J. Chem. Thermodynamics, 9, 75 (1979).

(56) Larkin, J. A., J. Chem. Thermodynamics, 7, 137 (1975).

(57) Mrazek, R. V. and H. C. Van Ness, AIChE J., 7, 190 (1961).

(58) Veselý F., P. Uchytil, M. Zabransky, and J. Pick, Collect. Czech. Chem. Commun., 44, 2869 (1979).

(59) Bondi, A., J. Phys. Chem., 68(3), 441 (1968).

(60) Kehiaian, H. V., Fluid Phase Equil., 13, 243 (1983).

(61) Bondi, A., Physical Properties of Molecular Crystals, Liquids and Gases, John Wiley, N.Y. (1968).

(62) Chao, K. C. and R. A. Greenkorn, Thermodynamics of Fluids, in: Chemical Processing and Engineering, L. F. Albright, R. N. Maddox, and J. J. Mcketta, Eds., Dekker, Inc., N.Y. (1975).

(63) Chandler, J. P., MARQ 2.6, A.N.C.I. Standard Fortran, Dept. of Computing and Information Science, Oklahoma State University, Stillwater, Oklahoma (1979).

(64) Rivkin, S. L. and A. N. Vinnikova, Thermal Eng., 11(6), 76 (1964).

APPENDIX A

TABULATION OF HEAT CAPACITY DATA CREATED FROM HEAT OF MIXING DATA

TABLE XI

METHANOL(A)-N-HEXANE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
306.85	0.0250	5.374	201.46
	0.0500	8.138	201.31
	0.0750	9.640	199.90
	0.1000	10.416	197.76
	0.1500	10.916	192.44
	0.2000	10.983	186.68
	0.2500	11.126	181.00
	0.3000	11.457	175.50
	0.4000	12.254	164.65
	0.5000	12.092	152.83
	0.6000	10.144	139.23
	0.7000	6.755	124.19
	0.7500	4.922	116.53
	0.8000	3.269	109.06
	0.8500	1.967	101.93
	0.9000	1.089	95.22
	0.9500	0.546	88.85
313.15	0.0250	5.813	204.35
	0.0500	8.938	204.54
	0.0750	10.722	203.38
	0.1000	11.703	201.42
	0.1500	12.402	196.24
	0.2000	12.436	190.39
	0.2500	12.386	184.46
	0.3000	12.439	178.64
	0.4000	12.681	167.12
	0.5000	12.277	154.95
	0.6000	10.523	141.44
	0.7000	7.605	126.76
	0.7500	5.997	119.27
	0.8000	4.487	111.88
	0.8500	3.185	104.70
	0.9000	2.120	97.75
	0.9500	1.171	90.92
318.15	0.0250	6.161	206.63
	0.0500	9.573	207.08
	0.0750	11.581	206.13
	0.1000	12.725	204.32
	0.1500	13.582	199.25
	0.2000	13.589	193.34
	0.2500	13.387	187.22
	0.3000	13.218	181.13
	0.4000	13.020	169.09
	0.5000	12.424	156.66
	0.6000	10.824	143.22

TABLE XI (Continued)

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
318.15	0.7000	8.279	128.83
	0.7500	6.851	121.48
	0.8000	5.453	114.17
	0.8500	4.153	106.95
	0.9000	2.938	99.81
	0.9500	1.666	92.62
323.15	0.0250	6.509	209.03
	0.0500	10.208	209.75
	0.0750	12.440	209.00
	0.1000	13.746	207.32
	0.1500	14.761	202.37
	0.2000	14.743	196.39
	0.2500	14.387	190.08
	0.3000	13.997	183.72
	0.4000	13.360	171.16
	0.5000	12.570	158.45
	0.6000	11.125	145.08
	0.7000	8.953	130.98
	0.7500	7.704	123.77
	0.8000	6.419	116.52
	0.8500	5.120	109.26
	0.9000	3.756	101.94
	0.9500	2.162	94.38

1. MFR "A" is the molar fraction of component A.
2. C_p^E stands for excess heat capacity in Joule/mol/K.
3. C_p^M represents total heat capacity in Joule/mol/K.

TABLE XII

1-PENTANOL(A)-N-HEPTANE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
293.15	0.2956	8.889	223.54
	0.4235	11.446	222.63
	0.5120	12.283	221.08
	0.5668	11.728	219.04
	0.5671	11.723	219.03
	0.6539	9.355	214.31
	0.7729	5.481	207.22
	0.8949	3.760	202.20
	0.9447	2.976	200.07
298.15	0.1741	10.868	230.90
	0.2964	10.641	227.49
	0.4244	10.693	224.21
	0.5129	10.072	221.28
	0.5779	9.088	218.61
	0.5854	8.950	218.27
	0.6254	8.157	216.44
	0.6966	6.667	213.09
	0.7536	5.614	210.56
	0.8120	4.799	208.22
	0.9018	3.730	204.82
303.15	0.1724	11.446	233.57
	0.2941	12.407	225.83
	0.4215	9.994	221.53
	0.5100	7.925	219.33
	0.5593	6.966	218.67
	0.5750	6.706	216.53
	0.6310	5.974	214.86
	0.6808	5.563	213.11
	0.7392	5.280	211.00
	0.8099	4.957	207.99
	0.8910	3.990	231.46

TABLE XIII

1-OCTANOL(A)-N-DECANE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
293.15	0.0060	0.433	311.97
	0.0370	2.223	312.53
	0.0967	4.422	312.35
	0.1499	5.440	311.25
	0.2009	5.865	309.65
	0.2791	5.939	306.61
	0.3500	5.810	303.65
	0.4116	5.756	301.15
	0.4593	5.799	299.29
	0.5020	5.829	297.68
	0.5384	5.911	296.33
	0.5548	6.035	295.72
	0.5739	6.079	295.01
	0.5952	6.115	294.19
	0.6071	6.126	293.73
	0.6442	6.105	292.23
	0.6986	5.855	289.82
	0.7396	5.443	287.77
	0.7940	4.555	284.72
	0.8608	2.983	280.49
	0.8985	1.968	277.97
	0.9419	0.710	274.70
298.15	0.0126	1.910	315.52
	0.0281	3.683	316.82
	0.0913	7.791	318.98
	0.1447	9.172	318.72
	0.1961	9.611	317.58
	0.2397	9.628	316.26
	0.3118	9.363	313.78
	0.3712	9.110	311.70
	0.4278	8.909	309.76
	0.4755	8.774	308.16
	0.5127	8.670	306.91
	0.5393	8.585	306.01
	0.5463	8.560	305.77
	0.5693	8.465	304.96
	0.5739	8.444	304.80
	0.6034	8.282	303.73
	0.6400	8.009	302.34
	0.6812	7.578	300.64
	0.7264	6.927	298.60
	0.7793	5.905	295.95
	0.8105	5.172	294.26
	0.8420	4.347	292.46
	0.8764	3.372	290.43

TABLE XIII (Continued)

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.9141	2.260	288.16
	0.9572	1.029	285.60
308.15	0.0056	1.970	320.71
	0.0200	5.815	324.13
	0.0789	13.964	330.56
	0.1448	16.777	331.45
	0.1969	17.151	330.30
	0.2840	16.601	327.21
	0.3539	15.937	324.50
	0.4137	15.349	322.17
	0.4635	14.807	320.17
	0.5072	14.248	318.34
	0.5411	13.739	316.84
	0.5690	13.263	315.55
	0.5804	13.052	315.00
	0.6010	12.649	314.00
	0.6347	11.923	312.29
	0.6740	10.980	310.20
	0.7184	9.805	307.73
	0.7631	8.529	305.15
	0.8166	6.908	302.96
	0.8793	4.885	298.11
	0.9153	3.628	295.80
	0.9569	2.009	292.97
313.15	0.0086	3.641	324.93
	0.0337	10.711	331.28
	0.0896	18.212	337.18
	0.1433	20.550	337.98
	0.2223	20.785	335.95
	0.2986	19.985	332.97
	0.3605	19.233	330.45
	0.4164	18.510	328.13
	0.4810	17.512	325.28
	0.5300	16.562	322.93
	0.5754	15.500	320.57
	0.5773	15.452	320.47
	0.6276	14.068	317.64
	0.6654	12.912	315.41
	0.7098	11.466	312.69
	0.7598	9.781	309.53
	0.8156	7.887	306.08
	0.8784	5.717	302.12
	0.9139	4.386	299.77
	0.9553	2.574	296.77

TABLE XIV

METHANOL(A)-BENZENE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.1000	8.056	136.48
	0.2000	10.904	134.08
	0.3000	11.882	129.81
	0.4000	11.712	124.40
	0.5000	10.591	118.03
	0.6000	8.705	110.90
	0.7000	6.398	103.35
	0.8000	4.102	95.80
	0.9000	2.081	88.54
308.15	0.1000	8.180	140.41
	0.2000	11.370	138.21
	0.3000	12.434	133.89
	0.4000	12.355	128.42
	0.5000	11.584	122.23
	0.6000	10.178	115.47
	0.7000	8.298	108.20
	0.8000	5.936	100.45
	0.9000	3.139	92.27
318.15	0.1000	8.304	142.70
	0.2000	11.835	140.83
	0.3000	12.986	136.59
	0.4000	12.997	131.20
	0.5000	12.506	125.31
	0.6000	11.651	119.05
	0.7000	10.198	112.20
	0.8000	7.769	104.37
	0.9000	4.196	95.40

TABLE XV

ETHANOL(A)-BENZENE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.0500	4.951	137.53
	0.1000	8.516	140.01
	0.2000	12.981	142.30
	0.3000	14.974	142.12
	0.4000	15.307	140.27
	0.5000	14.478	137.27
	0.6000	12.767	133.38
	0.7000	10.340	128.74
	0.8000	7.177	123.44
	0.9000	3.576	117.66
308.15	0.0500	5.020	141.57
	0.1000	8.693	144.17
	0.2000	13.306	146.63
	0.3000	15.325	146.50
	0.4000	15.618	144.65
	0.5000	14.763	141.65
	0.6000	13.085	137.82
	0.7000	10.707	133.30
	0.8000	7.649	128.09
	0.9000	3.973	122.27
318.15	0.0500	5.088	144.45
	0.1000	8.870	147.26
	0.2000	13.632	150.06
	0.3000	15.675	150.15
	0.4000	15.929	148.45
	0.5000	15.048	145.62
	0.6000	13.402	142.02
	0.7000	11.100	137.77
	0.8000	8.121	132.83
	0.9000	4.369	127.12

TABLE XVI

1-PENTANOL(A)-BENZENE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.0500	5.039	142.90
	0.1000	8.200	149.26
	0.2000	11.275	157.92
	0.3000	12.363	165.49
	0.4000	12.702	172.32
	0.5000	12.498	178.60
	0.6000	11.556	184.14
	0.7000	9.690	188.76
	0.8000	6.935	192.49
	0.9000	3.576	195.62
308.15	0.0500	4.187	145.12
	0.1000	7.398	151.65
	0.2000	11.439	162.33
	0.3000	13.158	170.68
	0.4000	13.408	177.57
	0.5000	12.777	183.57
	0.6000	11.550	188.98
	0.7000	9.740	193.80
	0.8000	7.183	197.88
	0.9000	3.752	201.09
318.15	0.0500	3.335	147.13
	0.1000	6.597	153.84
	0.2000	11.603	165.76
	0.3000	13.952	175.01
	0.4000	14.115	182.08
	0.5000	13.056	187.93
	0.6000	11.545	193.33
	0.7000	9.790	198.48
	0.8000	7.431	203.03
	0.9000	3.927	206.43

TABLE XVII

1-PROPANOL(A)-TOLUENE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.0500	5.656	163.53
	0.1000	9.547	166.89
	0.2000	13.946	170.23
	0.3000	15.554	170.77
	0.4000	15.785	169.95
	0.5000	15.392	168.49
	0.6000	14.497	166.54
	0.7000	12.743	163.72
	0.8000	9.629	159.55
	0.9000	5.038	153.90
308.15	0.0500	4.471	164.47
	0.1000	8.380	167.83
	0.2000	13.886	172.23
	0.3000	16.614	173.86
	0.4000	17.361	173.50
	0.5000	16.841	171.88
	0.6000	15.435	169.37
	0.7000	13.150	165.98
	0.8000	9.775	161.50
	0.9000	5.212	155.84
318.15	0.0500	3.285	165.87
	0.1000	7.214	169.29
	0.2000	13.826	174.90
	0.3000	17.674	177.74
	0.4000	18.936	177.99
	0.5000	18.291	176.34
	0.6000	16.374	173.41
	0.7000	13.557	169.58
	0.8000	9.920	164.94
	0.9000	5.386	159.40

TABLE XVIII

1-BUTANOL(A)-ETHYLBENZENE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.0500	6.001	190.99
	0.1000	9.906	194.12
	0.2000	14.811	197.48
	0.3000	17.512	198.63
	0.4000	18.656	198.23
	0.5000	18.364	196.39
	0.6000	16.654	193.13
	0.7000	13.633	188.56
	0.8000	9.568	182.95
	0.9000	4.868	176.71
308.15	0.0500	5.210	194.35
	0.1000	9.282	197.70
	0.2000	14.737	201.70
	0.3000	17.449	202.97
	0.4000	18.268	202.34
	0.5000	17.786	200.41
	0.6000	16.283	197.46
	0.7000	13.769	193.50
	0.8000	10.129	188.41
	0.9000	5.370	182.21
318.15	0.0500	4.419	197.71
	0.1000	8.658	210.27
	0.2000	14.663	205.93
	0.3000	17.386	207.31
	0.4000	17.880	206.46
	0.5000	17.208	204.44
	0.6000	15.911	201.80
	0.7000	13.905	198.41
	0.8000	10.689	193.88
	0.9000	5.871	187.72

TABLE XIX

1-PENTANOL(A)-ETHYLBENZENE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.0500	6.192	192.59
	0.1000	10.720	197.76
	0.2000	15.710	104.02
	0.3000	16.933	206.52
	0.4000	16.266	207.13
	0.5000	15.001	207.15
	0.6000	13.607	207.03
	0.7000	11.807	206.51
	0.8000	8.946	204.92
	0.9000	4.679	201.93
308.15	0.0500	4.985	195.55
	0.1000	8.939	200.21
	0.2000	14.033	206.72
	0.3000	16.224	210.32
	0.4000	16.594	212.10
	0.5000	15.949	212.86
	0.6000	14.644	212.97
	0.7000	12.596	212.33
	0.8000	9.480	210.36
	0.9000	5.108	207.67
318.15	0.0500	3.778	198.51
	0.1000	7.158	202.66
	0.2000	12.356	209.44
	0.3000	15.515	214.11
	0.4000	16.922	217.06
	0.5000	16.898	218.58
	0.6000	16.681	218.90
	0.7000	13.384	218.15
	0.8000	10.014	216.33
	0.9000	5.538	213.39

TABLE XX

1-PROPANOL(A)-CYCLOHEXANE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.0452	6.388	162.08
	0.0858	9.180	164.46
	0.1173	10.365	165.33
	0.1295	10.666	165.51
	0.1390	10.851	165.60
	0.1680	11.203	165.66
	0.1996	11.312	165.45
	0.2619	11.044	164.56
	0.3036	10.690	163.79
	0.3216	10.520	163.44
	0.3670	10.079	162.54
	0.4562	9.227	160.80
	0.4729	9.070	160.48
	0.4951	8.859	160.04
	0.5191	8.625	159.57
	0.5517	8.290	158.91
	0.5836	7.935	158.23
	0.6476	7.102	156.76
	0.6918	6.410	155.63
	0.7502	5.332	153.96
	0.7918	4.458	152.67
	0.8540	3.036	150.63
	0.2906	1.494	148.42
303.15	0.0805	9.287	166.51
	0.1003	10.227	167.25
	0.1273	11.097	167.84
	0.1632	11.743	168.12
	0.1984	12.013	168.03
	0.2189	12.063	167.87
	0.2518	12.037	167.51
	0.3067	11.825	166.73
	0.3782	11.401	165.57
	0.4262	11.054	164.74
	0.4632	10.746	164.05
	0.5126	10.255	163.05
	0.5648	9.612	161.87
	0.6282	8.624	160.24
	0.6593	8.052	159.34
	0.6946	7.334	158.26
	0.7581	5.887	156.17
	0.8128	4.526	154.24
	0.8438	3.732	153.13
	0.8797	2.815	151.85
	0.9080	2.106	150.85

TABLE XX (Continued)

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
308.15	0.0493	7.359	166.80
	0.0781	9.524	188.67
	0.1274	11.580	170.21
	0.1542	12.176	170.53
	0.1982	12.712	170.60
	0.2203	12.851	170.51
	0.2660	12.982	170.16
	0.3077	12.987	169.73
	0.3795	12.827	168.82
	0.4300	12.575	168.05
	0.4689	12.280	167.35
	0.5222	11.701	166.21
	0.5701	10.988	165.00
	0.6280	9.878	163.28
	0.6652	9.034	162.05
	0.7013	8.133	160.77
	0.7440	6.991	159.18
	0.7801	5.985	157.80
	0.8189	4.889	156.30
	0.8540	3.906	154.95
	0.9046	2.526	153.04
	0.9431	1.507	151.62
313.15	0.0602	8.625	169.86
	0.1078	11.381	172.11
	0.1397	12.397	172.79
	0.1982	13.412	173.18
	0.2410	13.806	173.12
	0.3036	14.140	172.79
	0.3527	14.257	172.39
	0.3786	14.263	172.12
	0.4225	14.147	171.51
	0.4605	13.935	170.93
	0.5100	13.422	169.89
	0.5360	13.045	169.24
	0.5637	12.561	168.46
	0.5903	12.019	167.64
	0.6122	11.518	166.91
	0.6604	10.266	165.14
	0.7181	8.564	162.83
	0.7672	7.028	160.77
	0.8110	5.653	158.93
	0.8574	4.240	157.03
	0.9195	2.434	154.57
318.15	0.0532	8.336	171.63
	0.0906	11.001	173.89
	0.1365	12.818	175.20
	0.1715	13.650	175.66

TABLE XX (Continued)

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
318.15	0.2152	14.358	175.89
	0.2457	14.734	175.93
	0.2680	14.970	175.93
	0.3046	15.298	175.86
	0.3413	15.546	175.54
	0.3780	15.693	175.45
	0.4275	15.685	174.91
	0.4642	15.491	174.31
	0.5096	14.997	173.33
	0.5483	14.346	172.26
	0.5703	13.883	171.55
	0.6091	12.914	170.16
	0.6371	12.109	169.05
	0.6438	11.906	168.78
	0.6758	10.881	167.41
	0.7099	9.722	165.88
	0.7459	8.459	164.22
	0.7731	7.502	162.97
	0.8242	5.750	160.66
	0.8741	4.140	158.51
	0.9215	2.677	156.53
323.15	0.0763	10.552	175.59
	0.1105	12.369	177.08
	0.1399	13.426	177.84
	0.1671	14.153	178.28
	0.1970	14.789	178.61
	0.2510	15.711	178.97
	0.2987	16.379	179.14
	0.3655	17.047	179.12
	0.3772	17.120	179.07
	0.4189	17.238	178.76
	0.4682	17.045	178.05
	0.5210	16.383	176.85
	0.5677	15.397	175.38
	0.6202	13.886	173.32
	0.6567	12.635	171.69
	0.6954	11.190	169.85
	0.7342	9.325	167.49
	0.7953	7.317	164.94
	0.8403	5.685	162.84
	0.8975	3.764	160.33
	0.9411	2.320	158.43

TABLE XXI

1-BUTANOL(A)-CYCLOHEXANE(B) MIXTURES

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
298.15	0.0370	1.904	158.59
	0.0830	5.364	162.70
	0.1091	7.172	164.87
	0.1402	8.975	167.12
	0.1822	10.700	169.43
	0.2336	11.731	171.19
	0.2628	11.866	171.74
	0.2863	11.788	171.99
	0.3215	11.435	172.14
	0.3503	11.002	172.11
	0.3784	10.512	172.02
	0.4133	9.876	171.88
	0.4554	9.154	171.75
	0.4926	8.615	171.74
	0.5213	8.276	171.80
	0.5840	7.738	172.15
	0.6189	7.505	172.41
	0.6538	7.254	172.65
	0.6932	6.874	172.83
	0.7367	6.240	172.81
	0.7834	5.217	172.45
	0.8386	3.532	171.54
303.15	0.0550	4.988	163.85
	0.1061	8.432	168.05
	0.1393	10.016	170.13
	0.1683	11.013	171.55
	0.2057	11.828	172.92
	0.2315	12.129	173.60
	0.2664	12.260	174.25
	0.3050	12.124	174.68
	0.3689	11.503	175.01
	0.4094	10.992	175.10
	0.4535	10.423	175.18
	0.4866	10.016	175.26
	0.5327	9.488	175.42
	0.5650	9.138	175.54
	0.5962	8.800	175.67
	0.6264	8.454	175.77
	0.6610	8.008	175.83
	0.7246	6.950	175.72
	0.7914	5.370	175.12
	0.8505	3.574	174.20
	0.9347	0.932	172.81
308.15	0.0726	8.039	169.12
	0.1170	10.345	172.11

TABLE XXI (Continued)

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
308.15	0.1386	11.083	173.18
	0.1700	11.837	174.42
	0.1981	12.264	175.28
	0.2374	12.578	176.20
	0.2674	12.656	176.74
	0.3112	12.600	177.36
	0.3577	12.390	177.87
	0.3838	12.225	178.11
	0.4188	11.963	178.39
	0.4502	11.693	178.60
	0.4845	11.359	178.79
	0.5163	11.012	178.94
	0.5322	10.823	179.00
	0.5641	10.411	179.08
	0.6066	9.782	179.10
	0.6318	9.360	179.07
	0.6668	8.709	178.96
	0.7140	7.703	178.68
	0.7592	6.599	178.27
	0.8018	5.447	177.78
	0.8516	2.024	176.15
313.15	0.0601	8.885	171.72
	0.1058	11.334	174.90
	0.1666	12.578	177.13
	0.2097	12.885	178.13
	0.2629	13.044	179.14
	0.3092	13.116	179.96
	0.3358	13.140	180.41
	0.3726	13.141	181.00
	0.4134	13.073	181.59
	0.4438	12.954	181.96
	0.4728	12.772	182.24
	0.5165	12.351	182.53
	0.5613	11.720	182.62
	0.6283	10.411	182.38
	0.6610	9.637	182.14
	0.6980	8.682	188.78
	0.7418	7.486	181.28
	0.7934	6.049	180.68
	0.8815	3.658	179.70
	0.9242	2.492	179.22
318.15	0.0555	10.251	175.05
	0.1035	12.735	178.33
	0.1396	13.281	179.48
	0.1720	13.390	180.13
	0.2141	13.382	180.82
	0.2460	13.401	181.37

TABLE XXI (Continued)

Temp., K	MFR "A"	C_p^E, J/mol/K	C_p^M, J/mol/K
318.15	0.2742	13.471	181.92
	0.3002	13.581	182.46
	0.3349	13.771	183.23
	0.3678	13.958	183.96
	0.4163	14.145	184.96
	0.4397	14.161	185.37
	0.4629	14.111	185.70
	0.5162	13.695	186.18
	0.5605	13.007	186.23
	0.5803	12.601	186.15
	0.6172	11.703	185.87
	0.6670	10.269	185.26
	0.6918	9.499	184.91
	0.7320	8.236	184.32
	0.7755	6.923	183.73
	0.8235	5.615	183.22
	0.8788	4.274	182.80
	0.9358	2.789	182.27
323.15	0.0616	12.500	179.45
	0.1050	14.241	181.95
	0.1271	14.388	182.49
	0.1672	14.187	183.00
	0.2095	13.883	183.44
	0.2361	13.798	183.28
	0.2638	13.833	184.35
	0.3077	14.123	185.41
	0.3681	14.775	187.13
	0.4137	15.208	188.37
	0.4598	15.381	189.35
	0.4832	15.320	189.70
	0.5210	14.975	190.03
	0.5748	14.540	190.06
	0.5982	13.323	189.74
	0.6338	12.209	189.25
	0.6686	10.993	188.65
	0.7041	9.705	187.99
	0.7372	8.535	187.40
	0.7969	6.687	186.60
	0.8800	4.793	186.18

APPENDIX B

SAMPLE CALCULATION FOR PREDICTING HEAT CAPACITY OF A LIQUID MIXTURE USING THE PROPOSED METHOD

We want to predict the liquid heat capacity of a mixture composed of 1-pentanol(1) and ethylbenzene(2) at 318.15 K. The mole fraction of 1-pentanol is 0.40.

$$C_p^M = C_p^{ID} + C_p^E \qquad \text{(B-1)}$$

$$C_p^{ID} = x_1\, C_{p1}^o + x_2\, C_{p2}^o \qquad \text{(B-2)}$$

Since the heat capacity of 1-pentanol (C_{p1}^o) at 318.15 K is 209.4 J/mol/K and the heat capacity of ethylbenzene (C_{p2}^o) is 194.0 J/mol/K, we have

$$C_p^{ID} = (0.4)(209.4 \text{ J/mol/K}) + (0.6)(195.0 \text{ J/mol/K})$$

$$= 200.14 \text{ J/mol/K}$$

In this mixture, we have three pairs of surface contacts: aliphatic/aromatic (CH_2,ACH), aliphatic/hydroxyl (CH_2,OH), and aromatic/hydroxyl (ACH,OH). To calculate the excess heat capacity of the mixture, we need to know the values of the interchange parameters C_{pst}^* for those three pairs of groups. According to Eqs. 3-8, 3-10, 3-13, and 3-14 for a binary mixture:

$$C_p^E = \{q_1\, q_2\, x_1\, x_2 \,/\, (q_1\, x_1 + q_2\, x_2)\}\, C_{p12} \qquad \text{(B-3)}$$

If we represent the group pairs (CH_2,ACH), (CH_2,OH), and (ACH,OH) by (a,c), (a,d), and (c,d) respectively, we can write C_{p12} as:

$$C_{p12} = -\{(f_{a1} - f_{a2})(f_{c1} - f_{c2})\, Z_{ac}\, C_{pac}^* +$$

$$(f_{a1} - f_{a2})(f_{d1} - f_{d2})\, Z_{ad}\, C_{pad}^* +$$

$$(f_{c1} - f_{c2})(f_{d1} - f_{d2})\ Z_{cd}\ C^*_{pcd}\ \} \qquad \text{(B-4)}$$

Using the constants, A_{mn}, for the group pair (a,c) from Table I, the interchange heat capacity C^*_{pac} can be obtained from the following equations:

$$C^*_{pac} = \{A_0 + A_1\ (x_1 - x_2) + A_2\ (x_1 - x_2)^2\} \qquad \text{(B-5)}$$

where

$$A_0 = A_{00} + A_{10}\ T + A_{20}\ T^2$$

$$A_1 = A_{01} + A_{11}\ T + A_{21}\ T^2$$

$$A_2 = A_{02} + A_{12}\ T + A_{22}\ T^2 \qquad \text{(B-6)}$$

For the case in which the system temperature is 318.15 K, and the mole fraction of 1-pentanol is 0.400, we have

$$A_0 = 8.51116 \quad A_1 = 13.9256 \quad A_2 = 26.6918$$

$$C^*_{pac} = 6.79371$$

Similarly, using the constants, A_{mn}, in Table I for the group pair (a,d), we have

$$A_0 = 175.548 \quad A_1 = -212.780 \quad A_2 = 74.4906$$

$$C^*_{pad} = 221.083$$

and for the group pair (c,d), we have

$$A_0 = 180.209 \quad A_1 = -199.477 \quad A_2 = 47.5624$$

$$C^*_{pcd} = 222.007$$

From Table XXII, the molecular surface areas q_1 (1-pentanol) and q_2 (ethylbenzene) can be calculated:

$$q_1 = q_{CH_3} + 4\, q_{CH_2} + q_{OH}$$

$$= 0.73103 + 4(0.46552) + 0.50345$$

$$= 3.09656$$

$$q_2 = q_{CH_3} + q_{CH_2} + q_{C_6H_5}$$

$$= 0.73103 + 0.46552 + 1.83793$$

$$= 3.03448$$

TABLE XXII

RELATIVE GROUP SURFACE INCREMENTS FOR MOLECULAR AREAS, $q_s = A_s/A_{CH_4}$, CALCULATED BY BONDI'S METHOD (61) ($A_{CH_4} = 2.9 \times 10^9$ CM^2/MOL)

Groups	q_s	Groups	q_s
CH_4	1.00000	a-O-a	0.20690
CH_3-	0.73103	a-C_6H_{11}	2.36123
-CH_2-	0.46552	C_6H_{12}	2.59660
a-C_6H_5	1.83793	a-OH	0.50345
C_6H_6	2.07240	H_2O	0.76896

a = aliphatic chain

The group surface fractions of 1-pentanol(1) and ethylbenzene(2) can then be calculated:

$$f_{a1} = (q_{CH_3} + 4\, q_{CH_2})_1 / q_1 = 0.83742$$

$$f_{c1} = (q_{C_6H_5})_1 / q_1 = 0.0$$

$$f_{d1} = (q_{OH})_1 / q_1 = 0.16258$$

$$f_{a2} = (q_{CH_3} + q_{CH_2})_2 / q_2 = 0.39432$$

$$f_{c2} = (q_{C_6H_5})_2 / q_2 = 0.60528$$

$$f_{d2} = (q_{OH})_2 / q_2 = 0.0$$

The weighting correction factors can be evaluated using Eq. 3-10

$$Z_{ac} = 1,\ Z_{ad} = 3.6239, \text{ and } Z_{cd} = 3.6239$$

Substituting into Eqs. 3-13 and 3-14, C_{p12} and the predicted value of C_p^E become:

$$C_{p12} = 23.276 \text{ J/mol/K}$$

$$(C_p^E)\text{calc.} = 17.158 \text{ J/mol/K}$$

The predicted heat capacity, (C_p^M)calc., for the mixture 1-pentanol-ethylbenzene is

$$(C_p^M)\text{calc.} = 200.14 + 17.158 = 217.30 \text{ J/mol/K}$$

When compared with the experimental value of 217.06 J/mol/K, the percent deviation is

$$PD = \{(217.30 - 217.06) / 217.06\}100 = 0.109\ \%$$

VITA

Chein-Hsiun Tu

Candidate for the Degree of

Doctor of Philosophy

Thesis: PREDICTION OF LIQUID-MIXTURE HEAT CAPACITY BY GROUP CONTRIBUTION METHOD

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Changhua, Taiwan, ROC, April 14, 1951, the son of Chiao-Yun and Chen-Mien Tu.

Education: Graduated from Changhua High School, Changhua, Taiwan, ROC, in June 1969; received Bachelor of Science degree in Chemical Engineering from Tatung Institute of Technology, Taipei, Taiwan, ROC, in June 1974; received Master of Science degree in Chemical Engineering from Washington State University, Pullman, Washington, in February, 1981; completed requirements for Doctor of Philosophy degree at Oklahoma State University in December, 1985.

Professional Experience: Chemical Engineer, Chung-Tai Chemical Industries, Kaoshiung Plant, Kaoshiung, Taiwan, ROC, 1976-1978; Teaching and Research Assistant, Chemical Engineering Department, Washington State University, Pullman, Washington, 1979-1981; Teaching Assistant, Oklahoma State University, Stillwater, Oklahoma, 1983-present.