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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RÉCU
VAPOR-LIQUID EQUILIBRIA FOR THE
ETHANOL-METHYL METHACRYLATE SYSTEM

by
Jin-Min Yu

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENT FOR THE DEGREE OF
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J.-M. Yu, Ottawa, Canada, 1979
ABSTRACT

A modified Dvorak and Boulik (1) recirculation still was used in the determination of isothermal vapor-liquid equilibrium data for the binary system ethanol - methyl methacrylate at 313.15, 323.15 and 333.15K. Liquid activity coefficients, \( \gamma_i^L \), and excess Gibbs free energies \( \Delta G^E \) were evaluated and correlated by a three-constant Redlich-Kister equation (2); a binary azeotrope exists at all three temperatures studied and the mole fraction of ethanol in the azeotrope increases with increasing temperature.

In order to evaluate liquid activity coefficients, a new empirical correlation of second virial coefficients for pure polar compounds has been developed by extending a modified Pitzer-Curl correlation of non-polar gases proposed by Tsonopoulos (3).

In this development, the effect of hydrogen-bonding on the second virial coefficients was correlated separately from the effect of polarity. For each compound, only one more parameter is required to describe the effect of polarity. Using this parameter, expressed as a function of reduced dipole moment \( \mu_R \), the second virial coefficients of non-hydrogen-bonding polar substances can be predicted in good agreement with the experimental data. As for the explanation of the hydrogen-bonding effect, two additional parameters are needed. Together with the parameter for polar effect, the second virial coefficients of hydrogen-bonding polar substances (alcohols) can be fitted satisfactorily.
ACKNOWLEDGEMENTS

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APPENDIX II

A-II Calibration of Composition - Refractive Index for the System Ethanol - Methyl Methacrylate
NOMENCLATURE

\( a, c \) = parameters of polar contribution term, \( f(2) \); see Equation (4.8)

\( a_T, b_T \) = parameters in Equations (2.20) and (2.22)

\( B, C \) = Virial Coefficients of the Virial Equation

\( B_{12}, C_{12}, D_{12} \) = Constants in the Redlich-Kister Equation in the Binary System

\( G \) = Gibbs Free Energy

\( b, d, g \) = Parameters of Hydrogen-Bonding Contribution Term, \( f(3) \); see Equation (4.12)

\( f^0 \) = Fugacity of a Component at standard State

\( f \) = Fugacity of a Component in the Solution

\( f_B^{(0)}, f_B^{(1)} \) = Dimensionless Terms of Equation (2.2), the Pitzer-Curl Correlation of Second Virial Coefficients

\( f_T^{(0)}, f_T^{(1)}, f_T^{(2)} \) = Dimensionless Terms of Equation (2.19), the Tsonopoulos Correlation of Second Virial Coefficients

\( f^{(2)}, f^{(3)} \) = Dimensionless Polar and Hydrogen-Bonding Contribution Terms of Equation (4.5), the New Correlation of Second Virial Coefficient

\( f_a, f_\mu \) = Dimensionless Polar Contribution Terms of Equation (2.5), the O'Connell-Prausnitz Correlation of Second Virial Coefficient

\( k_{ij} \) = Characteristic Binary Constant, see Equation (2.23)

\( n \) = Refractive Index of Sodium Light

\( N \) = Number of Data

\( P^0 \) = Vapor Pressure, Torr

\( P \) = Total Pressure, Torr

\( R \) = Gas Constant
$T$ = Absolute Temperature, K
$V^0$ = Molar Volume of Pure Component, cm$^3$ mol$^{-1}$
$V$ = Volume, cm$^3$
$x$ = Mole Fraction in Liquid Phase
$y$ = Mole Fraction in Vapor Phase
$z$ = Compressibility
$a_0, a_1, a_2$ = Parameters in Equation (4.10)
$\rho$ = Density, g cm$^{-3}$
$\mu$ = Dipole Moment, Debye
$P$ = Parachor
$\gamma$ = Activity Coefficient
$\omega$ = Acentric Factor
$\omega_H$ = Acentric Factor of Homomorph
$\delta_{12}$ = $2B_{12} - B_{11} - B_{22}$
$n$ = Association Factor

SUPERSCRIPTS
$L$ = Liquid Phase
$V$ = Vapor Phase

SUBSCRIPTS
$c$ = Critical Property
$E$ = Excess Property
$i, j$ = Component Identification
$R$ = Reduced Property
$l, 2$ = Component Identification
$l2$ = Mixture Identification
CHAPTER 1

INTRODUCTION

Methacrylate esters of higher alcohols are produced commercially by either direct esterification or the ester interchange reaction between the lower methacrylates and higher alcohols. In the preparation of ethyl methacrylate the vapor-liquid equilibrium data for the binary mixture ethanol - methyl methacrylate (MMA) are useful in the design of a distillation column for separating the mixture. However, these data have not yet been reported in the literature. The purpose of the present work is to establish isothermal vapor-liquid equilibrium data for the mixture at 313.15, 323.15 and 333.15K by means of a modified Dvorak and Boublík (1) recirculation still.

In order to analyze and correlate vapor-liquid equilibrium data, it is necessary to take the non-ideal behavior of vapor phase into account. For isothermal data and at subcritical temperature, up to a pressure of about 15 atm, the effect of vapor phase imperfection can be reliably calculated using only the second virial coefficients of the pure components and the cross second virial coefficients of the binary mixtures concerned (4). Several empirical methods for predicting the second virial coefficients have been developed (Pitzer and Curl (1957) (5), O'Connell and Prausnitz (1967) (6), Tsonopoulos (1974) (3)), but all of these correlations are not satisfactory in some aspects. For example, the value of one or two of the parameters must be obtained empirically; methods are only applicable in a narrow temperature range; or the results are simply not accurate enough to be acceptable. Because of these weaknesses,
a new empirical correlation for the second virial coefficients of pure polar compounds was developed in this study.
CHAPTER 2

LITERATURE SURVEY

The purpose of this chapter is to give a brief review of literature covering those points which are of interest to this study, i.e., methods for the direct experimental determination of vapor-liquid equilibrium and empirical correlations for the second virial coefficients.

2.1 Experimental Methods

The direct experimental determination of vapor-liquid equilibrium means that samples of the liquid and vapour which are in true equilibrium are separated and the concentrations of both phases are determined analytically.

In their work entitled "Vapor-Liquid Equilibrium" Hala et al. (7) presented a bibliography for experimental methods, which can be classified into the following groups:

1. Distillation Method
2. Static Method
3. Dew and Bubble-Point Method
4. Flow Method
5. Circulation Method

2.1.1 Distillation Method

In this oldest method, a small amount of liquid is distilled off from the boiling flask which contains a large
charge. During such distillation, a large amount of liquid sample is required and only a very small sample of condensate is allowed to be withdrawn for analysis. This method is very simple but has marked disadvantages and causes large errors in determining the equilibrium temperature, pressure and composition. At present, it is rarely used.

2.1.2 Static Method.

In this method, the liquid sample is charged into a closed evacuated equilibrium cell which is agitated at constant temperature until the equilibrium is reached between the vapor and the liquid. Then the samples of the two phases are withdrawn and analyzed.

The main disadvantage of this method is that of pressure changes in the equilibrium cell during sampling, causing disturbance to the equilibrium.

2.1.3 Dew and Bubble-point Method

This method employs an apparatus similar to the static method, but omitting the analyses of the compositions in two phases. A mixture of known composition is introduced into an evacuated equilibrium cell of variable volume which is maintained at constant temperature.

By varying the volume of the equilibrium cell, the system pressure, at which condensation commenced and is completed, is observed. The dew point and bubble point
pressures are measured directly. From these data, the saturation curves of the two phases at constant temperature can be plotted against composition.

One great advantage with this method is that in the determination of the equilibrium diagrams, it is not necessary to take samples of liquids or vapors for analysis. However, the dew and bubble points are not easily defined very sharply, hence highly refined precision instrument has to be used to detect the occurrence of vapor or liquid sensitively.

2.1.4 Flow Method

The flow method is used to measure equilibrium data in systems of limited miscibility in the liquid phase. A steady stream of vapor mixture is passed through equilibrium cell where it is cooled and partially liquified. Then the vapor which is in equilibrium with the condensate, is separated and removed for analysis. The samples are withdrawn and analyzed continuously.

It is obvious that during passing of the vapor mixture, there are pressure drops which will affect the equilibrium. Hence the main difficulties of this method are in the maintenance of constant system pressure and temperature during rapid condensation.

2.1.5 Circulation Method

This method is the most widely used. Vapor-liquid equilibrium data are obtained by continuously circulating the vapor formed by the vaporization of the liquid through the system and bringing it back into contact with the liquid until no further change in the composition of either phase can be detected. In the meantime,
condensed vapor and liquid are kept separate to allow the removal of samples for analysis.

This method is convenient to use both in the region of medium and low pressures.

Even though there are various equilibrium stills with simple circulation, they differ significantly from one another in their construction details.

According to the manner of circulation of the phases, these stills can be classified into two groups:

1. Stills with circulation of vapor phase
2. Stills with circulation of the liquid and vapor phases

The most typical stills of these two groups are those of Othmer (8), Jones, Schoenborn and Colburn (9), and Gillespie (10).

The Othmer still and the Jones still belong to the first group. In the Othmer still, the vapor produced by boiling the liquid mixture in an insulated still is removed, condensed and the overflow of condensate is returned to the still. An immersion heater is used to provide turbulent mixing and boiling.

The Jones still operates in a similar manner. But the overflow condensate is vaporized outside the still before it makes contact with the liquid phase contained therein again.

A Cottrell pump is used in one family of Gillespie still for the purpose of recirculating both the liquid and the vapor phases. The liquid mixture in the still is boiled by an internal heater form vapor bubbles that thoroughly mix with the liquid
mixture to ensure quiet and steady boiling.

The evolved vapors carry a flow of liquid with them into the cottrell pump from which this mixture spurts into the equilibrium chamber. Equilibrium is assumed to have been attained as the contact phases separate after leaving the upper end of cottrell pump. The overflow condensate then returns to the base of cottrell pump and makes contact with the liquid in the still. The conditions in the cottrell pump are ideal for obtaining the desired equilibrium between the phases.

Following a systematic study, Dvorak and Boublík (11) stated that intense stirring is necessary both in the liquid and in the condensate receivers. Accordingly, they proposed an apparatus which is suitable even for systems having a very high relative volatility. Two additional modifications were made by Boublíková and Lu (1): the circulation loop in the evacuated chamber was shortened to reduce the pressure drop, a well for an electrical heater was made in the boiling vessel. (Details of design are presented in Chapter 5.)

So far it has not been possible to construct a still which would yield thermodynamically consistent data for all systems. The relative merits of the various types of still were summarized and discussed by Gillespie (10) and Hala et al. (7).

2.2 Empirical Correlations of the Second Virial Coefficient

Experimental determination of second virial coefficients (B) for all systems is a formidable proposition; it is a usual practice to predict these data by the use of suitable correlations.
Correlations for second virial coefficients can be obtained from statistical mechanical formulas using an expression for the pair intermolecular potential energy (16), or by empirical or semi-empirical methods. The most popular method has been the last, since the computation is usually the easiest (although not always the most accurate).

In 1957, Pitzer and Curl (5) developed a very successful empirical correlation of the B of the nonpolar gases. Because of the soundness and reliability of this correlation, it was used as the basis to develop a correlation of the B of polar gases by O'Connell and Prausnitz (6) and by Tsonopoulos (3). Along this line, a predictive method for the B of polar gases is developed in this study. These three correlations are presented in the following sections. Other correlations (13)(14)(15), which have not originated from the Pitzer-Curl correlation are not as accurate as the above correlations, so they are not considered here.

2.2.1 The Correlation of Pitzer and Curl

By extending the theory of corresponding states originally proposed by van der Waals (17), Pitzer and Curl (15) used critical temperature ($T_c$), critical pressure ($P_c$) and an additional parameter called acentric factor ($\omega$) which is a macroscopic measure of the effect of acentricity, i.e., the non-spherical nature of intermolecular forces, to correlate the B of pure nonpolar gases characterized by zero dipole moment.
The definition of $\omega$ is given below:

$$
\omega_i = -\log_{10}\left(\frac{P_i}{P_{ci}}\right)_{T_{Ri}=0.7} - 1.000
$$

(2.1)

where $P_{ci}$ is the vapor pressure of component $i$ at reduced temperature $T_{Ri}=0.7$. $P_i$ is the critical pressure of component $i$. The values of $\omega$ can be evaluated directly from the above equation. Fluids consisting of spherical molecules, for example Ar, Kr, have an acentric factor equal to zero, the quantum gases, for example, He, H$_2$ have negative $\omega$'s and everything else has a positive value of $\omega$. Acentric factors of substances can be found in the compilation of Reid, Sherwood and Prausnitz (1977) (18).

The Pitzer-Curl correlation provides good predictions for the $B$ of nonpolar gases. In the reduced dimensionless form, it is:

$$
\frac{P_{ci} B_{ii}}{RT_{ci}} = f_B^{(0)} + \omega_i f_B^{(1)}
$$

(2.2)

where $R$ is the gas constant.

The function $f_B^{(0)}$ gives the reduced second virial coefficients for simple fluids ($\omega_i=0$) while $f_B^{(1)}$ is a correlation function which is multiplied by $\omega_i$, gives the effect of acentricity on the second virial coefficient. The two functions $f_B^{(0)}$ and $f_B^{(1)}$ were determined from experimental data for a number of nonpolar or slightly polar substances. Highly polar substances such as ammonia, nitriles or alcohols were not included.
The empirically determined functions are:

\[ f_B^{(0)} = 0.1445 - \frac{0.330}{T_{R_1}} - \frac{0.1385}{T_{R_1}^2} - \frac{0.0121}{T_{R_1}^3} \]  \hspace{2cm} (2.3)

\[ f_B^{(1)} = 0.073 + \frac{0.46}{T_{R_1}} - \frac{0.50}{T_{R_1}^2} - \frac{0.097}{T_{R_1}^3} - \frac{0.0073}{T_{R_1}^8} \]  \hspace{2cm} (2.4)

Pitzer and Curl did not extend their correlation to mixtures by defining mixing rules for the parameters in Equations (2.3) and (2.4) to estimate the cross second virial coefficient \( B_{ij} \).

2.2.2 The Correlation of O'Connell and Prausnitz

The O'Connell and Prausnitz method (6), uses the Pitzer-Curl correlation to calculate the \( B_{ii} \) for pure, nonpolar gases. They also use the Pitzer-Curl correlation as the basis for their correlation for polar gases. In place of \( \omega_i \), they use \( \omega_{Hi} \), the acentric factor of the polar compound's homomorph (19), i.e., a nonpolar compound having approximately the same size and shape as the polar compound, to present the effect of acentricity on the \( B \). By examining the \( B \) of 41 polar gases, (10 alcohols, 6 ethers, an aldehyde, ketones, 6 esters, 7 amines, 4 heterocyclic and 4 other polar gases), they established two empirically determined functions for the \( B \) of polar gases, \( f_\mu \) for the polar effect induced by the dipole moments among molecules, and \( f_\alpha \), an "association" function for compounds which exhibit special forces, such as hydrogen bonds.
For pure polar gases, the correlation has the form:

\[
\frac{P_{C_i} B_{ii}}{RT_{C_i}} = f_B(0) + \omega_{Hi} f_B(1) + f_\mu - \eta_i f_a
\]  

(2.5)

where the association constant \( \eta_i \) is an empirically determined quantity which reflects the tendency of compound \( i \) (e.g., an alcohol) to associate with itself to form dimers.

The empirical function \( f_\mu \) depends on the reduced temperature, \( T_R \), and on \( \mu_{Ri} \), the reduced dipole moment, defined by

\[
\mu_{Ri} = \frac{10^5 \mu_i^2 P_{C_i}^{\frac{1}{2}}}{T_{C_i}^{\frac{2}{3}}}
\]

(2.6)

in which \( \mu_i \) is the dipole moment of pure component \( i \) in Debye units, the critical pressure in atmospheres, and the critical temperature in degree Kelvin. The function \( f_\mu \) was determined from experimental data for 17 polar fluids which do not exhibit specific chemical forces.

For \( \mu_{Ri} > 4 \), it is given by

\[
f_\mu = -5.237220 + 5.665807 (\ln \mu_{R_i})
-2.133816 (\ln \mu_{R_i})^2 + 0.2525373 (\ln \mu_{R_i})^3
+ \frac{1}{T_{R_i}} [5.769770 - 6.181427 (\ln \mu_{R_i})
+ 2.283270 (\ln \mu_{R_i})^2 - 0.2649074 (\ln \mu_{R_i})^3]
\]

(2.7)

For the compounds with \( \mu_{Ri} < 4 \), \( f_\mu \) is set to be zero. The association function \( f_a \) is given by:

\[
f_a = \exp[6.6 (0.7 - T_{R_i})]
\]

(2.8)
The values for \( \mu_{R_i} \), \( \mu_{R_j} \), and \( \eta_i \) for some components are presented in Tables (4-1), (4-3), and (4-6).

The two polar terms, \( f_\mu \) and \( f_a \) in this correlation are set equal to zero for \( T_{R_i} > 0.95 \).

To estimate cross second virial coefficient \( B_{ij} \), O'Connell and Prausnitz proposed the following mixing rules for the various parameters in the above correlation equations.

For the case where \( i \) and \( j \) are both nonpolar gases, Equations (2.1), (2.2), (2.3) and (2.4) give values of \( B_{ij} \), where \( P_{C_i} \), \( T_{C_i} \), \( \omega_{ij} \) replaces \( T_{C_i} \), \( \omega_{ij} \) replaces \( T_{C_i} \), and \( \omega_{ij} \) replaces \( \omega_{ij} \). The mixing rules have the forms:

\[
T_{C_{ij}} = (T_{C_i} T_{C_j})^{1/2} \quad (2.9)
\]

\[
\omega_{ij} = 0.5(\omega_i + \omega_j) \quad (2.10)
\]

\[
P_{C_{ij}} = 4 T_{C_{ij}} \left[ \frac{P_{C_i} V_{C_i}}{T_{C_i}} + \frac{P_{C_j} V_{C_j}}{T_{C_j}} \right] / (V_{C_i}^{1/3} + V_{C_j}^{1/3})^3 \quad (2.11)
\]

For the case where \( i \) is a polar substance, and \( j \) is nonpolar, Equations (2.1), (2.2), (2.3) and (2.4) are used for \( B_{ij} \) where Equation (2.9) is used for \( T_{C_{ij}} \). For \( \omega_{ij} \), the mixing rule is:

\[
\omega_{ij} = 0.5(\omega_i + \omega_j) \quad (2.12)
\]

Equation (2.11) is used for \( P_{C_{ij}} \).

For the case where both components \( i \) and \( j \) are polar, Equation (2.5) is used for \( B_{ij} \), where \( T_{C_{ij}} \) is replaced by \( T_{C_{ij}} \).
from Equation (2.9), $\omega_H_i$ is replaced by $\omega_{H_{ij}}$:

$$\omega_{H_{ij}} = 0.5(\omega_{H_i} + \omega_{H_j})$$  \hspace{1cm} (2.13)

$P_C_i$ is replaced from (2.11), where the reduced dipole moment $\mu_{R_{ij}}$ is given by:

$$\mu_{R_{ij}} = 10^{-5} \mu_i \mu_j \frac{P_{C_{ij}}}{T_{C_{ij}}}$$  \hspace{1cm} (2.14)

Finally, $\eta_i$ is replaced by $\eta_{ij}$ according to:

$$\eta_{ij} = 0.5(\eta_i + \eta_j)$$  \hspace{1cm} (2.15)

For cross second virial coefficients of nonpolar compounds, this correlation based on the above mixing rules works well if the components are similar in size. However, for extremely different molecules, the predicted values are somewhat too negative.

In fact, the O'Connell-Prausnitz correlation has been used widely (for example, in two important monographs on computer calculation for vapor-liquid equilibria: Prausnitz et al. 1967 (20), Renon et al. (1971) (21)). Nevertheless, several drawbacks contained in their method are:

1. Eubank and Smith (22) have stated that the homomorph concept shall be limited to organic compounds. However, O'Connell and Prausnitz applied this concept to inorganic compounds, (e.g. methane was considered as the homomorph of both water and ammonia; propane the homomorph of sulfur dioxide) thus leading to unsatisfactory results.
2. The homomorph concept introduces another difficulty. Which critical constants should be used in Equations (2.3) and (2.4) - those of the homomorph or those of the polar compounds? Inconsistently, O'Connell and Prausnitz use the polar compound's critical constants, but not its acentric factor. This results in the overcorrection of the values of B for polar gases.

3. The association factor is strictly an empirical correlation. Some substances which could be expected to associate (e.g., H₂O and NH₃) do not have association constants. On the other hand, some substances which might not actually "associate" have associate constants (e.g., ketones and ethers).

4. The polar terms (2.7) and (2.8) are arbitrarily set to equal to zero for \( T_{R_i} > 0.95 \). This leads to a discontinuity that can frequently be very substantial, as shown in Chapter 4.

2.2.3 The Correlation of Tsonopoulos

By using up to date data of Ar and Kr, Tsonopoulos (3) modified the Pitzer-Curl correlation for nonpolar gases. A slight modification of \( f_B^{(0)} \) in Equation (2.3) made it possible to fit all the B data of simple fluids (\( \omega = 0 \)) to within 1% error. The modified \( f_B^{(0)} \) is

\[
f^{(0)} = f_B^{(0)} - \frac{0.000607}{T_{R_i}^8}
\]  

(2.16)

Tsonopoulos checked \( f_B^{(1)} \) against reliable B values for compounds with large acentric factors and then established a modified function \( f^{(1)} \) with one term less than \( f_B^{(1)} \). The modified \( f_B^{(1)} \) has the form:

\[
f^{(1)} = 0.0637 + \frac{0.331}{T_{R_i}^2} - \frac{0.423}{T_{R_i}^3} - \frac{0.008}{T_{R_i}^8}
\]  

(2.17)
Thus,

\[ \frac{P_{Ci}B_{ii}}{R T_{Ci}} = f(0) + \omega_i f(1) \]  \hspace{1cm} (2.18)

This equation improves the fit to the B values of nonpolar gases at low reduced temperatures \( T_{Ri} < 0.75 \), and was used by Tsonopoulos as a basis for establishing a new correlation for polar gases.

Polar gases considered in his study included alcohols, phenol, water, ketones, ethers, aldehydes, and alkyl nitriles. They were classified into two classes: hydrogen-bonding gases (alcohols, phenol, and water), and non-hydrogen-bonding gases (ketones etc.).

The polar effects of these two classes were treated separately. In order to obviate the need of determining and using homomorphs, Tsonopoulos used the actual acentric factor for all polar gases.

For the non-hydrogen-bonding gases, a one-parameter function was established to account for the polar contribution. By adding this polar contribution term to Equation (2.18) the B values of non-hydrogen-bonding gases were fitted satisfactorily. It has the form:

\[ \frac{P_{Ci}B_{ii}}{R T_{Ci}} = f(0) + \omega_i f(1) + f_T^2 \]  \hspace{1cm} (2.19)

where the polar term is given by

\[ f_T^2 = \frac{a_{Ti}}{T_{Ri}^6} \]  \hspace{1cm} (2.20)
For each non-hydrogen-bonding gas, parameter $a_{T_i}$ is an average value taken within a lower temperature range (usually at $T_{R_i} \leq 0.95$) in which the individual value of $a_{T_i}$ is determined from the corresponding B value, and does not vary very much with temperature.

A satisfactory correlation between $a_{T_i}$ and $\mu_{R_i}$ was established as:

$$a_{T_i} = -2.140 \times 10^{-4} (\mu_{R_i}) - 4.30 \times 10^{-21} (\mu_{R_i})^8$$

(2.21)

In fact, parameter $a_{T_i}$ has a negative value for the non-hydrogen-bonding gas.

The association effect of the hydrogen-bonding gases makes it difficult to express the temperature dependence of the polar contribution to the second virial coefficients; Tsonopoulos developed a two-parameter function for the polar contribution.

The polar term of Equation (2.22) then has the form:

$$f_T^{(2)} = \frac{a_{T_i}}{T_{R_i}^6} - \frac{b_{T_i}}{T_{R_i}^8}$$

(2.22)

Both $a_{T_i}$ and $b_{T_i}$ were assumed to be positive. The B values of eight alcohols, phenol and water were analyzed with equations (2.19) and (2.22).

A constant value of $a_{T_i}$, 0.0878 is used for all eight alcohols; values of $b_{T_i}$ for eight alcohols are listed in Table (4-3). No further generalization of $b_{T_i}$ for alcohols was made in his study. For water, the $a_{T_i}$ value is 0.0279 and $b_{T_i}$ value is 0.0229. On the contrary, phenol has a negative value for
a_{Ti} and zero value for b_{Ti}.

In general, Tsonopoulos' method provides reliable predictions for the second virial coefficients of hydrogen-bonding gases.

To estimate cross second virial coefficient B_{ij} of mixture, Tsonopoulos presented the following mixing rules. The expressions for \omega_{ij} and P_{ij} are the same as those of O'Connell and Prausnitz:

\[
\omega_{ij} = 0.5 \left( \omega_i + \omega_j \right) \quad (2.10)
\]

\[
P_{C_{ij}} = \frac{4 \, T_{C_{ij}} \left( \frac{P \, V_i / T_i + P \, V_j / T_j}{C_i C_j} \right)}{\left( V_{C_i}^{1/3} + V_{C_j}^{1/3} \right)^3} \quad (2.11)
\]

However, for T_{C_{ij}}, Tsonopoulos introduced an empirically determined characteristic constant k_{ij} for each binary mixture to account for the deviation of T_{C_{ij}} from the geometric mean as expressed in Equation (2.9). Thus T_{C_{ij}} is expressed as

\[
T_{C_{ij}} = \left( T_{C_i} T_{C_j} \right)^{1/2} (1-k_{ij}) \quad (2.23)
\]

Tsonopoulos suggested that T_{C_{ij}} can be assumed to be the geometric mean of T_{C_i} and T_{C_j} (i.e., k_{ij}=0) only when i and j are very similar in size and chemical nature. Values of k_{ij} for non-polar systems were reported by Chueh and Prausnitz (23).

Equations (2.10), (2.11) and (2.23) are used for nonpolar-nonpolar binary mixtures.

For polar-nonpolar binary mixtures Tsonopoulos assumed that
Bij has no polar term:
\[ a_{Tij} = 0 \]
\[ b_{Tij} = 0 \]

For polar-polar binary mixtures, mixing rules for the parameters in the polar term are presented as
\[ a_{Tij} = 0.5(a_{T_i} + a_{T_j}) \quad (2.24) \]
\[ b_{Tij} = 0.5(b_{T_i} + b_{T_j}) \quad (2.25) \]

With a temperature-independent \( k_{ij} \) for each binary mixture, this correlation provides much better predictions for Bij than those of the O'Connell-Prausnitz correlation.

However, his correlation still has several shortcomings.
1. Instead of assuming the polar contribution parameter, \( a_{T_i} \), of non-hydrogen-bonding gases to be independent of temperature values of \( a_{T_i} \) are obtained as an average value within an arbitrary low temperature range. This approach raises a question whether equation (2.20) is reliable beyond the temperature range as mentioned above.
2. Fixing values of the polar contribution parameter \( a_{T_i} \) for alcohols creates difficulties to generalize the parameter \( b_{T_i} \) in Equation (2.22).
3. The characteristic constant \( k_{ij} \) is an empirically determined value, and therefore is not available for many polar-polar binary mixtures.
CHAPTER 3
THEORETICAL CONSIDERATION

Complete description of vapor-liquid equilibria for a system gives equilibrium composition of both phases as well as temperature and total pressure. In a typical experimental investigation temperature or total pressure is held constant.

Usually chemical processing is operated at low or moderate pressure. Therefore particular attention has been given the subject of vapor-liquid equilibrium at low pressures - up to several atmospheres. Under these conditions certain quite reliable assumptions can be made about the behavior of the vapor phase which allow development of an accurate equation for the calculation of liquid phase activity coefficients from phase equilibrium data. Since the activity coefficients are useful in data reduction for vapor-liquid equilibrium calculations, their calculation and correlation are required.

3.1 Evaluation of Liquid Phase Activity Coefficients at Low and Moderate Pressures

Through the definition of activity coefficient $\gamma_i$ and some assumptions, Van Ness (24) derived an equation to evaluate the liquid phase activity coefficient ($\gamma_i^L$) at low and moderate pressures.

By definition:

$$\gamma_i = \frac{f_i}{x_i f_i^0}$$

(3.1)
For the liquid phase

\[ \gamma_i^L = \frac{f_i^L}{x_i(f_i^0)} \]  

(3.2)

For the vapor phase

\[ \gamma_i^V = \frac{f_i^V}{y_i(f_i^0)} \]  

(3.3)

where the superscripts L and V indicate the liquid and vapor phase respectively, and,

\[ f_i \] = fugacity of component i in the solution

\[ f_i^0 \] = fugacity of pure component i at the standard state

(i.e., at the temperature and pressure of the solution).

\[ \gamma_i \] = activity coefficient of component i in the solution

\[ x_i \] = mole fraction of component i in the liquid phase

\[ y_i \] = mole fraction of component i in the vapor phase

Three assumptions were made by Van Ness to derive the equation:

1. The vapor phase of the mixture, as well as the vapors in equilibrium with the pure components, are adequately described by the virial equation terminated after the second virial coefficient (B), i.e., \( Z = 1 + BP/RT \), where \( R \) is the gas constant, \( P \) is the system pressure, \( T \) is the system temperature, and \( Z \) is the compressibility.

2. The pure component liquid volumes (\( V_i^0 \)) are incompressible over the pressure range in question.
3. The standard states for the activity coefficients are the pure components at the same temperature and pressure as those of mixture.

Finally, an equation for liquid phase activity coefficient is found as

$$\log \gamma_i^L = \log \frac{\gamma_i^P}{x_i P_i^0} + \frac{(B_{ii} - V_i^0)(P - p_i^0)}{2.303 RT} + \log \gamma_i^V \quad (3.4)$$

In this equation, the quantities $p_i^0, B_{ii}, V_i^0, P$ are the vapor pressure, second virial coefficient, liquid molar volume of component $i$, and the total pressure of the system, respectively.

Thus, for a binary solution at low or moderate pressure, $\log \gamma_i^L$ is expressed by:

$$\log \gamma_i^L = \log \frac{\gamma_i^P}{x_i P_i^0} + \frac{(B_{ii} - V_i^0)(P - p_i^0)}{2.303 RT} \quad + \frac{(1 - \gamma_i^P)^2 p \delta_{12}}{2.303 RT} \quad (3.5)$$

in which $\delta_{12} = 2B_{12} - B_{11} - B_{22}$, and $B_{12}$ is the cross second virial coefficient.

In equation (3.5), the second and third terms of the right-hand side represent the departure of the vapor phase from ideal behavior.

In order to obtain values of $B_{11}, B_{22},$ and $B_{12}$, for the system studied in this investigation, a new empirical correlation of the second virial coefficient for polar gases was developed (see Chapter 4).
3.2 Correlation of Experimental Liquid Phase Activity Coefficients

A number of integrated forms of the Gibbs-Duhem equation are available for correlating liquid phase activity coefficients for binary mixtures, for example, the Margules equation (25), the Van Laar equation (26), the Redlich-Kister equation (22), and the Wilson equation (27).

The Redlich-Kister equations (22) are commonly used for correlating the liquid phase activity coefficient with the liquid phase composition. These equations were deduced from the relation between the liquid phase activity coefficient \( \gamma_i^L \) and molar excess Gibbs free energy \( G^E \) as described below.

An excess Gibbs free energy is defined as the difference between an actual Gibbs free energy and the Gibbs free energy that would be calculated under the same conditions of \( T, P \) and \( x_i \) by the equation for an ideal solution. Thus by definition (4):

\[
G^E = G \text{ (actual solution at } T, P, x_i) - G \text{ (ideal solution at same } T, P, x_i) 
\]

or in another form:

\[
\frac{G^E}{2.303RT} = \sum_i x_i \log \gamma_i^L \tag{3.6}
\]

For a binary system, equation (3.6) has zero values for \( x_i = 0 \) and \( x_i = 1 \). In this application, the usual conversion of \( \gamma_1^L = 1 \) for \( x_i = 1 \) and \( \gamma_2^L = 1 \) for \( x_1 = 0 \) is adopted.
Differentiating Equation (3.6) with respect to \( x_1 \) gives

\[
\log \left( \frac{L_1}{L_2} \right) = \left[ \frac{dG^E}{2.303RT} \right]_{T,P,x_2} \text{d}x_1 \quad (3.7)
\]

By taking advantage of the relation between \( G^E \) and \( x_1 \) illustrated above, Redlich and Kister assumed the pressure dependence of \( G^E \) can be neglected at low or moderate pressure, and proposed that \( G^E/RT \) can be presented by an appropriate power series of the liquid composition \( x_1 \).

The expansion for a binary mixture if given by,

\[
\frac{G^E}{2.303RT} = x_1 x_2 \left[ B_{12} + C_{12}(x_1-x_2) + D_{12}(x_1-x_2)^2 + \ldots \right] \quad (3.8)
\]

where the empirical parameters \( B_{12}, C_{12}, D_{12} \ldots \) depend on temperature only.

From equation (3.6), liquid phase activity coefficients are expressed as:

\[
\log \gamma_1^L = x_2 \left[ B_{12} + C_{12}(3x_1-x_2) + D_{12}(x_1-x_2)(5x_1-x_2) + \ldots \right] \quad (3.9)
\]

\[
\log \gamma_2^L = x_1 \left[ B_{12} + C_{12}(x_1-3x_2) + D_{12}(x_1-x_2)(x_1-5x_2) + \ldots \right] \quad (3.10)
\]

From equation (3.7), \( \log \gamma_1^L / \gamma_2^L \) can be expressed as:

\[
\log \frac{\gamma_1^L}{\gamma_2^L} = B_{12}(x_2-x_1) + C_{12}(6x_1x_2-1) + D_{12}(x_1-x_2)(8x_1x_2-1) + \ldots \quad (3.11)
\]

The Redlich-Kister equations provide not only a convenient method for representing liquid phase activity coefficients, but also for classifying different types of liquid solutions. According to Redlich, Kister and Turnquist (28), only the first term is
required for nearly ideal solutions. For a solution containing an associated component, such as alcohols and acids, the third term is necessary. However, only when very accurate and extensive data are available, the use of four or more terms is warranted. This is further reported by Ho et al. (29), that three-constant Redlich-Kister equations are adequate for representing liquid phase activity coefficients for most of binary systems.

The values of $y_i$ and $p$ can be calculated using these three-constant equations together with Equation (3.4) by means of the Newton-Raphson method of iteration (30). (A detailed description is presented in Appendix III). Computer programs for evaluating and correlating the vapor-liquid equilibrium data of the system studied are presented in Appendix VIII.

3.3 Thermodynamic Consistency Test of Binary Vapor-Liquid Equilibrium Data Obtained at Isothermal Conditions

At isothermal conditions, the integral form of the Gibbs-Duhem equation can be expressed as

$$
\int_{x_1=0}^{x_1=1} \log \left( \frac{v_1}{L} \right) dx_1 = - \int_{P_2}^{P_1} \frac{v^E}{2.303RT} dp
$$

(3.11)

where $v^E$ is the excess molar volume.

Observing that:

(a) Values of $v^E$ are small

(b) The range of system pressure is small

Redlich and Kister (2) proposed a very good approximation for the thermodynamic consistency test by simply setting the right-hand
side of Equation (3.11) equal to zero, i.e.,

$$\int_{x_1=0}^{x_1=1} \log \left( \frac{\gamma_1^L}{\gamma_2^L} \right) dx_1 = 0 \tag{3.12}$$

Equation (3.12) provides what is called the area test of Redlich and Kister. The integral can be evaluated by plotting $\log(\gamma_1^L/\gamma_2^L)$ versus $x_1$ and then measuring the net area under the curve. The requirement of thermodynamic consistency is met if the net area is very close to zero.
CHAPTER 4

DEVELOPMENT OF A NEW EMPIRICAL CORRELATION FOR SECOND VIRIAL COEFFICIENTS OF POLAR COMPOUNDS

At moderate pressure, the second virial coefficient provides a good measure of the departure of the vapor phase from ideal gas behavior arising from two body interactions. In this study, the second virial coefficients, $B$, for ethanol and methyl methacrylate are needed. Although values of $B$ for ethanol are available in the literature, no experimental data are reported for methyl methacrylate (an ester).

The correlation proposed by Tsonopoulos for polar gases, unfortunately did not include esters. For this reason, an attempt was made to develop a generalized empirical correlation for obtaining the second virial coefficient for methyl methacrylate by modifying the Tsonopoulos correlation. The Pitzer-Curl correlation for non-polar gases modified by Tsonopoulos provides a means for estimating the polar effects on the second virial coefficients for polar gases, and was used in this study as suggested.

In the present study the following polar compounds: esters, ketones, ethers, acetaldehyde, and alcohols were included in the development of the new correlation.

4.1 The Virial Equation of State

The virial equation (4) gives the compressibility factor as a power series in terms of reciprocal molar volume $1/V$:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} \ldots$$  \hspace{1cm} (4.1)
where $Z$ is the compressibility factor, $B$ is the second virial coefficient and $C$ is the third virial coefficient. All of the virial coefficients are independent of pressure or density and are functions of temperature and composition.

At low or moderate pressure, the virial equation of state, truncated at the second virial coefficient:

$$Z = 1 + \frac{B}{V}$$ \hspace{1cm} (4.2)

can accurately represent the p-V-T behavior of vapors.

The composition dependence of $B$ for an $N$-component mixture is given accurately by the following relationship:

$$B_{\text{mix}} = \sum_{j=1}^{N} \sum_{i=1}^{N} y_i y_j B_{ij}$$ \hspace{1cm} (4.3)

where $B_{ii}$ and $B_{jj}$ are the pure component second virial coefficients, and $B_{ij}$ ($i \neq j$) is the cross second virial coefficient.

For a binary mixture, $B_{\text{mix}}$ becomes:

$$B_{\text{mix}} = y_1^2 B_{11} + 2y_1y_2 B_{12} + y_2^2 B_{22}$$ \hspace{1cm} (4.4)

### 4.2 Development of an Empirical Correlation

It is known that polar compounds are characterized by a non-zero dipole moment $\mu$ which shows the effect of electrostatic forces between molecules. The polar compounds considered in this study are alcohols, esters, ketones, ethers and acetaldehyde as listed in Table (4-1). The $B$ values available in the literature for these compounds are listed in Appendix VIII. These compounds are further classified into hydrogen-bonding and non-hydrogen-bonding classes. Hydrogen bonding compounds have
bonding between the hydrogen atom attached to the oxygen atom in one molecule with the oxygen atom of another molecule; this makes their behavior in the vapor phase different and more complex than that of non-hydrogen bonding polar compounds (esters ... etc.). These two classes of compounds are treated separately.

Hálm (3) reported that the deviations of the reduced second virial coefficients of polar from non-polar behavior are small at reduced temperature greater than one but increase rapidly with decreasing temperature. The Pitzer-Qurl correlation as modified by Tsonopoulos yields excellent estimation of the B values for non-polar compounds. For this reason, it was used for detecting the deviation of second virial coefficients for polar compounds from that of non-polar compounds. The deviation due to the effect of polarity on the compounds can be corrected by an additional function \( f^{(2)} \) of reduced dipole moment and reduced temperature. For hydrogen-bonding polar compounds where both polar effects and hydrogen-bonding effects prevail, the deviations can be accounted for by adding an extra correction function \( f^{(3)} \) of reduced temperature to the polar correction function \( f^{(2)} \).

As a result, the reduced second virial coefficient for the polar compounds can then be expressed by combining functions \( f^{(2)} \) and \( f^{(3)} \) with Equation (2.18) as follows:

\[
\frac{P_{c_i} B_{ii}}{RT_{c_i}} = f^{(0)} + \omega_i f^{(1)} + f^{(2)} + f^{(3)}
\]  

(4.5)
### Table 4-1
VALUES OF PARAMETERS FOR THE COMPOUNDS USED IN THIS DEVELOPMENT

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_{c_i}^{R(14)}$</th>
<th>$p_i^{(14)}$</th>
<th>$c_{i,atm}$</th>
<th>$\omega_i^{(14)}$</th>
<th>$\omega_i^{(6)}$</th>
<th>$\mu_i^{(32)}$</th>
<th>$\eta_i^{(6)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Ether</td>
<td>400</td>
<td>53.0</td>
<td>0.192</td>
<td>0.152</td>
<td>1.3</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td>466.7</td>
<td>35.9</td>
<td>0.281</td>
<td>0.252</td>
<td>1.3</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>508.1</td>
<td>46.4</td>
<td>0.309</td>
<td>0.187</td>
<td>2.8</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Methyl-Ethyl Ketone</td>
<td>535.6</td>
<td>41.0</td>
<td>0.329</td>
<td>0.187</td>
<td>2.8</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Methyl-N-Propyl Ketone</td>
<td>564.0</td>
<td>38.4</td>
<td>0.348</td>
<td>0.278</td>
<td>2.8</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Ketone</td>
<td>553.4</td>
<td>38.0</td>
<td>0.349</td>
<td></td>
<td></td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>Diethyl Ketone</td>
<td>561.0</td>
<td>36.9</td>
<td>0.347</td>
<td></td>
<td></td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>461.0</td>
<td>55.0</td>
<td>0.303</td>
<td>0.152</td>
<td>2.7</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Ethyl Formate</td>
<td>508.4</td>
<td>46.8</td>
<td>0.283</td>
<td>0.252</td>
<td>2.0</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>N-Propyl Formate</td>
<td>538.0</td>
<td>40.1</td>
<td>0.315</td>
<td>0.297</td>
<td>1.9</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>506.8</td>
<td>46.3</td>
<td>0.324</td>
<td>0.215</td>
<td>1.7</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>523.2</td>
<td>37.8</td>
<td>0.363</td>
<td>0.278</td>
<td>1.9</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>N-Propyl Acetate</td>
<td>549.4</td>
<td>32.9</td>
<td>0.392</td>
<td></td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>N-Butyl Acetate</td>
<td>579.0</td>
<td>31.0</td>
<td>0.417</td>
<td></td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Methyl Propanoate</td>
<td>530.6</td>
<td>39.5</td>
<td>0.352</td>
<td>0.326</td>
<td>1.7</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Ethyl Propanoate</td>
<td>546.0</td>
<td>33.2</td>
<td>0.395</td>
<td></td>
<td></td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>512.6</td>
<td>79.9</td>
<td>0.599</td>
<td>0.105</td>
<td>1.7</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>516.2</td>
<td>43.0</td>
<td>0.635</td>
<td>0.152</td>
<td>1.7</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>N-Propanol</td>
<td>536.7</td>
<td>51.0</td>
<td>0.624</td>
<td>0.201</td>
<td>1.7</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>N-Butanol</td>
<td>562.9</td>
<td>63.6</td>
<td>0.590</td>
<td>0.252</td>
<td>1.7</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>Isopropanol</td>
<td>508.3</td>
<td>47.0</td>
<td>0.666</td>
<td>0.187</td>
<td>1.7</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>2-Butanol</td>
<td>536.0</td>
<td>41.4</td>
<td>0.576</td>
<td>0.215</td>
<td>1.7</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Isobutanol</td>
<td>547.7</td>
<td>42.4</td>
<td>0.588</td>
<td>0.215</td>
<td>1.7</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Tert-Butanol</td>
<td>506.2</td>
<td>39.2</td>
<td>0.618</td>
<td>0.201</td>
<td>1.7</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>
where $P_{C_i}$ = critical pressure of component $i$
$T_{C_i}$ = critical temperature of component $i$
$\omega_i$ = acentric factor of component $i$

$$f(0) = 0.1445 - 0.330/RT_{R_i} - 0.1385/T_{R_i}^2 - 0.0121/T_{R_i}^3$$
$$- 0.000607/T_{R_i}^8$$

$$f(1) = 0.0637 + 0.331/T_{R_i}^2 - 0.423/T_{R_i}^3 - 0.008/T_{R_i}^8$$

(2.16)

(2.17)

The numerical values of $T_{C_i}$, $P_{C_i}$, $\omega_i$, and $\mu_i$ for the compounds investigated in this work are presented in Table (4-1). The development of $f$ functions $f^{(2)}$ and $f^{(3)}$ are discussed below.

4.2.1 Non-Hydrogen-Bonding Polar Gases

In this work, eight esters, five ketones, two ethers, and acetaldehyde were studied. The data source and the temperature range of the available second virial coefficient data for these compounds are listed in Table (4-2).

The contribution of the non-hydrogen-bonding polar effect, $f^{(2)}$, for each individual compound was obtained by subtracting $f(0)$ from $f^{(1)}$ from

$$f(2) = f^{C_i}\frac{RT}{C_i B_{ii}}$$

When values of $f^{(2)}$ were plotted against $(1/T_{R_i})^C$, the curvature of the resulting curve was reduced by increasing the value of $C$ from unity as illustrated in Figure (4-1) for methyl acetate. It appears that the value of $f^{(2)}$ approaches zero at extremely high temperature, as dictated by the fact that the polar effect diminishes as temperature increases.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Number of Data</th>
<th>Reduced Temp. Range</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Ether</td>
<td>7</td>
<td>0.68-0.81</td>
<td>(33)(36)</td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td>28</td>
<td>0.63-0.87</td>
<td>(33)</td>
</tr>
<tr>
<td>Acétone</td>
<td>7</td>
<td>0.59-0.71</td>
<td>(33)</td>
</tr>
<tr>
<td>Methyl-Ethyl Ketone</td>
<td>5</td>
<td>0.59-0.69</td>
<td>(33)</td>
</tr>
<tr>
<td>Methyl N-Propyl Ketone</td>
<td>5</td>
<td>0.59-0.70</td>
<td>(33)</td>
</tr>
<tr>
<td>Methyl Isopropyl Ketone</td>
<td>3</td>
<td>0.59-0.66</td>
<td>(34)</td>
</tr>
<tr>
<td>Diethyl Ketone</td>
<td>3</td>
<td>0.60-0.67</td>
<td>(34)</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>16</td>
<td>0.63-1.03</td>
<td>(33)</td>
</tr>
<tr>
<td>N-propyl Formate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
<tr>
<td>N-Propyl Acetate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
<tr>
<td>N-Butyl Acetate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
<tr>
<td>Methyl Propanoate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
<tr>
<td>Ethyl Propanoate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
<tr>
<td>Ethyl Formate</td>
<td>23</td>
<td>0.50-5.00</td>
<td>(35)</td>
</tr>
</tbody>
</table>
Figure 4-1 Relationship Between $f^{(2)}$ and $1/T_{Ri}^C$ for Methyl Acetate
Accordingly, the function $f^{(2)}$ was expressed by:

$$f^{(2)} = \frac{a_i}{T_{R_i}^c}$$  \hspace{1cm} (4.8)

In this equation, the quantity of $a_i$ was considered only as a function of reduced dipole moment ($\mu_{R_i}$). Value of $\mu_{R_i}$ are listed in Table (4-3). In order to find an optimum value of $c$ which gives the minimum value of the RMS deviation of Equation (4.8), the Golden section search method (37) was employed. In this method, several values of $c$ were assumed within a probable region in which the optimum value of $c$ lies, and the corresponding RMS deviations of Equation (4.8) were calculated and compared. Simultaneously, the value of $a_i$ for each $c$ was obtained during the calculation of RMS. By sequentially reducing the region, the optimum $c$ together with $a_i$ were found. The values thus obtained together with the RMS deviations for each compound are listed in Table (4.3).

The values of $c$ vary from 3.1 to 11.0. This large difference caused difficulties in selecting an appropriate value of $c$. It was then arbitrarily decided to adopt the value of 6 as used by Tsonopoulos. Values of $a_i$ were again calculated by means of the least-squares method.

Therefore, Equation (4.8) was:

$$f^{(2)} = \frac{a_i}{T_{R_i}^6}$$  \hspace{1cm} (4.9)

Values of $a_i$ and RMS deviations of B using Equation (2.18) and Equations (4.9) are listed in Table (4.4). Figure (4-2) depicts the values of $a_i$ plotted against $\mu_R$ for all the non-hydrogen bonding polar compounds studied in this work. Figure (4-2) displays two important characteristics which should be considered in the calculation of a correlating functional form. It demonstrated that $f^{(2)}$ diminishes to zero as $\mu_R$ approaches
Table 4-3
VALUES OF $\mu_{R_i}$ AND VALUES OF $c_i$ AND $a_i$ FOR EQUATION (4.8)
AND RMS DEVIATION OF B FROM EQUATIONS (2.18) AND (4.8)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\mu_{R_i}$</th>
<th>$a_i$</th>
<th>$c_i$</th>
<th>RMS* Deviation of B cm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Ether</td>
<td>56.0</td>
<td>-0.02874</td>
<td>4.2</td>
<td>15.0</td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td>27.9</td>
<td>-0.00010</td>
<td>11.0</td>
<td>45.0</td>
</tr>
<tr>
<td>Acetone</td>
<td>140.9</td>
<td>-0.02825</td>
<td>6.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Methyl-Ethyl Ketone</td>
<td>112.1</td>
<td>-0.03515</td>
<td>4.6</td>
<td>26.4</td>
</tr>
<tr>
<td>Methyl N-Propyl Ketone</td>
<td>94.6</td>
<td>-0.00601</td>
<td>9.2</td>
<td>31.7</td>
</tr>
<tr>
<td>Methyl Isopropyl Ketone</td>
<td>97.3</td>
<td>-0.02311</td>
<td>4.7</td>
<td>2.3</td>
</tr>
<tr>
<td>Diethyl Ketone</td>
<td>85.5</td>
<td>-0.02302</td>
<td>5.6</td>
<td>1.9</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>188.7</td>
<td>-0.05570</td>
<td>5.8</td>
<td>33.9</td>
</tr>
<tr>
<td>Ethyl Formate</td>
<td>72.4</td>
<td>-0.005131</td>
<td>6.7</td>
<td>7.0</td>
</tr>
<tr>
<td>N-Propyl Formate</td>
<td>50.0</td>
<td>-0.003056</td>
<td>7.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>52.1</td>
<td>-0.06021</td>
<td>3.9</td>
<td>28.2</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>49.9</td>
<td>-0.01600</td>
<td>5.1</td>
<td>17.2</td>
</tr>
<tr>
<td>N-Propyl Acetate</td>
<td>35.3</td>
<td>-0.008189</td>
<td>5.6</td>
<td>15.7</td>
</tr>
<tr>
<td>N-Butyl Acetate</td>
<td>30.0</td>
<td>-0.02597</td>
<td>5.0</td>
<td>21.6</td>
</tr>
<tr>
<td>Methyl Propanoate</td>
<td>40.6</td>
<td>-0.05149</td>
<td>3.1</td>
<td>21.2</td>
</tr>
<tr>
<td>Ethyl Propanoate</td>
<td>36.1</td>
<td>-0.02993</td>
<td>3.2</td>
<td>23.3</td>
</tr>
</tbody>
</table>

*RMS deviation = $\sqrt{\frac{\sum |B_{cal.} - B_{exp.}|^2}{N}}$ in which $B_{cal.}$ refers to the calculated values from the correlation, $B_{exp.}$ represents the experimental values and $N$ is the number of data points.
Table 4-4
VALUES OF $a_i$ FOR EQUATIONS (4.9) AND RMS DEVIATION OF $B$ FROM EQUATIONS (2.18) AND (4.9)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$a_i$</th>
<th>RMS Deviation of $B \text{ cm}^3\text{mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl Ether</td>
<td>-0.01651</td>
<td>16.1</td>
</tr>
<tr>
<td>Ethyl Ether</td>
<td>-0.00135</td>
<td>47.7</td>
</tr>
<tr>
<td>Acetone</td>
<td>-0.03391</td>
<td>11.9</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>-0.01825</td>
<td>38.6</td>
</tr>
<tr>
<td>Methyl N-Propyl Ketone</td>
<td>-0.02581</td>
<td>97.8</td>
</tr>
<tr>
<td>Methyl Iso-Propyl Ketone</td>
<td>-0.01245</td>
<td>14.9</td>
</tr>
<tr>
<td>Keto</td>
<td>-0.01898</td>
<td>7.3</td>
</tr>
<tr>
<td>Diethyl Ketone</td>
<td>-0.05289</td>
<td>34.0</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>-0.00780</td>
<td>12.8</td>
</tr>
<tr>
<td>Ethyl Formate</td>
<td>-0.00528</td>
<td>15.4</td>
</tr>
<tr>
<td>N-Propyl Formate</td>
<td>-0.02060</td>
<td>88.7</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>-0.01006</td>
<td>27.0</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>-0.00643</td>
<td>17.7</td>
</tr>
<tr>
<td>N-Propyl Acetate</td>
<td>-0.01559</td>
<td>57.0</td>
</tr>
<tr>
<td>N-Butyl Acetate</td>
<td>-0.01258</td>
<td>91.6</td>
</tr>
<tr>
<td>Methyl Propanoate</td>
<td>-0.00744</td>
<td>68.7</td>
</tr>
<tr>
<td>Ethyl Propanoate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-2 Relationship Between $a_i$ and Reduced Dipole Moment for Non-Hydrogen-Bonding polar Substances (—— calculated by Equation (4.10)).
zero, and the representative function should be exponential at higher \( \nu_{R_i} \) and linear at lower \( \nu_{R_i} \) as indicated in Figure (4-2). The function chosen to be the best suited is the following:

\[
a_i = a_0 \nu_{R_i} + a_1 (\exp a_2 \nu_{R_i})
\]  

(4-10)

The optimum value of \( a_2 \) for minimizing the RMS deviation of Equation (4.10) was also obtained by means of the Golden section search method (37). It should be mentioned that values of \( a_0 \), and \( a_1 \) were simultaneously evaluated during the calculation of RMS deviation of Equation (4.10). A good fit of this equation was obtained as shown in Figure (4-2). The obtained values of \( a_0 \), \( a_1 \), and \( a_2 \), are -0.0001799, -0.00002169 and 0.03605, respectively. RMS deviation of this fit is 0.04.

The complete equation for the second virial coefficient of non-hydrogen-bonding polar gases then can be represented by adding the one-parameter function \( f^{(2)} \) to Equation (2.18) as shown below:

\[
\frac{P_{C_i}}{RT_{C_i}} = f^{(0)} + \omega_i f^{(1)} + f^{(2)}
\]

(4.11)

where

\[
f^{(2)} = a_i / T_{R_i}^6
\]

(4.9)

\[
a_i = 0.0001799 \nu_{R_i} - (0.00002169) (\exp 0.03605 \nu_{R_i})
\]

(4.10)

In general, the results obtained from a generalized expression are inferior to those obtained from the expression representing the individual compound. This is also true for the results obtained in this study. This can be seen from
Table (4-4) of this section and Table (4-9) of Section 4.4, particularly for 1-butyl acetate, acetone and methyl n-propyl ketone.

The discrepancy observed for these three compounds as depicted in Figures (4-3), (4-4), and (4-5) indicates that the discrepancy tends to increase with decreasing temperature. The results of fitting Equation (4.11) to $B$ values for the compounds studied in this work, will be discussed in Section 4.4.

4.2.2 Hydrogen-Bonding Polar Gases

With hydrogen linked to an electronegative atom (for example $O$, $N$) molecules tend to associate with each other by forming hydrogen bonds.

It is generally acknowledged that along with the polar character, alcohols display strong hydrogen bonded association, and show much greater deviations from the perfect gas laws than do non-hydrogen-bonding polar gases. Consequently, the second virial coefficients of alcohols are more negative than those of non-hydrogen-bonding polar gases (at the same corresponding states), thus reflecting the additional effect of hydrogen-bonding. In Table 4-5 the data source and the temperature range of the experimental $B$ values are listed for the eight alcohols.

To study the effect of hydrogen-bonding apart from the effect of polarity, the polar correction function $f^{(2)}$ developed in 4.2.1 was extended to alcohols.
Figure 4-3  Comparisons of Experimental and Calculated Values for N-Butyl Acetate (o Experimental, —— Calculated from Equations (2.18) and (4.8), —— Calculated from Equations (2.18) and (4.9))
Figure 4-4 Comparisons of Experimental and Calculated Values for Acetone (○ Experimental, —— Calculated from Equations (2.18) and (4.8), —— Calculated from Equations (2.18) and (4.9))
Figure 4-5  Comparisons of Experimental and Calculated Values for Methyl N-Propyl Ketone (○ Experimental, ——— Calculated from Equations (2.18) and (4.8), --- Calculated from Equations (2.18) and (4.9))
<table>
<thead>
<tr>
<th>Substance</th>
<th>Number of Data</th>
<th>Reduced Temp. Range</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>16</td>
<td>0.58-1.12</td>
<td>(33)(38)(39)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6</td>
<td>0.61-0.76</td>
<td>(33)(38)</td>
</tr>
<tr>
<td>N-Propanol</td>
<td>4</td>
<td>0.70-0.79</td>
<td>(33)</td>
</tr>
<tr>
<td>N-Butanol</td>
<td>6</td>
<td>0.62-0.78</td>
<td>(33)</td>
</tr>
<tr>
<td>Iso-Propanol</td>
<td>12</td>
<td>0.66-0.93</td>
<td>(33)</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>4</td>
<td>0.71-0.79</td>
<td>(33)</td>
</tr>
<tr>
<td>Iso-Butanol</td>
<td>4</td>
<td>0.72-0.80</td>
<td>(33)</td>
</tr>
<tr>
<td>Tert-Butanol</td>
<td>4</td>
<td>0.75-0.84</td>
<td>(33)</td>
</tr>
</tbody>
</table>
Along with this extension, the function \( f^{(3)} \) was developed to account for the hydrogen-bonding effect. A similar method as mentioned in 4.2.1 was employed to obtain values of \( f^{(3)} \) for each alcohol and further to find an expression for \( f^{(3)} \).

In order to evaluate the contribution of \( f^{(3)} \) on \( B \), values of \( f^{(3)} \) for each of the individual alcohols were obtained in terms of \( \Delta B \).

\[
\Delta B = B - \frac{RT_{C_i}}{p} (f^{(0)} + \omega_i f^{(1)} + f^{(2)})
\]

Consequently, the quantity \( \Delta B \) was plotted against \( 1/T_{R_i} \) as shown in Figure (4-6). It is shown that \( \Delta B \) changes more drastically with temperature for \( T_{R_i} < 0.8 \) than for \( T_{R_i} > 0.8 \). This indicates that the behavior of \( f^{(3)} \) is in good agreement with the observed behavior of the temperature dependence of the hydrogen-bonding effect. The figure further displays that it is appropriate to extend the polar correction function \( f^{(2)} \) to alcohols to demonstrate their effects. In order to formulate a suitable expression for \( f^{(3)} \), methanol was chosen for further analysis because there are more experimental \( B \) values reported for this compound. Therefore, values of \( f^{(3)} \) for methanol were plotted against \( 1/T_{R_i} \) in Figure (4-7).

This figure indicates that at higher temperatures \( T_{R_i} > 0.8 \), there is a tendency for the curve to approach zero as the temperature increases, and at lower temperatures \( T_{R_i} < 0.8 \), the effect of temperature on \( f^{(3)} \) is more profound.

According to the above analysis, a typical model of \( f^{(3)} \)
Figure 4.6 Relationship between $\Delta B$ and $\frac{1}{T_{R_1}}$ for eight alcohols.
was developed for each alcohol:

\[ f^{(3)} = \frac{b_i}{R_i} + \left( \frac{1}{R_i} - \frac{1}{R_C} \right) (d_i \exp \frac{g_i}{R_i})^{(4.12)} \]

in which \( b_i, g_i \) and \( d_i \) are constants for each alcohol, and \( R_C \) is the reduced temperature at which the behavior of \( f^{(3)} \) starts changing. By using an appropriate value of \( 1/R_C \), Equation (4.12) may accurately describe \( f^{(3)} \) for all the alcohols, that is, at \( R_i < 0.8 \), the exponential term in Equation (4.12) predominates, while at \( R_i > 0.8 \) the linear term predominates. First of all, a trial-and-error procedure together with the Golden section search method (37) were used to obtain the values of \( R_C, b_i, d_i \) and \( g_i \) for methanol. Initially, several possible values of \( R_C \) were estimated from Figure (4-7) and used in the Golden section search method (37). The procedure used in the calculation may be described as following:

1) Designate a search interval for \( g_i \)
2) Select a value for \( R_C \) in Equation (4.12)
3) Apply the Golden section search method to find a value for \( g_i \) which minimizes the RMS deviation of \( B \). Values of \( b_i \) and \( d_i \) are thus obtained during the calculation.
4) Repeat steps (2) and (3) by using different values of \( R_C \)

Consequently, several sets of values for \( R_C, g_i, b_i, d_i \) and RMS deviation of \( B \) were obtained. The final selection was based on the set which yields the smallest RMS deviation of second virial coefficient. The values of \( R_C, g_i, b_i \) and \( d_i \) thus obtained are 1.24, 5.5938, 0.05014 and -0.00023065, respectively.
In Figure (4-7), values of $f^{(3)}$ obtained from the experimental data of B for methanol were plotted along with the curve calculated from the Equation (4.12). The figure indicates that the equation fits the data satisfactorily over the whole temperature range.

Since Equation (4.12) gives an excellent fit of methanol, values of $g_i$, $d_i$ and $b_i$ for the other seven alcohols were determined by fixing $1/T_{R_c} = 1.24$ (i.e., $T_{R_i} = 0.81$). The values of $g_i$, $d_i$, $b_i$ and RMS deviation of B obtained from Equations (4.12) and (4.5) for eight alcohols are listed in Table (4-6).

The values of $b_i$ and $g_i$ for n-propanol and C$_4$ alcohols are much greater than those for the other alcohols. These differences caused difficulties in obtaining a generalized expression for these values.

In order to generalize Equation (4.12), it was hoped that one of the three parameters, $b_i$, $g_i$, and $d_i$ be kept constant so that values of the other two parameters might be generalized in terms of some physical properties. Values of $b_i$, $g_i$, and $d_i$ for methanol were used as the basis for this attempt.

By a trial-and-error method, it was found that by fixing $d_i = 0.00023065$ for all the alcohols, reasonable values of $b_i$ and $g_i$ were obtained. Equation (4.12) was then expressed as

$$f^{(3)} = \frac{b_i}{T_{R_i}} + \left( -\frac{1}{T_{R_i}} - 1.24 \right) (0.00023065) \exp \frac{g_i}{T_{R_i}}$$ (4.13)

The recalculated values of $b_i$ and $g_i$ are listed together with the RMS deviations of B as obtained from Equations (4.5) and (4.13).
Table 4-6

VALUES OF $\mu_{R_i}^i$, $b_i$, $d_i$, $q_i$, AND RMS DEVIATIONS OF B FOR ALCOHOLS

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\mu_{R_i}^i$</th>
<th>$b_i$</th>
<th>$d_i$</th>
<th>$q_i$</th>
<th>RMS of B cm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>87.9</td>
<td>0.05014</td>
<td>-2.3065x10$^{-4}$</td>
<td>5.5938</td>
<td>15.4</td>
</tr>
<tr>
<td>Ethanol</td>
<td>68.3</td>
<td>0.02135</td>
<td>-1.4401x10$^{-6}$</td>
<td>8.8251</td>
<td>17.6</td>
</tr>
<tr>
<td>N-Propanol</td>
<td>51.2</td>
<td>0.02259</td>
<td>2.6124x10</td>
<td>-13.081</td>
<td>1.8</td>
</tr>
<tr>
<td>N-Butanol</td>
<td>39.8</td>
<td>0.1767</td>
<td>-1.7923x10$^{-7}$</td>
<td>-2.1523</td>
<td>5.4</td>
</tr>
<tr>
<td>Iso-Propanol</td>
<td>52.6</td>
<td>0.02603</td>
<td>-2.3110x10</td>
<td>8.6906</td>
<td>5.6</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>41.6</td>
<td>0.09351</td>
<td>-3.4823x10$^{-3}$</td>
<td>-2.6700</td>
<td>2.3</td>
</tr>
<tr>
<td>Iso-Butanol</td>
<td>40.8</td>
<td>0.1006</td>
<td>-6.2145x10$^{-3}$</td>
<td>-6.4277</td>
<td>4.7</td>
</tr>
<tr>
<td>Tert-Butanol</td>
<td>44.2</td>
<td>0.06691</td>
<td>-1.8652x10</td>
<td>-2.3252</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 4-7

VALUES OF PARAMETERS IN EQUATION 4-13 AND THE PARACHORS ($\Phi$) FOR ALCOHOLS

<table>
<thead>
<tr>
<th>Substance</th>
<th>$b_i$</th>
<th>$q_i$</th>
<th>RMS deviation of B cm$^3$ mol$^{-1}$</th>
<th>$\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.05014</td>
<td>5.5938</td>
<td>15.4</td>
<td>88.8</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.07455</td>
<td>5.7764</td>
<td>28.4</td>
<td>126.8</td>
</tr>
<tr>
<td>N-Propanol</td>
<td>0.08943</td>
<td>4.4005</td>
<td>8.1</td>
<td>165.0</td>
</tr>
<tr>
<td>N-Butanol</td>
<td>0.02339</td>
<td>5.6447</td>
<td>28.7</td>
<td>203.4</td>
</tr>
<tr>
<td>Iso-Propanol</td>
<td>0.10540</td>
<td>4.4353</td>
<td>17.0</td>
<td>164.4</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>0.06095</td>
<td>5.5199</td>
<td>13.3</td>
<td>201.9</td>
</tr>
<tr>
<td>Iso-Butanol</td>
<td>0.06925</td>
<td>5.5812</td>
<td>21.4</td>
<td>202.1</td>
</tr>
<tr>
<td>Tert-Butanol</td>
<td>0.07056</td>
<td>5.1979</td>
<td>20.4</td>
<td>201.3</td>
</tr>
</tbody>
</table>
in Table (4-7). It can be seen that the RMS deviations of B obtained are acceptable.

In this work, the parachor, \( \text{\( P \)} \), which has been shown to characterize the molecular structure (40) is regarded as one of the most promising physical constant to generalize \( b_i \) and \( g_i \). Values of parachor for alcohols are listed in Table (4-7).

As shown in Figures 8 and 9, \( b_i \) and \( g_i \) are plotted against \( \text{\( P \)} \) respectively. A weak dependence of \( b_i \) and \( g_i \) on \( \text{\( P \)} \) was found. These results need to be validated when adequate and reliable data of B are available.

For the time being, the two-parameter hydrogen-bonding correction function \( f(3) \) is used to account for the hydrogen-bonding effect of the compounds. A complete expression for the B of hydrogen-bonding polar gases then can be expressed as follows:

\[
\frac{P_{C_i} B_{ii}}{R T_{C_i}} = f(0) + \omega_i f(1) + f(2) + f(3) \tag{4.5}
\]

In Figure (4-10), the experimental and calculated values of B for ethanol were plotted against \( \frac{1}{T_{R_i}} \). It indicates that Equations (4.5) and (4.13) give good fit of the experimental values of B.

The comparison of this development with experimental data of B and those obtained by using the methods of O'Connell-Prausnitz (1967) and Tsonopoulos (1974), is discussed in Section 4.4.

4.3 Cross Second Virial Coefficients for Mixtures

The correlation developed here for the second virial coefficients of pure gases, provides a basis for calculating the
Figure 4-8 Dependence of $b_i$ on Parachor, $\phi$, for Alcohols
Figure 4-9 Dependence of $g_i$ on Parachor, $\varphi$, for Alcohols
Figure 4-10 Comparison of Experimental and Calculated Values for Ethanol (--- Experimental, —— Calculated)
second virial coefficient for polar-polar gaseous mixtures.

The only requirement for extending this correlation to mixtures is to determine suitable mixing rules. The cross second virial coefficient $B_{ij}$ has the same temperature dependence as $B_{ii}$ and $B_{jj}$ have, but the parameters to be used with the present correlation are $P_{ci,j}$, $T_{ci,j}$, $\omega_{ij}$, $a_{ij}$, $b_{ij}$, and $g_{ij}$.

There are no "universal" mixing rules, but in the absence of experimental data for a given $i$-$j$ binary mixture mixing rules similar to those suggested by Prausnitz (4) were employed in this study:

\[
T_{ci,j} = \left( \frac{T_{ci} T_{cj}}{T_{ci,j}} \right)^{1/2}
\]

\[
P_{ci,j} = \frac{4 T_{ci,j} (P_{ci} V_{ci}/T_{ci} + P_{cj} V_{cj}/T_{cj})}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3}
\]

\[
\omega_{ij} = 0.5 (\omega_i + \omega_j)
\]

\[
a_{ij} = 0.5 (a_i + a_j)
\]

\[
b_{ij} = 0.5 (b_i + b_j)
\]

\[
g_{ij} = 0.5 (g_i + g_j)
\]

The suitability of these mixing rules needs to be further examined by the experimental data of $B_{ij}$ for polar-polar binary mixtures.

4.4 Comparisons of the Proposed Correlation with Those Proposed by O'Connell and Prausnitz (4) and Tsonopoulos (3).

The correlation proposed by O'Connell and Prausnitz and
by Tsonopoulos and the correlation developed in this study were evaluated in detail to study their relative merits in predicting second virial coefficients of pure polar substances.

Values of parameters used in the O'Connell-Prausnitz correlation and the Tsonopoulos correlation are listed in Tables (4-1) and (4-8), respectively.

The three correlations evaluated here were tested against a data set comprising of 314 experimental points for 24 polar compounds listed in Table (4-1). These 24 compounds include esters, ethers, ketones, alcohols and acetaldehyde.

The results of the evaluation study were summarized in Table (4-9). For convenience in assessing the merits of each correlation for different groups of compounds, the results have been broken down into two classes, that is, non-hydrogen-bonding polar compounds and hydrogen-bonding polar compounds.

The RMS deviations and absolute average deviations between the experimental and calculated B values were employed as the basis for comparison. Although this approach is not sufficient enough for the purpose of statistical analysis, it still offers some insight about the differences among these three correlations.

In the RMS calculations, the expression used was

\[ \text{RMS} = \sqrt{\frac{\sum (B_{\text{exp.}} - B_{\text{cal.}})^2}{N}} \]  \hspace{1cm} (4.20)

instead of

\[ \text{RMS} = \sqrt{\frac{\sum (B_{\text{exp.}} - B_{\text{cal.}})^2}{(N-n)}} \]  \hspace{1cm} (4.21)

in which, n refers to number of parameters in the correlation.
Table (4-8)

VALUES OF PARAMETERS $a_{Ti}$ and $b_{Ti}$ FOR EQUATION (2.22)
USED IN THE TSONOPOULOS CORRELATION

<table>
<thead>
<tr>
<th>Substance</th>
<th>$a_{Ti}$</th>
<th>$b_{Ti}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.0878</td>
<td>0.0560</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.0878</td>
<td>0.0560</td>
</tr>
<tr>
<td>N-Propanol</td>
<td>0.0878</td>
<td>0.0447</td>
</tr>
<tr>
<td>N-Butanol</td>
<td>0.0878</td>
<td>0.0367</td>
</tr>
<tr>
<td>Iso-Propanol</td>
<td>0.0878</td>
<td>0.0537</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>0.0878</td>
<td>0.0487</td>
</tr>
<tr>
<td>Iso-Butanol</td>
<td>0.0878</td>
<td>0.0481</td>
</tr>
<tr>
<td>Tert-Butanol</td>
<td>0.0878</td>
<td>0.0508</td>
</tr>
</tbody>
</table>
Nevertheless this difference does not affect the comparison between the proposed correlation and the Tsonopoulos correlation as both correlations contain the same number of parameters. Another reason for adopting Equation (4.20) is that in some cases the number of available data points is less than the number of parameters of the generalized expression. The number of parameters used in the correlations of O'Connell and Prausnitz is larger than that of the proposed correlation. The calculated RMS deviations obtained by means of Equation (4.20) for the O'Connell and Prausnitz correlation should be less than observed by means of Equation (4.21). The RMS deviations obtained from Equation (4.20) for the O'Connell and Prausnitz correlation are generally larger than those obtained from the proposed and the Tsonopoulos correlations. Therefore, the selection of Equation (4.20) for calculating RMS deviations does not affect the conclusion of the comparison.

For non-hydrogen-bonding polar gases, the Tsonopoulos correlation is not applicable to esters, since the polarity constants ($a_T^i$) used in the correlation are only available for ethers, ketones and acetaldehyde. Likewise, the empirical parameters (association constants) used in the O'Connell-Prausnitz correlation are not available for some of the compounds shown in Table (4-1). As a result, it is not possible to have overall comparison for these three correlations. It is shown in Table (4-9) that the new correlation gives satisfactory estimations for the 16 non-hydrogen-bonding polar compounds. In prediction of $B$ for ketones, ethers, and acetaldehyde, the deviations of the new
correlation are almost the same as those of Tsonopoulos correlation. However, the O'Connell-Prausnitz correlation gives the largest deviations among the three correlations.

The experimental and calculated B values for ethyl ether and ethyl acetate were plotted in Figures (4-11) and (4-12), respectively. It is shown in Figure (4-11) that at lower temperatures, the new correlation gives better fit to the B values of ethyl ether than the other two correlations. The O'Connell-Prausnitz correlation seems to over-correct the B values in the lower temperature range. In Figure (4-12), the new correlation fits the B values of ethyl acetate excellently over the whole temperature range from \( T_{R_i} = 0.5 \) to \( T_{R_i} = 5.0 \). While the O'Connell-Prausnitz correlation only gives good fit in the range between \( T_{R_i} = 0.5 \) and \( T_{R_i} = 0.95 \). However, the discontinuity at \( T_{R_i} = 0.95 \) is because the polar correction terms in this correlation are set to zero for \( T_{R_i} > 0.95 \). The Tsonopoulos correlation is not applicable for ethyl acetate.

With respect to the available data of alcohols, the new correlation gives very accurate prediction of B. As shown in Table (4-9), the deviation of the new correlation for each alcohol falls within the experimental error range of B (i.e. \( \pm 2\% \)). However, the Tsonopoulos correlation also gives good results even though its deviations are somewhat larger than those obtained from the new correlation.

The O'Connell-Prausnitz correlation gives very poor results for alcohols, the deviations of this correlation are several
Table 4-9

COMPARISONS OF THREE CORRELATIONS WITH EXPERIMENTAL DATA FOR PURE POLAR SUBSTANCES

<table>
<thead>
<tr>
<th>Non-Hydrogen-Bonding Substance</th>
<th>THIS WORK</th>
<th>TSONOPOLOUS</th>
<th>O'CONNELL &amp; PRausNITZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RMS Deviation of B</td>
<td>RMS Deviation of B</td>
<td>RMS Deviation of B</td>
</tr>
<tr>
<td></td>
<td>Average Absolute Deviation of B</td>
<td>Average Absolute Deviation of B</td>
<td>Average Absolute Deviation of B</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>28.1</td>
<td>22.6</td>
<td>30.1</td>
</tr>
<tr>
<td>Ethyl ether</td>
<td>50.1</td>
<td>54.1</td>
<td>85.3</td>
</tr>
<tr>
<td>Aceton</td>
<td>74.3</td>
<td>47.5</td>
<td>241.1</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>71.4</td>
<td>111.7</td>
<td>105.8</td>
</tr>
<tr>
<td>Methyl n-propyl ketone</td>
<td>195.1</td>
<td>156.9</td>
<td>299.0</td>
</tr>
<tr>
<td>Methyl diisopropyl ketone</td>
<td>127.7</td>
<td>183.4</td>
<td></td>
</tr>
<tr>
<td>Diethyl ketone</td>
<td>63.5</td>
<td>13.2</td>
<td>91.4</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>34.6</td>
<td>47.8</td>
<td>33.6</td>
</tr>
<tr>
<td>Ethyl formate</td>
<td>72.1</td>
<td>44.5</td>
<td>29.4</td>
</tr>
<tr>
<td>N-propyl formate</td>
<td>59.5</td>
<td>54.1</td>
<td>24.3</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>93.7</td>
<td>44.5</td>
<td>47.7</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>14.0</td>
<td>44.5</td>
<td>38.6</td>
</tr>
<tr>
<td>N-propyl acetate</td>
<td>17.7</td>
<td>80.0</td>
<td></td>
</tr>
<tr>
<td>N-butyl acetate</td>
<td>205.5</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>Methyl propanoate</td>
<td>44.9</td>
<td>47.8</td>
<td></td>
</tr>
<tr>
<td>Ethyl propanoate</td>
<td>53.1</td>
<td>47.8</td>
<td></td>
</tr>
<tr>
<td>Hydrogen-Bonding Substance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>15.4</td>
<td>26.2</td>
<td>205.3</td>
</tr>
<tr>
<td>Ethanol</td>
<td>28.4</td>
<td>62.9</td>
<td>222.0</td>
</tr>
<tr>
<td>N-propanol</td>
<td>8.1</td>
<td>15.1</td>
<td>22.0</td>
</tr>
<tr>
<td>N-butanol</td>
<td>28.7</td>
<td>61.4</td>
<td>117.0</td>
</tr>
<tr>
<td>Iso-propanol</td>
<td>17.0</td>
<td>22.2</td>
<td>127.2</td>
</tr>
<tr>
<td>2-butanol</td>
<td>13.3</td>
<td>14.7</td>
<td>51.4</td>
</tr>
<tr>
<td>Iso-butanol</td>
<td>21.4</td>
<td>23.2</td>
<td>96.7</td>
</tr>
<tr>
<td>Tert-butanol</td>
<td>20.5</td>
<td>33.2</td>
<td>72.2</td>
</tr>
<tr>
<td>Ave.**</td>
<td>19.1</td>
<td>32.4</td>
<td>114.2</td>
</tr>
</tbody>
</table>

* Average absolute deviation = \(|\frac{\text{cal} - B_{exp}}{B_{exp}}| \times 100\%.

** Over-all average values of RMS deviations or average absolute deviations for alcohols.
Figure 4.11 Comparisons of Calculated Results Obtained from Three Correlations with Experimental Data for Ethyl Ether. (O Experimental)
Figure 4-12 Comparisons of Calculated Results Obtained from Two Correlations with Experimental Data for Ethyl Acetate. (O Experimental)
times larger than those obtained from the new correlation and the Tsonopoulos correlation. A good example of the fit of the new correlation is illustrated in Figure (4-13) for methanol - for which we have the most extensive information. For comparison, the results from the O'Connell-Prausnitz correlation and the Tsonopoulos correlation were also plotted. It is shown that the new correlation provides an excellent fit to the data over the whole temperature range, and is somewhat more accurate than the fit provided by the Tsonopoulos correlation. While, the O'Connell-Prausnitz correlation leads to serious errors. The discontinuity in the correlation at \( T_{R_i} = 0.95 \) is \(-298 \text{ cm}^3 \text{ mol}^{-1}\).

4.5 Discussion and Conclusions

The values of \( B \) for methanol were used in the development of Equations (4.12) and (4.13) for representing the contribution of the hydrogen bonding effect to the \( B \) values. This choice may not be the best as it is often found that the first compound of a homologous series may differ considerably from the general behavior of the remaining series. Further justification of the proposed expression should be made when more data for second virial coefficients become available.

The calculated values of \( B \) for methyl methacrylate by means of the proposed correlation may not be as good as desired because the correlation is a generalized one; not restricted to esters. The effect of the possible variation of \( B \) values for methyl methacrylate on the calculation of the liquid phase activity coefficients will be discussed in Chapter 6.
An empirical correlation for predicting second virial coefficients for pure polar compounds has been developed by using 314 data points of 24 polar compounds. The proposed mixing rules for estimating second virial cross coefficients need to be further examined by experimental data of $B_{ij}$ for polar-polar binary mixtures.

In general, the present method seems to be better than those proposed by O'Connell and Prausnitz and by Tsonopoulos. It offers a good framework for further improvements.
Figure 4-13 Comparisons of Calculated Results Obtained from Three Correlations with Experimental Data for Methanol. (O Experimental)
CHAPTER 5
EXPERIMENTAL DETAILS

5.1 Materials
Aldrich analyzed grade MMA, containing 65 PPM hydroquinone monomethyl ether, supplied by Aldrich Chemical Company Inc., and absolute alcohol supplied by Canadian Industrial Alcohols and Chemicals Ltd. were used without further purification. The purity of both liquids as determined by gas chromatographic analyses was estimated to be 99.9% minimum. (The analytical results are reported in Appendix I). Physical constants of these materials are given in Table (5-1). The vapor pressure data available in the literature for pure methyl methacrylate are generally not in good agreement (41). The values obtained in this work were preferred to the literature values.

5.2 Apparatus
5.2.1 Equilibrium Still
In this work, vapor-liquid equilibrium data were studied by means of a modified Dvorak and Boublik still which was originated from the family of the Gillespie still and has been described previously (1). Details of the design are shown in Figure (5-1). The still was made by pyrex glass.
The Cottrell pump (K) together with the recirculation loop ensured that equilibrium was achieved. The long
Table 5-1

PHYSICAL CONSTANTS OF PURE COMPONENT LIQUIDS

\( n^D \) refractive index of sodium light; \( \rho \) density and \( \rho^o \), vapour pressure; \( V^o \), molar volume

<table>
<thead>
<tr>
<th>Component</th>
<th>( n^D ) (298.15K)</th>
<th></th>
<th>( \rho ) (298.15)/g cm(^{-3})</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
<td>Lit.</td>
<td>Obs.</td>
<td>Lit.</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.35914</td>
<td>1.35914(^{(42)})</td>
<td>0.78523</td>
<td>0.78522(^{(44)})</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>1.41198</td>
<td>1.4120(^{(43)})</td>
<td>0.9379</td>
<td>0.9375(^{(45)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9380 (^{(46)})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>313.15K</th>
<th></th>
<th>( \rho^o ) Torr.</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Obs.</td>
<td>Lit.</td>
<td>Obs.</td>
<td>Lit.</td>
</tr>
<tr>
<td>Ethanol</td>
<td>134.37</td>
<td>134.32(^{(47)})</td>
<td>221.49</td>
<td>221.20(^{(47)})</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>75.88</td>
<td>75.2(^{(48)})</td>
<td>119.45</td>
<td>115.2 (^{(48)})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>181.91</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>( V^o ) cm(^3) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>313.15K</td>
</tr>
<tr>
<td>Ethanol</td>
<td>59.66(^{(44)})</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>108.79(^{(45)})</td>
</tr>
</tbody>
</table>
Figure 5-1 Schematic Diagram of the Modified Dvorak and Boublík Still

A boiling vessel, B liquid reservoir, C vapor and liquid separator, D evacuated chamber, E thermometer well,
F condenser, G condensate reservoir, H mixing vessel,
I cooling jacket, J heater well, K Cottrell pump
thermometer well (E) ensured good temperature measurement. Magnetic stirrers were placed in the liquid reservoir and the condensate reservoir, as stirring prevents any possible density gradient occurring in the reservoirs. The total amount of liquid required in the still is about 120 ml.

5.2.2 Accessory Equipment Used With Still

They are divided into two parts.

a) Temperature Measurement Device

Temperature measurement was made with a quartz thermometer, Hewlett-Packard Model 2801A, which was checked at the triple point of water. The accuracy in temperature measurements is estimated to be ± 0.01K at higher concentration of ethanol in the liquid, but to be ± 0.02K at lower concentration of ethanol. The difference in the estimated accuracy is due to the large change in P with x in the lower ethanol concentration region.

For isothermal operation, the desired temperatures 313.5, 322.15 and 333.15K were obtained and regulated by adjusting the total pressure of the system.

b) Pressure Measurement Device

A Texas Instrument Pressure Gauge (Type 144-01) together with a Bourdon Capsule (0 to 174 Kpa) was used to measure the pressure of the still. This gauge was calibrated by measuring the vapor pressure of demineralized and distilled water at different temperature using a Świetoslawski type ebulliometer (7), and checked by a mercury manometer in conjunction with a cathetometer. System pressure was controlled by a two-liquid monostate.
The accuracy of pressure measurement is estimated to be \( \pm 0.05 \) Torr.

5.2.3 Equipment for Quantitative Analysis

Refractometer

A Baush and Lomb Abbe-3L precision refractometer equipped with a sodium lamp was used to determine the refractive indices of the compositions of the condensed vapor and liquid samples. The calibration values and curve which were obtained by measuring the refractive indices of mixture with known composition are reported in Appendix II. The error in the determined composition is estimated to be less than \( \pm 0.002 \) mole fraction.

5.3 Experimental Procedure

5.3.1 Test of the Equilibrium Still

Before this study, a series of runs were performed on the system methanol-methyl methacrylate at 313.15, 323.15 and 333.15K, the results were in complete agreement with those of Ishikawa and Lu (41). Besides, the total vapor pressures of methanol and ethanol were measured from 303.15K to 348.15K. The results agree well with the vapor pressures calculated from the Antoine equation constants reported in the literature (47).

5.3.2 Determination of Total Pressures for the Binary Systems

a) Preparation of the Binary Liquid Mixture

For the very first run, the still was usually filled with the more volatile component, and then certain amounts of content
at both reservoirs were withdrawn and replaced by the same amount of the less volatile component for the successive runs.

b) Experimental Procedure

The boiling vessel, the liquid reservoir and the condensate reservoir were charged with the desired mixture at the beginning of each run. Pressure was adjusted manually to obtain the desired temperature in the equilibrium chamber.

The boiling of the liquid was continued for 24 hours at the desired temperature to ensure attainment of equilibrium, and then after recording the system pressure and temperature, discontinued by a sudden increase of pressure to the atmosphere. Samples of the liquid and the condensed vapor were taken and their refractive indices were measured. Equilibrium temperature was maintained within ± 0.005K for liquid solutions rich in the more volatile component, and otherwise maintained within ± 0.02K.

An attempt was made to detect the possible occurrence of polymerization of MMA throughout this work. There was no change of density of pure MMA after boiling for 5 hours, and no manifestation of haziness or turbidity was observed when the boiled monomer was subject to the solvent test of Luskin (43). In determination of vapor-liquid equilibrium data, pure ethanol was used as the initial solution in one series of runs while pure MMA in another. The results obtained from both series are in good agreement. It appears that the volatility of the shipping inhibitor is adequate for preventing the polymerization of MMA in the condensed vapor.
CHAPTER 6

RESULTS AND DISCUSSION

The experimentally determined values of \( P, T, x_i \) and \( y_i \) together with liquid phase activity coefficients \( \gamma_i^L \) evaluated from Equation (3.5) and the corresponding Gibbs free energy \( G^E \) evaluated from Equation (3.6) at each of the three temperatures studied (313.15, 323.15 and 333.15K) are listed in Table (6-1). The second virial coefficients \( (B_{11} \text{ and } B_{22}) \) and the cross second virial coefficients \( (B_{12}) \) for the ethanol - MMA system were calculated by the correlation developed in Chapter 4. At the temperatures 313.15, 323.15 and 333.15K the values obtained for \( B_{11} \) are -2116, -1662, and -1342, for \( B_{22} \), -2543, -2258, and -2021; and for \( B_{12} \), -1860, -1639, and -1456 cm\(^3\) mol\(^{-1}\), respectively.

As discussed in Chapter 4, the B values for ethanol calculated from the generalized correlation are acceptable. However, the validity of the predicted B values for methyl methacrylate cannot be directly confirmed because there is no data available in the literature. An attempt was made to estimate the possible variations of \( B_{22} \) (for MMA), and its effect on the calculation of \( \gamma_1^L \) and \( \gamma_2^L \).

The reduced temperature range of B values used to develop the proposed correlation is from 0.5 to 5.0. It was found that the deviations between the calculated and the literature results of B increase with decreasing temperature, and the maximum deviation is about 35% at \( T_{Ri} = 0.5 \). Based on this result,
calculations were made by varying the $B_{22}$ value (for MMA) at 323.15K by $\pm$ 20%, $\pm$ 40%, and $\pm$ 50%. These values were then used in Equation (3.5) to evaluate $\gamma_1^L$ and $\gamma_2^L$. The results were then compared with those obtained previously.

The variations of the $\gamma_1^L$ values are less than those of the $\gamma_2^L$ values, and the greatest variation of $\gamma_2^L$ is $\pm$ 0.44% when $B_{22}$ value is varied by $\pm$50%, but reduced to $\pm$ 0.18% when $B_{22}$ value is varied by $\pm$ 20%. On the right-hand side of Equation (3.5), the contribution of the last two terms, which contain the second virial coefficients is much less important than that of the first term. Because only the $B_{22}$ value is varied, $\gamma_1^L$ is only affected slightly by the third term, however, $\gamma_2^L$ is affected by both of the last two terms.

These calculated results indicate that even with a variation of 50% in the second virial coefficient of methyl methacrylate, the changes in the calculated $\gamma^L$ values are negligible.

The thermodynamic consistency of the data was tested by the area test of Redlich and Kister (2) as shown in Figures (6-1) to (6-3). The net area obtained is less than 1% of the total area for each of the isotherms.

The values of $\gamma_i^L$ and $G^E$ were correlated by means of the three-constant Redlich-Kister Equations (3.9), (3.10) and (3.8). The parameters $B_{12}$, $C_{12}$ and $D_{12}$ were determined by the least-squares method and the values obtained are listed below:

<table>
<thead>
<tr>
<th>Redlich-Kister Parameters</th>
<th>313.15</th>
<th>323.15</th>
<th>333.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{12}$</td>
<td>0.5273</td>
<td>0.4987</td>
<td>0.4722</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>0.0041</td>
<td>0.0098</td>
<td>0.0134</td>
</tr>
<tr>
<td>$D_{12}$</td>
<td>0.0213</td>
<td>0.0156</td>
<td>0.0108</td>
</tr>
</tbody>
</table>
To illustrate the agreement obtained, the calculated and the experimental values of \( \log \left( \frac{\gamma_1^L}{\gamma_2^L} \right) \), \( \log \gamma_1^L \), \( \log \gamma_2^L \) and \( G^E \) at three temperatures are compared in Figures (6.1) to (6.9). In addition, the calculated values of \( \gamma_1^L \), \( P \) at given \( T \) and \( x_1 \) which were obtained by means of the Newton-Raphson method are compared with the experimental values in Figures (6-10) to (6-13). In Table (6-2), the calculated values of \( \gamma_1^L \), \( P \), \( \gamma_1^L \) and \( G^E \) are listed together with the experimental values of \( x_1 \). Values of the average absolute deviations between the calculated and the experimental \( G^E \), \( \gamma_1^L \), \( \gamma_2^L \), \( \gamma \) and \( P \) are listed in Table (6-3).

An azéotrope exists in the binary mixture at the three temperatures studied. The calculated azéotropic compositions and pressures at these temperatures agree well with those values obtained graphically as shown in Table (6-4).
Table 6-1

Isothermal Vapor-Liquid Equilibrium Results for Ethanol (1) + Methyl Methacrylate (2): \( p \), Total Pressure; \( x \), Liquid Mole Fraction; \( y \), Vapor Mole Fraction; \( \gamma^L \), Activity Coefficient; and \( G^E \), Excess Gibbs Free Energy

<table>
<thead>
<tr>
<th>( P/\text{Torr.} )</th>
<th>( x_1 )</th>
<th>( y_1 )</th>
<th>( \gamma^L_1 )</th>
<th>( \gamma^L_2 )</th>
<th>( G^E/J \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>141.15</td>
<td>0.9400</td>
<td>0.9000</td>
<td>1.0051</td>
<td>3.0905</td>
<td>128.64</td>
</tr>
<tr>
<td>144.29</td>
<td>0.8898</td>
<td>0.8448</td>
<td>1.0186</td>
<td>2.6669</td>
<td>324.07</td>
</tr>
<tr>
<td>146.32</td>
<td>0.8320</td>
<td>0.7958</td>
<td>1.0405</td>
<td>2.3322</td>
<td>456.38</td>
</tr>
<tr>
<td>147.31</td>
<td>0.7598</td>
<td>0.7498</td>
<td>1.0808</td>
<td>2.0109</td>
<td>590.63</td>
</tr>
<tr>
<td>146.42</td>
<td>0.6388</td>
<td>0.6890</td>
<td>1.1746</td>
<td>1.6513</td>
<td>789.28</td>
</tr>
<tr>
<td>143.75</td>
<td>0.5243</td>
<td>0.6420</td>
<td>1.3098</td>
<td>1.4166</td>
<td>799.90</td>
</tr>
<tr>
<td>140.07</td>
<td>0.4252</td>
<td>0.6043</td>
<td>1.4822</td>
<td>1.2629</td>
<td>785.01</td>
</tr>
<tr>
<td>134.04</td>
<td>0.3931</td>
<td>0.5501</td>
<td>1.7653</td>
<td>1.1472</td>
<td>706.81</td>
</tr>
<tr>
<td>127.79</td>
<td>0.2388</td>
<td>0.5038</td>
<td>2.0112</td>
<td>1.0918</td>
<td>608.53</td>
</tr>
<tr>
<td>127.20</td>
<td>0.2338</td>
<td>0.5000</td>
<td>2.0294</td>
<td>1.0880</td>
<td>599.11</td>
</tr>
<tr>
<td>118.01</td>
<td>0.1569</td>
<td>0.4323</td>
<td>2.4290</td>
<td>1.0423</td>
<td>453.59</td>
</tr>
<tr>
<td>117.07</td>
<td>0.1524</td>
<td>0.4260</td>
<td>2.4450</td>
<td>1.0401</td>
<td>441.43</td>
</tr>
<tr>
<td>104.33</td>
<td>0.0912</td>
<td>0.3218</td>
<td>2.7557</td>
<td>1.0226</td>
<td>293.67</td>
</tr>
<tr>
<td>101.27</td>
<td>0.0793</td>
<td>0.2960</td>
<td>2.8309</td>
<td>1.0174</td>
<td>256.24</td>
</tr>
<tr>
<td>87.31</td>
<td>0.0320</td>
<td>0.1543</td>
<td>3.1597</td>
<td>1.0038</td>
<td>105.42</td>
</tr>
</tbody>
</table>

\( T = 313.15K \)

<table>
<thead>
<tr>
<th>( P/\text{Torr.} )</th>
<th>( x_1 )</th>
<th>( y_1 )</th>
<th>( \gamma^L_1 )</th>
<th>( \gamma^L_2 )</th>
<th>( G^E/J \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>230.55</td>
<td>0.9380</td>
<td>0.9068</td>
<td>1.0069</td>
<td>2.8816</td>
<td>193.54</td>
</tr>
<tr>
<td>234.51</td>
<td>0.8873</td>
<td>0.8528</td>
<td>1.0180</td>
<td>2.5440</td>
<td>325.18</td>
</tr>
<tr>
<td>236.83</td>
<td>0.8285</td>
<td>0.8070</td>
<td>1.0418</td>
<td>2.2118</td>
<td>456.90</td>
</tr>
<tr>
<td>237.38</td>
<td>0.7558</td>
<td>0.7620</td>
<td>1.0818</td>
<td>1.9204</td>
<td>587.84</td>
</tr>
<tr>
<td>235.03</td>
<td>0.6360</td>
<td>0.7028</td>
<td>1.1735</td>
<td>1.5908</td>
<td>727.51</td>
</tr>
<tr>
<td>229.83</td>
<td>0.5210</td>
<td>0.6528</td>
<td>1.3021</td>
<td>1.5811</td>
<td>785.03</td>
</tr>
<tr>
<td>223.16</td>
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<td>0.6120</td>
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<td>1.2461</td>
<td>270.25</td>
</tr>
<tr>
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<td>1.0819</td>
<td>587.14</td>
</tr>
<tr>
<td>200.68</td>
<td>0.2338</td>
<td>0.5053</td>
<td>1.9675</td>
<td>1.0762</td>
<td>576.28</td>
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<tr>
<td>184.04</td>
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<td>0.4270</td>
<td>2.3251</td>
<td>1.0363</td>
<td>429.26</td>
</tr>
<tr>
<td>159.03</td>
<td>0.0832</td>
<td>0.2970</td>
<td>2.5870</td>
<td>1.0166</td>
<td>293.03</td>
</tr>
<tr>
<td>137.48</td>
<td>0.0330</td>
<td>0.1543</td>
<td>2.9307</td>
<td>1.0045</td>
<td>107.30</td>
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\( T = 323.15K \)
<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
<th>Value 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>363.91</td>
<td>0.9360</td>
<td>0.9118</td>
<td>1.0054</td>
<td>2.7241</td>
<td>191.50</td>
</tr>
<tr>
<td>368.35</td>
<td>0.8870</td>
<td>0.8638</td>
<td>1.0171</td>
<td>2.4089</td>
<td>316.83</td>
</tr>
<tr>
<td>370.66</td>
<td>0.8252</td>
<td>0.8170</td>
<td>1.0405</td>
<td>2.1037</td>
<td>450.79</td>
</tr>
<tr>
<td>370.31</td>
<td>0.7640</td>
<td>0.7723</td>
<td>1.0756</td>
<td>1.8571</td>
<td>574.04</td>
</tr>
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<td>364.78</td>
<td>0.6335</td>
<td>0.7143</td>
<td>1.1671</td>
<td>1.5404</td>
<td>709.72</td>
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<td>0.5183</td>
<td>0.6630</td>
<td>1.2903</td>
<td>1.3404</td>
<td>762.68</td>
</tr>
<tr>
<td>343.66</td>
<td>0.4220</td>
<td>0.6200</td>
<td>1.4354</td>
<td>1.2251</td>
<td>747.49</td>
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<td>325.40</td>
<td>0.3136</td>
<td>0.5643</td>
<td>1.6677</td>
<td>1.1212</td>
<td>661.65</td>
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<td>0.5088</td>
<td>1.8903</td>
<td>1.0705</td>
<td>559.34</td>
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<td>0.5115</td>
<td>1.8882</td>
<td>1.0708</td>
<td>562.63</td>
</tr>
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<td>279.99</td>
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<td>0.4285</td>
<td>2.1980</td>
<td>1.0329</td>
<td>416.01</td>
</tr>
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<td>244.28</td>
<td>0.0872</td>
<td>0.3063</td>
<td>2.4597</td>
<td>1.0345</td>
<td>253.82</td>
</tr>
<tr>
<td>208.83</td>
<td>0.0349</td>
<td>0.1560</td>
<td>2.6840</td>
<td>1.0013</td>
<td>98.84</td>
</tr>
</tbody>
</table>
Table 6.2

CALCULATED RESULTS OF $y_1$, $P$, $\gamma^L_1$, $\gamma^L_2$ and $C^E$, TOGETHER WITH EXPERIMENTAL VALUES OF $x_1$

<table>
<thead>
<tr>
<th>P/Torr</th>
<th>$x_1$</th>
<th>$y_1$</th>
<th>$\gamma^L_1$</th>
<th>$\gamma^L_2$</th>
<th>$C^E$/J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>140.82</td>
<td>0.9400</td>
<td>0.9022</td>
<td>1.0052</td>
<td>3.0150</td>
<td>185.13</td>
</tr>
<tr>
<td>144.01</td>
<td>0.8898</td>
<td>0.8453</td>
<td>1.0172</td>
<td>2.6533</td>
<td>319.54</td>
</tr>
<tr>
<td>146.66</td>
<td>0.8320</td>
<td>0.7963</td>
<td>1.0393</td>
<td>2.3221</td>
<td>452.12</td>
</tr>
<tr>
<td>147.02</td>
<td>0.7598</td>
<td>0.7503</td>
<td>1.0794</td>
<td>2.0031</td>
<td>585.70</td>
</tr>
<tr>
<td>146.23</td>
<td>0.6388</td>
<td>0.6930</td>
<td>1.1798</td>
<td>1.6279</td>
<td>733.42</td>
</tr>
<tr>
<td>143.61</td>
<td>0.5243</td>
<td>0.6481</td>
<td>1.3209</td>
<td>1.3912</td>
<td>788.99</td>
</tr>
<tr>
<td>139.88</td>
<td>0.4252</td>
<td>0.6088</td>
<td>1.4913</td>
<td>1.2467</td>
<td>772.59</td>
</tr>
<tr>
<td>133.18</td>
<td>0.3113</td>
<td>0.5543</td>
<td>1.7672</td>
<td>1.1294</td>
<td>679.78</td>
</tr>
<tr>
<td>126.75</td>
<td>0.2388</td>
<td>0.5070</td>
<td>2.0075</td>
<td>1.0761</td>
<td>578.73</td>
</tr>
<tr>
<td>126.22</td>
<td>0.2338</td>
<td>0.5232</td>
<td>2.0265</td>
<td>1.0730</td>
<td>570.53</td>
</tr>
<tr>
<td>116.12</td>
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<td>0.4282</td>
<td>2.3678</td>
<td>1.0332</td>
<td>423.96</td>
</tr>
<tr>
<td>115.40</td>
<td>0.1524</td>
<td>0.4226</td>
<td>2.3911</td>
<td>1.0314</td>
<td>414.17</td>
</tr>
<tr>
<td>103.52</td>
<td>0.0912</td>
<td>0.3241</td>
<td>2.7533</td>
<td>1.0114</td>
<td>267.45</td>
</tr>
<tr>
<td>100.70</td>
<td>0.0793</td>
<td>0.2982</td>
<td>2.8351</td>
<td>1.0087</td>
<td>235.92</td>
</tr>
<tr>
<td>87.33</td>
<td>0.0320</td>
<td>0.1565</td>
<td>3.2048</td>
<td>1.0014</td>
<td>100.68</td>
</tr>
</tbody>
</table>

$T = 313.15K$

<table>
<thead>
<tr>
<th>P/Torr</th>
<th>$x_1$</th>
<th>$y_1$</th>
<th>$\gamma^L_1$</th>
<th>$\gamma^L_2$</th>
<th>$C^E$/J mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>229.86</td>
<td>0.9380</td>
<td>0.9080</td>
<td>1.0052</td>
<td>2.8364</td>
<td>186.84</td>
</tr>
<tr>
<td>233.87</td>
<td>0.8873</td>
<td>0.8543</td>
<td>1.0170</td>
<td>2.5114</td>
<td>319.04</td>
</tr>
<tr>
<td>236.22</td>
<td>0.8285</td>
<td>0.8067</td>
<td>1.0388</td>
<td>2.2091</td>
<td>450.00</td>
</tr>
<tr>
<td>236.86</td>
<td>0.7558</td>
<td>0.7615</td>
<td>1.0779</td>
<td>1.9181</td>
<td>579.89</td>
</tr>
<tr>
<td>234.49</td>
<td>0.6360</td>
<td>0.7047</td>
<td>1.1740</td>
<td>1.5772</td>
<td>719.82</td>
</tr>
<tr>
<td>229.32</td>
<td>0.5210</td>
<td>0.6581</td>
<td>1.3097</td>
<td>1.3571</td>
<td>770.75</td>
</tr>
<tr>
<td>222.60</td>
<td>0.4238</td>
<td>0.6175</td>
<td>1.4676</td>
<td>1.2255</td>
<td>751.82</td>
</tr>
<tr>
<td>210.90</td>
<td>0.3115</td>
<td>0.5602</td>
<td>1.7183</td>
<td>1.1182</td>
<td>659.85</td>
</tr>
<tr>
<td>199.82</td>
<td>0.2388</td>
<td>0.5098</td>
<td>1.9349</td>
<td>1.0690</td>
<td>559.96</td>
</tr>
<tr>
<td>198.92</td>
<td>0.2338</td>
<td>0.6057</td>
<td>1.9518</td>
<td>1.0661</td>
<td>551.91</td>
</tr>
<tr>
<td>181.21</td>
<td>0.1536</td>
<td>0.4225</td>
<td>2.2655</td>
<td>1.0286</td>
<td>401.75</td>
</tr>
<tr>
<td>158.18</td>
<td>0.0832</td>
<td>0.3018</td>
<td>2.6252</td>
<td>1.0085</td>
<td>236.65</td>
</tr>
<tr>
<td>137.18</td>
<td>0.0330</td>
<td>0.1552</td>
<td>2.9466</td>
<td>1.0014</td>
<td>99.36</td>
</tr>
</tbody>
</table>
Table 6-3

DEVIATIONS BETWEEN THE CALCULATED AND EXPERIMENTAL VALUES
Σ | ΔX_i | /N

<table>
<thead>
<tr>
<th>X</th>
<th>313.15K</th>
<th>323.15K</th>
<th>333.15K</th>
</tr>
</thead>
<tbody>
<tr>
<td>G_E/J mol^-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>14.8</td>
<td>11.3</td>
<td></td>
</tr>
<tr>
<td>0.0137</td>
<td>0.0129</td>
<td>0.0113</td>
<td></td>
</tr>
<tr>
<td>0.0174</td>
<td>0.0148</td>
<td>0.0122</td>
<td></td>
</tr>
<tr>
<td>0.0029</td>
<td>0.0023</td>
<td>0.0019</td>
<td></td>
</tr>
<tr>
<td>0.61</td>
<td>0.99</td>
<td>1.13</td>
<td></td>
</tr>
</tbody>
</table>

Table 6-4

AZEOTROPIC DATA FOR THE ETHANOL (1) - METHYL METHACRYLATE (2) SYSTEM

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Azeotropic Composition mole fraction of ethanol</th>
<th>Azeotropic Pressure Torr.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp.</td>
<td>calc.</td>
</tr>
<tr>
<td>313.15,</td>
<td>0.738</td>
<td>0.739</td>
</tr>
<tr>
<td>323.15,</td>
<td>0.769</td>
<td>0.769</td>
</tr>
<tr>
<td>333.15,</td>
<td>0.799</td>
<td>0.799</td>
</tr>
</tbody>
</table>
Figure 6.1 Thermodynamic Consistency Test of Vapor-Liquid Equilibrium Data for Ethanol (1) - Methyl Methacrylate (2) System at 313.15 K
Figure 6-2  Thermodynamic Consistency Test of Vapor-Liquid Equilibrium Data for Ethanol (1) - Methyl Methacrylate (2) System at 323.15K
Figure 6-3  Thermodynamic Consistency Test of Vapor-Liquid Equilibrium Data for Ethanol (1) - Methyl Methacrylate (2) System at 333.15K
Figure 6-4 Comparison of Calculated and Experimental $\gamma_i^L$ Values for Ethanol (1) - Methyl Methacrylate Methacrylate (2) System at 313.15K. (O, Experimental, - Calculated)
Figure 6-5 Comparison of Calculated and Experimental $\gamma_1^L$ Values for Ethanol (1) - Methyl Methacrylate (2). System at 323.15K. (O, Experimental; - Calculated)
Figure 6-6 Comparison of Calculated and Experimental $\gamma_i^L$ Values for Ethanol (1) - Methyl Methacrylate (2) System at 333.15K. (O, Experimental; -, Calculated)
Figure 6.7 Excess Gibbs Free Energy for Mixtures of Ethanol
(1) - Methyl Methacrylate (2) System at 313.15K.
(0, Experimental, - Calculated)
Figure 6-8 Excess Gibbs Free Energy for Mixtures of Ethanol (1) - Methyl Methacrylate (2) System at 323.15K. (0, Experimental; - Calculated)
Figure 6-9: Excess Gibbs Free Energy for Mixtures of Ethanol
(1) - Methyl Methacrylate (2) System at 333.15K.
(0, Experimental, Calculated)
Figure 6.10 Comparison of Calculated y values with Experimental Data for Ethanol (1) - Methyl Methacrylate (2) System at 313.15K. (O, Experimental, - Calculated)
Figure 6-11 Comparison of Calculated y Values with Experimental Data for Ethanol (1) - Methyl Methacrylate (2) System at 323.15K. (○, Experimental, - Calculated)
Figure 6-12 Comparison of Calculated $y$ Values with Experimental Data for Ethanol (1) - Methyl Methacrylate (2) System at 333.15K. (O, Experimental, - Calculated)
Figure 6-13 Comparison of Calculated P and y with Experimental Data for Ethanol (1) - Methyl Methacrylate (2) System at 313.15, 323.15 and 333.15K. (O, •, Experimental; - Calculated)
CHAPTER 7

CONCLUSIONS

Isothermal vapor-liquid equilibrium data measured for the ethanol-methyl methacrylate system at 313.15, 323.5 and 333.15K are thermodynamically consistent. A useful empirical correlation for the prediction of second virial coefficients for polar gases has been established and used in this study for the evaluation of the B values for ethanol and methyl methacrylate. The calculated and the experimental values of $\gamma_i^L$, $G^E$, $\gamma_i$ and $P$ are found to be in good agreement. A binary azeotrope exists at all three temperatures and its ethanol concentration increases with increasing temperature.
REFERENCES


35. Thermodynamics Research Center Data Project, Texas A&M University.


### Figure A-1 Result of a Gas Chromatographic Analysis for Determining the Purity of Ethanol

<table>
<thead>
<tr>
<th>RT</th>
<th>AREA</th>
<th>AREA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>9822</td>
<td>0.082</td>
</tr>
<tr>
<td>0.91</td>
<td>1653800000</td>
<td>99.997</td>
</tr>
<tr>
<td>4.28</td>
<td>144</td>
<td>0.008</td>
</tr>
<tr>
<td>4.48</td>
<td>423</td>
<td>0.008</td>
</tr>
<tr>
<td>4.64</td>
<td>4743</td>
<td>0.001</td>
</tr>
</tbody>
</table>

XF: 1.0000 E+0

### Figure A-2 Result of a Gas Chromatographic Analysis for Determining the Purity of MMA

<table>
<thead>
<tr>
<th>RT</th>
<th>AREA</th>
<th>AREA %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.10</td>
<td>6879</td>
<td>0.088</td>
</tr>
<tr>
<td>1.33</td>
<td>1622</td>
<td>0.008</td>
</tr>
<tr>
<td>2.55</td>
<td>24579</td>
<td>0.004</td>
</tr>
<tr>
<td>3.45</td>
<td>68900000</td>
<td>99.996</td>
</tr>
</tbody>
</table>

XF: 1.0000 E+0
APPENDIX II
### Table A-1

**CALIBRATION OF COMPOSITION - REFRACTIVE INDEX FOR SYSTEM ETHANOL (1) - MMA (2).**

<table>
<thead>
<tr>
<th>Run</th>
<th>( x_1 )</th>
<th>Refractive Index ( n^D ) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1.41194</td>
</tr>
<tr>
<td>2</td>
<td>0.0074</td>
<td>1.40945</td>
</tr>
<tr>
<td>3</td>
<td>0.1242</td>
<td>1.40807</td>
</tr>
<tr>
<td>4</td>
<td>0.2045</td>
<td>1.40532</td>
</tr>
<tr>
<td>5</td>
<td>0.3044</td>
<td>1.40159</td>
</tr>
<tr>
<td>6</td>
<td>0.4140</td>
<td>1.39708</td>
</tr>
<tr>
<td>7</td>
<td>0.5031</td>
<td>1.39301</td>
</tr>
<tr>
<td>8</td>
<td>0.6045</td>
<td>1.38778</td>
</tr>
<tr>
<td>9</td>
<td>0.7044</td>
<td>1.38207</td>
</tr>
<tr>
<td>10</td>
<td>0.8015</td>
<td>1.37566</td>
</tr>
<tr>
<td>11</td>
<td>0.8965</td>
<td>1.36836</td>
</tr>
<tr>
<td>12</td>
<td>0.9484</td>
<td>1.36442</td>
</tr>
<tr>
<td>13</td>
<td>1.000</td>
<td>1.35915</td>
</tr>
</tbody>
</table>
Figure A-3 Calibration Curve for Composition - Refractive Index for the System Ethanol (1) - MMA (2) at 298.15K
Calculation of $y_1$ and $P$

Using equation (3.5) for the two components and constants obtained from Equation (3.8), at given $T$ and $x_i$, values of $y_1$ and $P$ are calculated by means of the Newton-Raphson method of iteration (30) as described below:

For two components, we can have two non-linear equations in the form of Equation (3.5), while the relationship of $y_1 + y_2 = 1$ is introduced into Equation (3.5). Thus Equation (3.5) can be expressed for the two components as:

$$\log y_1^L = \log \frac{y_1 P}{x_1 P_0} + \frac{(B_{11} - v_1^0)(P - P_1)}{2.303 \, RT} + \frac{(1-y_1)^2 P}{2.303 \, RT} \quad (A3.1)$$

$$\log y_2^L = \log \frac{(1-y_1) P}{(1-x_1) P_0} + \frac{(B_{22} - v_2^0)(P - P_1)}{2.303 \, RT} + \frac{y_1^2 P}{2.303 \, RT} \quad (A3.2)$$

While $y_1$ and $P$ will be treated as variables.

These two equations are simplified as:

$$f_1(y_1, P) = 0 \quad (A3.3)$$

$$f_2(y_1, P) = 0 \quad (A3.4)$$

For solving functions $f_1$ and $f_2$, we may take an initial guess for a pair of $y_1$ and $P$ starting from the
experimental data say \((y_1, p_1)\) with reference to an \(x_1\) and \(T\). To set the next approximation, the following approach is established:

At \((k+1)\)th approximation, functions \(f_1(y_{k+1}, p_{k+1})\) and \(f_2(y_{k+1}, p_{k+1})\) can be expressed in terms of the functions and its derivative at \((y_k, p_k)\) by expanding a two-dimension Taylor series:

\[
f_1(y_{k+1}, p_{k+1}) = f_1(y_k, p_k) + (y_{k+1} - y_k) \frac{\partial f_1(y_k, p_k)}{\partial y_k} + (p_{k+1} - p_k) \frac{\partial f_1(y_k, p_k)}{\partial p_k} + \ldots \tag{A3.5}
\]

\[
f_2(y_{k+1}, p_{k+1}) = f_2(y_k, p_k) + (y_{k+1} - y_k) \frac{\partial f_2(y_k, p_k)}{\partial y_k} + (p_{k+1} - p_k) \frac{\partial f_2(y_k, p_k)}{\partial p_k} + \ldots \tag{A3.6}
\]

Suppose that \(y_{k+1}\) and \(p_{k+1}\) are both very close to the actual roots so that the values of \(f_1(y_{k+1}, p_{k+1})\) and \(f_2(y_{k+1}, p_{k+1})\) are almost equal to zero. Then Equations (A3-5) and (A3-6) simplify to
\[ 0 = f_1(y_k, p_k) + h \frac{\partial f_1(y_k, p_k)}{\partial y_k} + k \frac{\partial f_1(y_k, p_k)}{\partial p_k} \quad (A3.7) \]

\[ 0 = f_2(y_k, p_k) + h \frac{\partial f_2(y_k, p_k)}{\partial y_k} + k \frac{\partial f_2(y_k, p_k)}{\partial p_k} \quad (A3.8) \]

where \( h = y_{k+1} - y_k \), \( k = p_{k+1} - p_k \)

Thus, we can get the \((k+1)\)th approximation from the \(k\)th by

\[ y_{k+1} = h + y_k \quad (A3.9) \]
\[ p_{k+1} = k + p_k \quad (A3.10) \]

The values of \( h \) and \( k \) for each iteration can be obtained by solving Equations (A3.7) and (A3.8). Rearranging, we can get the simultaneous equations:

\[ h \frac{f_1(y_k, p_k)}{y_k} + k \frac{f_1(y_k, p_k)}{p_k} = -f_1(y_k, p_k) \quad (A3.11) \]
\[ h \frac{f_2(y_k, p_k)}{y_k} + k \frac{f_2(y_k, p_k)}{p_k} = -f_2(y_k, p_k) \quad (A3.12) \]

These resulting simultaneous equations can easily be solved for \( h \) and \( k \) by determinants, provided that the determinant is not zero, i.e.
\[ J = \begin{bmatrix} \frac{f_1(y_k, p_k)}{y_k} & \frac{f_1(y_k, p_k)}{p_k} \\ \frac{f_2(y_k, p_k)}{y_k} & \frac{f_2(y_k, p_k)}{p_k} \end{bmatrix} \neq 0 \quad \text{(A3.13)} \]

Hence
\[ h = \begin{bmatrix} -f_1(y_k, p_k) & \frac{\partial f_1(y_k, p_k)}{\partial y_k} \\ -f_2(y_k, p_k) & \frac{\partial f_2(y_k, p_k)}{\partial p_k} \end{bmatrix} \quad \text{(A3.14)} \]

\[ k = \begin{bmatrix} \frac{\partial f_1(y_k, p_k)}{\partial y_k} & -f_1(y_k, p_k) \\ \frac{\partial f_2(y_k, p_k)}{\partial p_k} & -f_2(y_k, p_k) \end{bmatrix} \quad \text{(A3.15)} \]

Having found \( h \) and \( k \), then we may use equations (A3.9) and (A3.10) to get the next approximation, and repeat.

Computing programme for this application is presented in Appendix VII.
DEPARTMENT OF CHEMICAL ENGINEERING
JIN-MIN YU

This program is using Golden Section Search of minimum to find optimal values of A and C in the equation \( F(2) = A + \frac{C}{T} \) which is used in the new developed correlation of second virial coefficient for the polar correction term.

Main program
This program is using experimental data of second virial coefficients and corresponding temperatures to calculate values of \( F(2) \).

```
1 IMPLICIT REAL*4(A-H,O-Z)
2 DIMENSION TC(30), FC(15), W(15), B(30), T(30), SP(30),
   * P(30), F1(30), F2(200), NJTA(15),
   * A(15), U(15), UF(15), NAME(20), PPP(30), AA(15), E2(30), S(30), TR(200)
3 DIMENSION RES(30)
4 DIMENSION AC(30)
5 DIMENSION DIF2(30)
6 DIMENSION RES(30), K(30)
7 DIMENSION K(30), A(30)
8 DIMENSION AA(30), AA1(30), AA2(30)
9 INTEGER NDATA
10 EXTERNAL F
11 TOL=1.0E-5
12 A=3.0
13 A=1.0
14 A=1.5
15 S=2.5
16 A=2.0
17 A=0.0
18 S=10.
19 S=20.
20 A=30.
21 S=30.
22 S=40.
23 S=0.0
24 A=0.0
25 S=11.
26 P=92.057
27 READ DD, BO, A2
28 PR=1.24
29 CC=6.0
30 PRINT 897, CC, DD, BO, A2
31 877 FORMAT(7/3X, CC=*, F10.4, 2X, BO=*, F20.10, 2X, A2=*)
32 READ NN
33 DII 20 I=1, NN
```
READ(5, 500) (NAME(K), K=1, 20)
600 FORMAT(20A4)
READ(NDATA(I), TC(I), PC(I), W(I))
READ(U1)
WRITE(6, 500) (NAME(K), K=1, 20)
500 FORMAT(16, TC(I), PC(I), W(I), U1)
UR(I) = C(I) * (W(I)**2) * 100000./TC(I)**2
UR(I) = C(I) * (W(I)**2) * 100000./TC(I)**2
700 FORMAT(//, 'X', 'U= ', 'F10.4', '2X', 'W= ', 'F10.4', '2X', 'U= ', 'F10.4')
SU(I) = R * TC(I) / PC(I)
N = NDATA(I)
PRINT 44, AA(I), HR(I)
44 FORMAT('//, 'X', 'AA0 = ', 'F10.6', '2X', 'AA1 = ', 'F20.10', '2X', 'AA2 = ', 'F13.6')
DO 55 K = 1, N
55 PRINT 7012, N
50 FORMAT('//, 'X', 'AAA = ', 'F20.10', '2X', 'HR = ', 'F20.10', '2X')
56 FORMAT('//, 'X', 'AAA0 = ', 'F10.6', '2X', 'AAA1 = ', 'F20.10', '2X', 'AAA2 = ', 'F13.6')
VO = 0.0
SUM = 0.0
PRINT 7012, N
DO 60 M = 1, N
60 SP(M) = (BM * PC(I)) / (2 * TC(I))
COND(M) = T(M) / TC(I)
FO(M) = 0.1645 - 0.330 / (TR(M)) - 0.1385 / (TR(M) ** 2) - 0.0121 / (TR(M) ** 3)
= -0.000607 / (TR(M) ** 8)
F1(M) = 0.0637 + 0.331 / (TR(M) ** 2) - 0.0423 / (TR(M) ** 3) - 0.006b / (TR(M) ** 8)
F2(M) = UP(M) - FO(M) - w(I) * F1(M)
TR(M) = 1. / TR(M)
PRINT 7005, T(M), TR(M), UP(M), BE(M), PCE2(M)
59 FORMAT('//, 'X', 'SF15.4')
60 TR(M) = T(K)
63 CONTINUE
70 PRINT 1, Z
71 CONTINUE
STOP
END

GOLDEN SECTION SEARCH OF MINIMUM

AN APPROXIMATION X TO THE POINT WHERE F ATTAINS A MINIMUM UN

FUNCTION FMIN(AX, BX, F, TOL, F2, TR, N)
IMPLICIT REAL*8(A-H, O-Z)
DIMENSION F2(200), TR(200)

THE INTERVAL (AX, BX) IS DETERMINED.

AX LEFT ENDPOINT OF INITIAL
UX = RIGHT ENDPONT

C IS THE SQUARED INVERSE OF THE GOLDEN RATIO

QQQQ = 5.00
C = 0.5*(3. - DSRT(QQQQ))

C EPS IS APPROXIMATELY THE SQUARE ROOT OF THE RELATIVE MACHINE
C PRECISION.

EPS = 1.00
10 EPS = EPS/2.0
TOL1 = 1.0 + EPS
IF(TOL1 GT 1.00) GO TO 10
EPS = DSRT(EPS)

C INITIALIZATION

A = AX
B = BX
V = A + C*(B - A)
W = V
X = V
E = V
FX = F(F2,TR,X,N)
FX = FX
Fw = FX

MAIN LOOP STARTS HERE

XM = 0.5*(A + B)
TUL1 = EPS*DABS(X) + TUL2/2.0
TUL2 = 2.0*TOL1

CHECK STOPPING CRITERION
IF(DABS(XM) LE. (TUL2 - 0.5*(B - A))) GO TO 90

C IS GOLDEN-SECTION NECESSARY
IF(DABS(X) LE. TOL1) GO TO 40

FIT PARABOLA
R = (XM - X)*(FX - FV)
Q = (X - V)*(FX - FW)
P = (X - V)*Q - (X - W)*R
Q = 2.000*(Q - R)
IF(Q < 0) R = 0
Q = DABS(Q)
R = E
E = 0

IS PARABOLA ACCEPTABLE
30 IF(DABS(P) GE. DABS(0.5*Q*R)) GO TO 40
IF(P LE. 0*(A - X)) GO TO 40
IF(P GE. C*(B - X)) GO TO 40

C A PARABOLIC INTERPOLATION STEP
C

109  D=P/D
110  U=X+D

C  FMUST NOT BE EVALUATED TOO CLOSE TO AX GH3X

111  IF(((U-A) *LT* TOL2) U=DSIGN(TOL1 XM-X) 112  IF((B-U) *LT* TOL2) D=DSIGN(TOL1 XM-X)

113  GO TO 50

C  GOLDEN-SECTION STEP

114  40 IF(X *GE* XM) E=A -X
115  IF(X *LT* XM) E=B -X
116  D=C*E

C  FMUST NOT BE EVALUATED TOO CLOSE TO X

117  50 IF(DABS(D) *GE* TOL1) U=X+D
118  IF(DABS(D) *LT* TOL1) U=X+DSIGN(TOL1,D)
119  FU=F(F2,TR,U,N)

C  UPDATE A,B,V,W,W AND X
120  IF(FU *GT* FX) GO TO 50

121  Q
122  IF(U *GE* X) A=X
123  IF(U *LT* X) B=X
124  V=W
125  FW=FW
126  W=X
127  FX=FX
128  U=X
129  FX=FU

130  GO TO 20

131  60 IF(U *LT* X) A=U
132  IF(U *GE* X) B=U
133  IF(FU *LE* FW) GO TO 70
134  IF(W *EQ* X) GO TO 70
135  IF(FU *LE* FW) GO TO 50
136  IF(W *EQ* X) GO TO 50
137  IF(V *EQ* W) GO TO 50

138  70 V=W
139  FW=FW
140  W=U
141  FW=FU
142  GO TO 20
143  30 V=U
144  FW=FU

145  GO TO 20

C  END OF MAIN LOOP

146  90 FMIN=X
147  RETURN
148  END

C  THIS PROGRAM IS USING LEAST-SQUARES METHOD
C  TO FIND ROOT-MEAN SQUARE DEVIATION OF
C  F(2)
FUNCTION f(F2, TR, CC, N)
IMPLICIT REAL*8(A-H, O-Z)
DIMENSION F2(200), TR(200), PP(100), SS(100), PPP(100).
* FF2(100), DIFF(200)
SUM = 0.0
SUM2 = SUM3 = 0.0
DO 66 I = 1, N
PP(I) = TR(I) ** CC
SS(I) = PP(I) ** 2
SUM = SUM + PP(I)
SUM1 = SUM1 + SS(I)
SUM2 = SUM2 + PP(I) * F2(I)
SUM3 = SUM3 + F2(I)
66 CONTINUE
COBIN = N * SUM1 - SUM ** 2
Q = SUM3 * SUM1 - SUM * SUM2
A = Q / COBIN
S = N * SUM2 - SUM3 * SUM
B = S / COBIN
A = 0.0
B = SUM3 / SUM
PRINT 55, A, B
55 FORMAT(4X, 'A=', F50.7, 'X=', B, F50.7)
SUM = 0.0
DO 666 KK = 1, N
PPP(KK) = TR(KK) ** CC
FF2(KK) = A + B * PPP(KK)
666 DIFF(KK) = (F2(KK) - FF2(KK)) ** 2
SSUM = SSSUM + DIFF(KK)
CONTINUE
F = DSQRT(SSUM / N)
Y = F
PRINT 777, Y
777 FORMAT(15X, 'Y=', F30.7)
RETURN
ENTRY
IMPLICIT REAL (A-H, O-Z)
DIMENSION TC(2), PC(2), VC(2), XX(2), AA(2), SE(2), TT(3), PP(20),
*E(20), FF(30), F12(30), F13(30), CAM1(30), CAM2(30), XJ(30),
SCAM(30), VJ(30), PJ(30), VJ(30), CAM1(30), CAM2(30), UJFF(30),
*SJFF(30), XJEN(30), CJ(30), CPT(30), B12JE(30), B13JE(30), JAP(30),
*VVI(30), VV2(30), X1(30), V1(30), PT(30), MM(30), PP(30), PP(30),
*PT(30), Cp(30), Cpt(30), CCCAM(30), CCCAM(30), YACI(30),
*PT(30).
DIMENSION U(30), VR(30)
R3D3, RNN

5 READ *, Do, Do, A2
6 P.INT A, B0, CD, DA2
7 R PRINT 'I', 'X1', 'X2', 'UD', 'F20.10', 'X2', 'A2', 'F20.10'
8 DD 11 I = 1, 2
9 READ, TC(1), PC(1), VC(1), XX(1), AA(1), SE(1)
10 READ, U(1)
11 U(I)=PC(I)*(U(I)=2.0)*1.00000/T(I)*#2
12 AA(I)=1.00000(1)+2.00000(1)+1.00000(I)
13 PRINT 2, I, (I), AA(I), BL(I)
14 2D F.INT 'I', 'X1', 'X2', 'UD', 'F10.4', 'X2', 'AA', 'F10.4, X2', 'BE', 'F10.4'
15 DD 12 I = 1, RNN
16 READ
17 READ, TT(J), PP(1), PP(2), VVI(J), VV2(J)
18 READ, YP, PPA
19 READ, VAC(1), VAC(1)
20 T=TT(J)+X(I)
21 V1=VVI(J)
22 V2=VV2(J)
23 TR=T/TC(1)
24 TV=TV/TC(1)
25 PP1=PP(1)*750.
26 PP2=PP(2)*750.
27 TC1=TC(1)
28 TC2=TC(2)
29 PC1=PC(1)
30 PC2=PC(2)
31 VC1=VC(1)
32 VC2=VC(2)
U=1=UN(1)
B=2=BC(2)
E1=E1(1)
AA2=AA(2)
AA1=AA(1)
WW2=WW(2)
WW1=WW(1)
CALL SECUN(1), TC1, TC2, FC1, FC2, WW1, WW2, AA1, AA2, 3C1, B2, VCL.

F=M2*0.057
PRINT 91
FORMAT(*'Q', 2X, 'EXPERIMENTAL KAMA')
DO 13 K=1, N
Q=AD, X1(K), Y1(K), OPT(K)
OPT(K)=OPT(K)*730.
F1(K)=Y1(K)*OPT(K)/(X1(K)*PF1).
FF1(K)=5LUG10(F1(K))
F12(K)=OPT(K)-PF1*(B1-V1)/(2.303*RT)
F13(K)=OPT(K)*5LUG((1.-Y1(K))*2)/(2.303*RT)
CAMIL(K)=FF1(K)F12(K)F13(K)
X2(K)=1.0-1(K)
Y2(K)=1.0-Y1(K)
F21(K)=Y2(K)*OPT(K)/(X2(K)*PF2)
FF2(K)=5LUG10(F21(K))
12
DO 6 M=1, N
PRINT 6, XI(K), Y1(K), CAMAL1(K), CAMAL2(K), CAMAL3(K)
6 CONTINUE
6M
PRINT 93
FORMAT(*'Q', 2X, 'CCWPAQ TERM 1, 2, 3, 1, 2, 3', 1)
DO 52 K=1, M
PRINT 64, F1(KM), F12(KM), F13(KM), FF2(KM), F22(KM), F23(KM)
54 CONTINUE
52
PRINT 17
17 FORMAT(*'CAL. CONST. OF P-K EQU. AND CAL. KAMAL')
2
DU .14 M=1, N
CAMALC1(M)=(X2(M)*2)+(B6+CC*(3*X1(M)-X2(M)))*DD*(X1(M)-X2(M))
CAMALC2(M)=(X1(M)*2)+(B6+CC*(X1(M)-X2(M)))*DD*(X1(M)-X2(M),
CAMAL(M)=CAMALC1(M)-CAMALC2(M)
CCAMAL(M)=CAMALC1(M)-CAMALC2(M)
CAMALC1(M)=1Q*X*(CAMECI(M))
CAMALC2(M)=1Q*X*(CAMALC2(M))
DIFF(M)=CAMALC1(M)-CAMALC2(M)
148 \text{SUM} = \text{SSUM} + \text{UABS(DYY)}
149 \text{SSU} = \text{SSUM} + \text{UABS(DPP)}
150 \text{SSUM} = \text{SSUM} + \text{UABS(PECEN(L))}
151 \text{SSU} = \text{SSUM} + \text{UABS(PCECEN(L))}
152 \text{PRINT} 41, 1, X1(L), Y1(L), CY1(L), PCECEN(L), PT(L), CPT(L), PCECEN1(L)
153 \text{FORMAT} (2X, 7F15.4)
154 \text{STAND} = \text{UABS(SUM)} / (\text{N}-3)
155 \text{DSTAND} = \text{DSTAND} / (\text{STAND})
156 \text{CENTA} = \text{UABS} / (\text{SSUM})
157 \text{APE} = \text{CENTA} / \text{UABS} / (\text{N}-3)
158 \text{PSTAND} = \text{STAND} / (\text{STAND})
159 \text{PPSTAND} = \text{STAND} / (\text{STAND})
160 \text{CENTAP} = \text{APE} / (\text{SSUM})
161 \text{DCENTAP} = \text{DCENTAPA}
162 \text{DCENTAPA}
163 \text{PRINT} 74
164 \text{PRINT} 79, \text{STAND}, \text{DCENTAPA}, \text{APE}
165 \text{PRINT} 79, \text{STAND}, \text{DCENTAPA}, \text{APE}
166 \text{PRINT} 54
167 \text{PRINT} 54
168 \text{PRINT} 54
169 \text{PRINT} 54
170 \text{PRINT} 54
171 \text{PRINT} 54
172 \text{PRINT} 54
173 \text{DSTAND} = \text{STAND} / (\text{N}-3)
174 \text{CENTA} = \text{UABS} / (\text{OMS} 2) / (\text{N})
175 \text{CENTA} = \text{UABS} / (\text{OMS} 2) / (\text{N})
176 \text{CENTA} = \text{UABS} / (\text{OMS} 2) / (\text{N})
177 \text{PRINT} 57, \text{X1(JJ)}, \text{DEGEC(JJ)}, \text{DEGEC(JJ)}, \text{DEGEC(JJ)}, \text{DEGEC(JJ)}
178 \text{FORMAT} (2X, 7F15.4)
179 \text{CONTINUE}
180 \text{CONTINUE}
181 \text{CONTINUE}
182 \text{CONTINUE}
183 \text{CONTINUE}
184 \text{CONTINUE}
185 \text{CONTINUE}
186 \text{CONTINUE}
187 \text{CONTINUE}
188 \text{CONTINUE}
189 \text{CONTINUE}
190 \text{CONTINUE}
191 \text{CONTINUE}
192 \text{CONTINUE}
193 \text{CONTINUE}
194 \text{CONTINUE}
195 \text{CONTINUE}
196 \text{CONTINUE}
197 \text{CONTINUE}
198 \text{CONTINUE}
199 \text{CONTINUE}
200 \text{CONTINUE}
201 \text{CONTINUE}
202 \text{CONTINUE}
203 \text{CONTINUE}
204 \text{CONTINUE}
205 \text{CONTINUE}
206 \text{CONTINUE}
207  12 CONTINUE
209   STOP
209   END

************************************************************************************************

PREDICTION OF THE SECOND VIRIAL COEFFICIENTS
BY USING THE N-2 DEVELOPED CORRELATION

SUBROUTINE SEC3N1(T,T1,T2,PC1,PC2,w1,w2,AA1,AA2,DEL)

IMPLICIT REAL*8(A-H,O-Z)
P=9.52957

HE=1.0
AI=0.02135
A2=-0.0000144
A2=5.0251
A9=0.00814
A1=-0.0022365
A2=5.33
A9=0.37455

AI=-0.0002265
A2=5.7764
FCO1=3.14455-0.33/PI1-0.1355/(TR1**2)-0.0121/(TR1**3)-0.000607/
*TR1**8
FCN1=0.5037+0.331/(TR1**2)-0.423/(TR1**3)-0.005/(TR1**8)
FC21=AA1/(TR1**6)-DE1/(TR1**8)
FC21=FC21+FG/TR1+AI1*(1/TR1-1.24)*(UEXP(A2/TR1))
TTL1=FC31+AA1+CI1+FC21

CALCULATION OF THE CROSS SECOND VIRIAL COEFFICIENTS

RR1=0.0
TT1=TC1+TC2
TTT=TC12+3.1412
TC12=TC12*(1,12)
TR12=7/7-12
VC12=VC1+VC2+VC2/TC2
VS=1.3
VC12=VC12*(5+VC2*DE2)*3
PC12=4.12PC12*VC12
AI12=(AA1+AA2)/2
AI12=(AA1+AA2)/2

PC012=0.14455-0.33/PC12-0.1355/(TR1**2)-0.0121/(TR1**3)-0.000607/

************************************************************************************************
CALCULATION OF THE SCALE-ROTATED CONSTANTS $\alpha_1, \beta_1, \cdots, \alpha_N, \beta_N$

---

```
* Calculation of the scale-rotated constants $\alpha_1, \beta_1, \cdots, \alpha_N, \beta_N$ *

250 FC=0.9537+1.31*(T12+5.412/(TR12+2.5))-0.423*(TR12**3)-0.036*(TR12**5)
251 FC12=A12/(TR12+2.5)+A12*(TR12+1.24)*DUP(A2/TR12)
252 TOL=1.25+0.612*TOL12+TOL12*FCM12
253 X12=FCM12+TOL12
254 DCM=2*(12-1)-12
255 X12=A12+DEL
256 X12=FCM12+DEL
257 RETURN END
```

---

```
** Subroutine CALSCI(NJ, X*, Y*, CAMALL, CAMALL2, 30, CC, DD) **

260 IMPLICIT REAL*8(A-H,O-Z)
261 DIMENSION A(3,4), Z1(30), Z2(30), Z3(30), X1(30), Y1(30), CAMALL(1)
262 CAMALL2(50), (20, 30), X(3)
263 A(1,1)=0.000
264 A(1,2)=0.000
265 A(1,3)=0.000
266 A(1,4)=0.000
267 A(2,1)=0.000
268 A(2,2)=0.000
269 A(2,3)=0.000
270 A(2,4)=0.000
271 A(3,1)=0.000
272 A(3,2)=0.000
273 A(3,3)=0.000
274 A(3,4)=0.000
275 DU=20**I=1, NJ
276 F(I)=CAMALL(I)**(1)-CAMALL2(I)
277 Z1(I)=CAMALL(I)**(1)
278 Z2(I)=Z1(I)*(1,-X1(I))-1.
279 Z3(I)=Z1(I)**(1,-X1(I))*(1,-X1(I))
280 A(1,4)=A(1,4)+Z1(I)**(1,-X1(I))
281 A(2,4)=A(2,4)+Z2(I)**(1,-X1(I))
282 A(3,4)=A(3,4)+Z3(I)**(1,-X1(I))
283 A(1,1)=A(1,1)+Z1(I)**(1,-X1(I))
284 A(2,1)=A(2,1)+Z2(I)**(1,-X1(I))
285 A(3,1)=A(3,1)+Z3(I)**(1,-X1(I))
286 CONTINUE
287 A(2,1)=A(2,1)+Z1(I)**(1,-X1(I))
288 A(3,1)=A(3,1)+Z2(I)**(1,-X1(I))
289 A(4,1)=A(4,1)+Z3(I)**(1,-X1(I))
290 DO 40 K=2,3
291 DO 40 J=K, I+1
292 A(J,K)=A(J,K)
293 A(J,K)=A(J,K)+Z(I)**(1,-X1(I))
294 X(J=Z(I)**(1,-X1(I))/A(J,J)
295 D0 40 J=K+1
296 J=K+1
297 RETURN
```
```
302  RAX=X(1)
303  C=Z=X(2)
304  J=Z=X(3)
305  PRINT 11
306  11 FORMAT('1', 'CONSTANT IN R-K EQU.')
307  PRINT 12: JU, CC, JD
308  12 FORMAT('JX, JF, J0, J4')
309  RETURN

CALCULATIONS OF VAPOR COMPOSITIONS
AND TOTAL Pressures BY MEANS OF
NEWTON-RAPHSON METHOD OR ITERATION

311  SUBROUTINE CALC (N,R,V,X,PO,PP,PT,X1,Y1,DEL,B2,T,CAMAC1,
*CAMAC2,CY1,CPT)
312  IMPLICIT REAL*4(A-L,Z)
313  DIMENSION R(T),X(T),Y(T),Z(J0),CAMAC1(J0),CAMAC2(J0),ZXI(J0),
*CY1(J0),CPT(J0),ZAMAC1(J0),ZAMAC2(J0),DECY1(J0),DECPT(J0)
314  19=SF, 057
315  DO 2, 250, 990
316  250 X(I)=X(I)
317  251 ZAMAC1(I)=CAMAC1(I)
318  ZAMAC2(I)=CAMAC2(I)
319  CY1(I)=Y(I)
320  CPT(I)=PT(I)
321  DO 23 J=1, 80
322  SF11=((CPT(I)-PP1)*(R1-V1))/(R*T)+(CPT(I)*DEL*((1.-CY1(I))*ZI)/
*SF11)
323  SF1=SF1-ZAMAC1(I)*ZXI(I)*PP1/(CY1(I)*CPT(I))
324  SF2=SF2-ZAMAC2(I)*ZXI(I)*PP2/(CY1(I)*CPT(I))
325  SF1=SF1-ZAMAC1(I)*ZXI(I)*PP1/(CY1(I)*CPT(I))
326  SF2=SF2-ZAMAC2(I)*ZXI(I)*PP2/(CY1(I)*CPT(I))
327  FF1=+ZCPT(I)*UL1*(1.-CY1(I))*SF1/(SF*T)+ZAMAC1(I)*ZXI(I)*PP1/
*SF11*(1.-SF11)*(1.-SF11)*SF11
328  FF2=+ZCPT(I)*UL1*(1.-CY1(I))*SF2/(SF*T)+ZAMAC2(I)*ZXI(I)*PP2/
*SF21*(1.-SF21)*(1.-SF21)*SF21
329  SF11=(1.-VL1)*(1.-CPT(I))*ZAMAC1(I)*ZXI(I)*PP1/(CPT(I)*ZI)
330  SF21=(1.-VL1)*(1.-CPT(I))*ZAMAC2(I)*ZXI(I)*PP2/(CPT(I)*ZI)
331  G2=(V2-V1)*SF1/(T*SF1)*(CPT(I)*ZI)/(T*SF21)
332  CONTINUE
333  RETURN
334  STOP
335  END

337  IF (DAHS(F1)>0.0000001.AND.DABS(F2)<.0.0000001) GO TO 22
338  IF (JU<50) G0 TO 707
339  DECAY1=CY1(I)*0.2
340  DECAY2=CPT(I)*0.2
341  IF (DAHS(DECY1(J))<0.0000001) DECY1(J)=SIGN(DECAY1, DECY1(J))
342  IF (DAHS(DECPT(J))<0.0000001) DECPT(J)=SIGN(DECAY2, DECPT(J))
343  CPT(I)=CPT(I)+DECPT(J)
344  GO TO 23
345  207 PRINT 595
346  595 FORMAT('0', 'ITERATION NO IS OUT OF RANGE')
373   " FORMAT('0',2X,F10.2,F20.2,F20.4)  \\
374      30 TO 32  \\
375      30 PRINT 31  \\
376      31 FORMAT('0'), 'ITERATION NO IS OUT OF RANGE')  \\
377      32 RETURN  \\
378      END
B VALUES OF POLAR COMPOUNDS AVAILABLE IN THE LITERATURE

<table>
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<tr>
<th>T (K)</th>
<th>B (cm³ mol⁻¹)</th>
<th>T (K)</th>
<th>B (cm³ mol⁻¹)</th>
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**Ethyl Propanoate**

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**2-Butanol**

**Methanol**

**Tert-Butanol**
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