ABSTRACT

EVALUATION OF KNOX GROUP CONTRIBUTION PARAMETERS USING QUANTUM BASED MOLECULAR AND GROUP PROPERTIES

by
Myriam Carrillo

Thermodynamic property prediction through the group contribution methods has been improving. However, the approaches considered in the past present not only limitations on the physical basis but often have restrictions as to certain substances, such as isomers. A new group contribution method is proposed that uses AIM theory, which is based on computational chemistry and quantum mechanics, to overcome these limitations by treating each molecule individually. An evaluation of this method as applied to the Knox model is proposed and analyzed for Vapor Liquid Equilibrium (VLE) of mixtures with the help of nine global parameters that are obtained by correlation.

This method is able to calculate with accuracy VLE for many systems. Both binary and ternary mixtures have been evaluated and have shown that the model can predict the behavior of the systems for several types of mixtures. The model has proved to work well with systems that have presented trouble in the past, such as isomers or polar mixtures, giving very small errors.

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by
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EVALUATION OF KNOX GROUP CONTRIBUTION PARAMETERS USING QUANTUM BASED MOLECULAR AND GROUP PROPERTIES

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To my husband and my parents
because their love is the most significant
encouragement that I have had.

A mi esposo y a mi papás
porque su amor es el mas valioso
incentivo que he tenido.

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LIST OF SYMBOLS

i,j	compounds
k,l,m	groups
q	charge of the group
μ	group dipole moment
α	polarizability
V	volume of the group
A	exposed surface area
r_{avg}	distance from center to exposed surface area
T	temperature
P_c	critical pressure
T_c	critical temperature
V_c	critical volume
T_r	reduced temperature
MW	molecular weight
R	universal gas constant
ω	acentric factor
μ_M	molecular dipole moment
μ_{Mr}	reduced dipole moment
V_{LIQ}	liquid molar volume
V_{LIQR}	reference liquid molar volume
T_{LIQR}	temperature of reference for liquid volume
P_{SAT}	vapor pressure
VPA	Antoine constants for vapor pressure
x_i	composition of the mixture
Q	canonical partition function
q_{c}	molecular partition function
N_i	number of molecules
M_k	group composition in the mixture
M_{kl}	the number of *k-l* interactions assigned to groups type *k*
M_k	group composition in the mixture
W^{ath}	combinatorial factor for an athermal mixture
Θ_I	Knox molecular surface area interaction fraction
ϕ_k	Knox volume fraction
v_k	Knox volume structural factor
Z_i	Knox area structural factor
Z_k	Knox structural contribution
Θ_k	Knox local group composition of *l* groups about *k* groups

y_{kl}	Knox group interaction fraction
ν_{ik}	multiplicity of groups
NG	number of groups
NC	number of compounds
G^E	excess molar Gibbs energy
E_{qq}	Coulombic interaction Energy
$E_{q\alpha}$	induction interaction energy caused by a charge
$E_{q\mu}$	charge-dipole interaction energy
$E_{\alpha\alpha}$	dispersion interaction energy
$E_{\mu\alpha}$	induction interaction energy caused by a dipole
$E_{\mu\mu}$	dipole-dipole interaction energy
ε_{kl}	interaction energy
u_{qq}	electric charge energy
$u_{\mu\mu}$	dipole moment energy
$u_{\alpha\alpha}$	polarizability energy
$u_{q\alpha}$	charge-polarizable energy
$u_{q\mu}$	charge-dipole energy
$u_{\mu\alpha}$	dipole- polarizable energy
$u_{q\alpha}$	charge- polarizable energy
P_A	global-energy parameter A
P_B	global-energy parameter B
P_C	global-energy parameter C
P_D	global-energy parameter D
P_F	global-energy parameter F
P_G	global-energy parameter G
P_H	global-energy parameter H
P_J	global-energy parameter J
P_K	global-structural parameter K
Φ_i	single fugacity correction
B	second virial coefficient
γ_i	activity coefficient
k_b	Boltzmann's Constant
γ_i^C	UNIFAC combinatorial contribution to the activity coefficient
γ_i^R	UNIFAC residual contribution to the activity coefficient
Φ_{Ui}	UNIFAC volume fraction
q_U	UNIFAC surface area fraction
θ_{Ui}	UNIFAC surface area fraction
λ_I	UNIFAC interchange surface area
Γ_k	UNIFAC group residual activity
Θ_{Um}	UNIFAC groups mole fraction

CHAPTER 1

INTRODUCTION

1.1 Objective

The primary objective of this research is to evaluate the thermodynamic property prediction model proposed by Knox (Knox, 1987) using a new group contribution method based on Atoms in Molecules (AIM) theory.

This research can be divided into four parts. The first part, presented in Chapter 2, introduces the basis of the Knox model theory, the UNIFAC model, and the background and steps followed to calculate the group properties that will be applied to the model. Chapter 3 describes the implementation, and is divided into two main sections; the first section shows the format in which the empirical data were collected and arranged in several tables, to facilitate the calculations and later evaluation of the results. The second section details how the model was coded into a program that not only calculates by the Knox model, but applies a regression that estimates the global parameters required to apply the new group contribution method.

Finally, the results of this research as well as a comparison with results from the UNIFAC method are presented in Chapter 4, followed by the conclusions and suggestions in Chapter 5.

1.2 Background Information

The calculation of thermodynamic properties has been a considerable help to the chemical industry, not only in the design process, but also as part of the quality control and simulation of process behavior. As is known, the estimation of such properties has been studied for decades, and in that process different methods - some more complex than others - have been established. Even though these methods have proved very useful for engineers, they present some limitations as well. These restrictions motivate the study of new approaches that allow the estimation of these properties to be more accurate utilizing fewer resources.

Acknowledging that, usually, experimental determination can be time consuming and sometimes prone to error, this research assesses a model that does not require the use of experimental data. Instead, the only tool required is a computer. This work will present a new way to use an established thermodynamic estimation property model that applies a functional group contribution method based purely on computational chemistry and quantum mechanics. The results of this evaluation will address the accuracy and usefulness of this model as well as offer new suggestions to obtain better results, and, therefore, contribute to the search for easier methods that could help the accuracy of the estimation of thermodynamic properties.

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CHAPTER 2

BACKGROUND

The Knox (Knox, 1987) and UNIFAC (Fredenslund et al. 1975) models predict thermodynamic properties for vapor-liquid equilibrium based on group-contribution methods. Although these methods have been useful in the prediction of thermodynamic properties, some disadvantages have been acknowledged. These methods are unable to distinguish between isomers because they don't consider the position of the group in the molecule. Additionally, different sets of parameters are required to calculate different properties, which make the group-contribution methods more complex, resulting in higher costs.

This research evaluates a possible solution for the Knox model based on quantum mechanics and computational chemistry that calculates the properties of atoms and groups utilizing Atoms in Molecules (AIM) theory. With these properties (dipole moment, charge, polarizability, external surface volume, area, and the distance from the center of the atom or group to its surface) the energy and structural contribution of the system are estimated with the help of nine global parameters. These are obtained by applying a nonlinear regression comparing the calculated pressures to a database containing several Vapor Liquid Equilibrium (VLE) systems. These results for the Knox model can be compared to similar results for the UNIFAC model.

In order to understand the approach of this study, Chapter 2 introduces the Knox model and the AIM theory. Additionally, some background about energy and a quick review of the UNIFAC model are presented.

2.1 Knox Model

The original Knox model (Knox et al. 1984) is based on a quasichemical expression for local composition. The model used a single energy parameter per molecular pair interaction, and one structural parameter per molecule. A later publication (Knox, 1987) proposed a group contribution version that requires one energy parameter per pair of groups and one structural parameter per each group. This work uses the Knox model with the group contribution approach, applying the AIM-properties method to evaluate the model parameters.

The development of the Knox model uses statistical thermodynamics, where the canonical partition function Q is represented by (Knox, 1987):

$$Q = \sum_{M_{kl}} W^{ath} \left[\frac{I! \prod_{k} \prod_{l} M_{kl}!}{\left(\prod_{k} \left({}^{Z_k M_k}\!/_{2} \right)! \right)^2} \right]^{-1} e^{-\sum_{k} \sum_{l} \left(\frac{M_{kl} \varepsilon_{kl}}{kT} \right)} \prod_{i} q_i N_i \qquad (2.1)$$

$M_{kl} = M_{lk}$ and is the number of *k-l* interactions assigned to groups type *k*. It must satisfy the relation:

$$\frac{Z_k M_k}{2} = \sum_l M_{kl} \tag{2.2}$$

The number of groups of type k in the mixture, M_k, is given by:

$$M_k = \sum_i N_i \nu_{ik} \tag{2.3}$$

Here, ν_{ik} is the number of groups type k in a molecule i, Z_k is the characteristic number of the interactions with other groups, and will be defined later as a structural parameter. N_i represents the number of molecules i. W^{ath} is a combinatorial factor for an athermal mixture, and q is the molecular partition function for the molecule i.

The Knox model uses the limiting case of the Guggenheim equation for athermal mixtures. The Knox expression for excess Gibbs energy (G^E) of mixing is expressed as follows (Knox et al. 1984):

$$\begin{aligned}\frac{G^E}{RT} = {} & \sum_i^{NC} x_i \ln\frac{\phi_i}{x_i} + \sum_i^{NC} \frac{z_i x_i}{2} \ln\frac{\Theta_i}{\phi_i} + \sum_i^{NC}\sum_k^{NG} \frac{Z_k x_i \nu_{ik}}{2} \ln\frac{\Theta_k}{\Theta_k^{(i)}} \\ & - \sum_i^{NC}\sum_k^{NG} \frac{Z_k x_i \nu_{ik}}{2} \ln\frac{y_{kk}}{y_{kk}^{(i)}}\end{aligned} \tag{2.4}$$

where Θ_i represents the surface area interaction fraction for component i and is given by:

$$\Theta_i = \frac{\left(z_i x_i / 2 \right)}{\sum_j^{NC} \left(z_j x_j / 2 \right)} \tag{2.5}$$

ϕ_i is the volume fraction for component i and is represented by

$$\phi_i = \frac{v_i x_i}{\sum_i^{NC} v_i x_i} \tag{2.6}$$

The structural quantities v_i and z_i are estimated by considering the volume and area of the groups respectively. Both v_i and z_i are given by the sum of the group values V_k and Z_k for all the groups in species *i*. The area quantity Z_k uses one of the global parameters P_K. Both factors need AIM group properties V_k and A_k that will be described in the next section.

Therefore, ν_i is expressed as:

$$v_i = \sum_k^{NG} \nu_{ik} * V_k \tag{2.7}$$

and z_i is given by

$$z_i = \sum_k^{NG} \nu_{ik} * Z_k \tag{2.8}$$

where Z_k is

$$Z_k = P_K * A_k \tag{2.9}$$

and ν_{ik}, as defined earlier in this section, is the multiplicity of groups; in other words, the number of times a group or atom is present in compound *i*.

The local compositions are defined as

$$y_{kl} = \frac{M_{kl}}{Z_k M_k / 2} \tag{2.10}$$

These equations relating the local composition are obtained by minimizing the free energy of the system subject to the conditions above, resulting in

$$1 = \sum_{l} y_{kl} \tag{2.11}$$

$$\theta_k y_{kl} = \theta_l y_{lk} \tag{2.12}$$

$$\frac{y_{kl} y_{lk}}{y_{kk} y_{ll}} = C_{kl} \tag{2.13}$$

The local group composition y_{kl} and the group interaction fraction Θ_k require a numerical solution for the mixture of the groups or for the pure component ($y_{kl}^{(i)}$). This numerical solution involves an iterative process as described in previews work (Knox et al. 1984; Knox, 1987), and is detailed here.

The first step is to determine the largest value of the group interaction fraction for the pure molecule $\Theta_k^{(i)}$ expressed with Equation (2.14), or for the mixture Θ_k, expressed with Equation (2.15)

$$\Theta_k^{(i)} = \frac{v_{ik} * Z_k}{\sum_{k}^{NG} v_{ik} * Z_k} \tag{2.14}$$

$$\Theta_k = \frac{X_i v_{ik} Z_k}{\sum_{k}^{NG} z_i X_i} \tag{2.15}$$

Once the group with the largest Θ, species k, is obtained, Equation (2.16) estimates the initial value for r_l,

$$r_l^{initial} = \frac{2t}{1 - t + \sqrt{(1-t)^2 - 4\beta t}} \tag{2.16}$$

where t is given by,

$$t = \frac{\Theta_l}{\Theta_k} \tag{2.17}$$

and β depends on the interchange energy C_{kl} – defined later in this section - and is expressed as:

$$\beta = \frac{C_{lk} - 1}{C_{lk}} \tag{2.18}$$

When $r_k^{initial}$ is obtained the iteration starts employing the following formula

$$r_k = \left(\frac{\Theta_l}{\Theta_k}\right) \frac{\sum_n r_n}{\sum_m \left(\frac{C_{lm}}{C_{lk} C_{mk}}\right)^{1/2} r_j} \tag{2.19}$$

$r_k^{initial}$ values are plugged into Equation (2.19). If the differences between the old and new r_k values are higher than the tolerance($1 \mathrm{x} 10^{-6}$), then the new calculated r_k values are plugged into the same equation until the limit is reached, or the maximum number of iterations exceeded. If the difference between the old and new r_k values are lower than the limit, then the r_k values are accepted and the y_{kl} values are calculated with Equation (2.20)

$$y_{kl} = \frac{r_m \left(\frac{C_{kl}}{C_{lk} C_{mk}} \right)^{1/2}}{\sum_m^{NG} r_m \left(\frac{C_{lm}}{C_{lk} C_{mk}} \right)^{1/2}} \tag{2.20}$$

for l = k this reduces to an identity.

As expressed in the Knox model (Knox et al. 1984), Equation (2.21) defines C_{kl} in relation to the interchange energy,

$$C_{kl} = \exp\left\{ \frac{-\left(2\varepsilon_{kl} - \varepsilon_{kk} - \varepsilon_{ll}\right)}{k_b T} \right\} \qquad k = l = 1,2,3 \ldots NG \tag{2.21}$$

where T is the temperature and k_B is the Boltzmann's Constant

The calculation of the energies is obtained by applying the properties of the groups and atoms calculated with AIM, using eight global parameters (P_A, P_B, P_C, P_D, P_F, P_G, P_H and P_J).

The Coulombic energy formula uses the charge q and is expressed as:

$$E_{qq} = P_A \frac{q_{(j)} * q_{(k)}}{R_{12}} \tag{2.22}$$

The contribution for the dipole moment μ is,

$$E_{\mu\mu} = P_C \frac{\mu_{(j)} \mu_{(k)}}{R_{12}{}^3} \tag{2.23}$$

the charge-dipole moment energy is calculated by,

$$E_{q\mu} = P_B \frac{q_{(j)}\mu_{(k)} + q_{(k)}\mu_{(j)}}{{R_{12}}^2} \tag{2.24}$$

the combination of the polarizability, α, and charge contribution is expressed as,

$$E_{\alpha q} = P_D \frac{q_{(j)}^2\alpha_{(k)} + q_{(k)}^2\alpha_{(j)}}{{R_{12}}^4} \tag{2.25}$$

the Polarizability-dipole moment contribution is:

$$E_{\alpha\mu} = P_F \frac{\mu_{(j)}^2\alpha_{(k)} + \mu_{(k)}^2\alpha_{(j)}}{{R_{12}}^6} \tag{2.26}$$

The contribution for polarizability is given by,

$$E_{\alpha\alpha} = P_G \frac{\alpha_{(j)} * \alpha_{(k)}}{{R_{12}}^6} \tag{2.27}$$

The combination of all the contributions formula is,

$$E_{q\mu\alpha} = P_H \frac{q_{(j)}\mu_{(j)}\alpha_{(k)} + q_{(k)}\mu_{(k)}\alpha_{(j)}}{{R_{12}}^5} \tag{2.28}$$

The repulsive contribution is expressed in terms of the orbital exponent ξ contribution and is expressed with the following equation (Arturo, 2005),

$$E_{rep} = P_J\left[\exp(-\rho_{12})\left(1+\rho_{12}+\frac{1}{3}\rho_{12}^2\right)\right]^2 \tag{2.29}$$

$$\rho_{12} = \frac{\left(\xi_{(j)}+\xi_{(k)}\right) * R_{12}}{2}$$

Where R_{12} is

$$R_{12} = r_{avg_{(j)}} + r_{avg_{(k)}} \tag{2.30}$$

$$\varepsilon_{jk} = E_{qq} + E_{\mu\alpha} + E_{\alpha\alpha} + E_{\mu\mu} + E_{q\mu} + E_{\mu\alpha} + E_{rep} \tag{2.31}$$

and where r_{avg} is the distance to the nuclei of the group. A deeper explanation of these energies is found later in this chapter.

In order to obtain the pressure of the system, the activity coefficient (γ_i) should be found. From the excess Gibbs energy, the γ_i can be expressed in terms of ϕ_I, Θ_i, ν_i, x_i, Θ_K, y_{kk} and Z_k as follows (Knox,1987):

$$\ln\gamma_i = \ln\frac{\phi_i}{x} - \left(1 - \frac{\phi_i}{x_i}\right) - \frac{z_i}{2}\left(1 - \frac{\phi_i}{\Theta_i} + \ln\frac{\phi_i}{\Theta_i}\right)$$

$$- \sum_{\mathrm{k}}^{\mathrm{NG}} \frac{\mathrm{Z_k} * \nu_{\mathrm{ik}}}{2} \ln\frac{\Theta_k}{\Theta_i^k} + \sum_{k}^{NG} \frac{Z_k \nu_{ik}}{2} \ln\frac{y_{kk}}{y_{kk}^{(i)}} \tag{2.32}$$

Once γ_i is calculated, the fugacity correction factor (Φ_i) for each component is estimated as follows (Smith et al. 2000)

$$\Phi_i = \exp\left\{\frac{\left(Bii - V_i^{liq}\right)\left(P - P_i^{sat}\right)}{RT} + \left(\frac{P}{RT}\frac{1}{2}\sum_{j}^{NC}\sum_{k}^{NC} y_j y_k \left(2\delta_{ji} - \delta_{jk}\right)\right)\right\} \tag{2.33}$$

where δ_{ji} is:

$$\delta_{ji} = 2B_{ij} - B_{ii} + B_{jj} \tag{2.34}$$

B_{ij} is the second virial coefficient and P_i^{SAT} the vapor pressure, and their calculations are shown in the next chapter.

Finally, the pressure of a VLE system is obtained by an iteration between Equations (2.33) and (2.35) (Knox, 2004)

$$y_i \Phi_i P = x_i \gamma_i P^{SAT} \tag{2.35}$$

The Knox model presented here requires nine global parameters that will be calculated by this work as well as the energy and structural properties of each molecule to be studied. An advantage over previous methods is that the molecular properties should be calculated only once and the acknowledged problems with the old group contribution methods based on binary interactions are eliminated. Furthermore, the number of parameters utilized by this method is limited and can be universally used for different types of substances.

2.2 UNIFAC Model

The Knox model was introduced as an alternative to the UNIQUAC and UNIFAC models. UNIQUAC, is based on the two-fluid theory that was also later employed by UNIFAC. Since one of the objectives of this work is to compare the Knox model results with analogous results by UNIFAC done by Kim (2005), this section makes an introduction to this model with the AIM properties functional groups treatment.

The original UNIFAC model (Fredenslund et al. 1975) is an extension of the Universal Quasi Chemical theory of liquid mixtures (UNIQUAC) combined with the functional group concept. UNIFAC activity coefficients are found using group interaction parameters. The molecular activity coefficient is divided into two contributions, the first one based on the molecular size difference, and the other on the molecular energy interaction contribution. Therefore, the activity coefficient of component *i* is given by:

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \tag{2.36}$$

where the combinatorial contribution is expressed as follows:

$$\ln \gamma_i^c = \ln \frac{\Phi_{Ui}}{x_i} + \frac{z}{2} q_U \ln \frac{\theta_{Ui}}{\Phi_{Ui}} + \lambda_i - \frac{\Phi_{Ui}}{x_i} \sum_j x_j \lambda_j \tag{2.37}$$

The volume fraction, Φ_{Ui}, is calculated by

$$\Phi_{Ui} = \frac{x_i r_i}{\sum_j x_j r_j} \tag{2.38}$$

where r_{Ui} is

$$r_{Ui} = \sum_k v_k^{(i)} V_k \tag{2.39}$$

and V_k is the volume of the group given by the AIM properties.

As for the surface area fraction, θ_{Ui}, the equations are

$$\theta_{Ui} = \frac{x_i q_{Ui}}{\sum_j x_j q_{Uj}} \tag{2.40}$$

$$q_{Ui} = \sum_k v_k^{(i)} Q_k \tag{2.41}$$

and Q_k is obtained with the area of the group from the AIM properties and a global parameter P_K,

$$Q_k = P_K * A_k \tag{2.42}$$

Finally, λ_i is given by,

$$\lambda_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \tag{2.43}$$

The residual contribution part γ_i^R requires the use of the energies and can be obtained with the following equations:

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} \left[\ln \Gamma_k - \Gamma_k^{(i)} \right] \tag{2.44}$$

where Γ_k is the group residual activity coefficient, and $\Gamma^{(i)}{}_k$ is the residual activity coefficient of group k in pure species i. Both are represented by,

$$\ln \Gamma_k = Q_k \left[\lambda - \ln \left(\sum_m \Theta_{Ui} \Psi_{mk} \right) - \sum_m \frac{\Theta_{Ui} \Psi_{km}}{\sum_n \Theta_{Un} \Psi_{nm}} \right] \tag{2.45}$$

where the area fraction of group m, Θ_{Um}, is calculated with the mole fraction of the group, X_m and Q_{Um} as follows,

$$\Theta_{Um} = \frac{Q_{Um} X_m}{\sum_n Q_{Un} X_n} \tag{2.46}$$

The group interaction parameter Ψ_{nm} is temperature dependent and is described as,

$$\Psi_{nm} = \exp \left[- \frac{\varepsilon_{mn} - \varepsilon_{nn}}{RT} \right] \tag{2.47}$$

where the energy contribution, ε_{nm}, is obtained using Equations (2.22) to (2.31).

A more detailed explanation of the application of the AIM group contribution method applied to the UNIFAC model can be found Kim (2005). Results of this research will be discussed in Chapter 4.

2.3 Energies

The energy between two molecules depends on the collection of different molecular forces. In the search for the energy contribution to the Knox model, these quantities should be estimated considering the different types of interaction contributions. This section presents a short introduction to these forces.

The electrostatic potential is given by Coulomb's relation, in which two electric charges, q_1 and q_2 that are separated by a distance r have an intermolecular energy given by

$$u_{qq} = \frac{q_1 q_2}{r^2} \tag{2.48}$$

Another electrostatic potential would occur when a particle has uneven spatial distributions between the negative electronic cloud and the positive charges of the nuclei. This particle would have a permanent dipole moment (μ), and the interaction of two such particles is given by Equation (2.49),

$$u_{\mu\mu} = \frac{\mu_1 \mu_2}{r^3}\left[2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \theta_2 \cos(\varphi_1 - \varphi_2)\right] \tag{2.49}$$

where θ and φ represent the orientations of the dipole axes.

Polarizability (α) measures how easily the electron cloud can be displaced by an external electric field. The quantum mechanical approach presented by London is given in Equation (2.50) (London, 1937)

$$u_{\alpha\alpha} = \frac{\alpha_1\alpha_2}{r^6}\left[\frac{h(v_0)_i h(v_0)_j}{h(v_0)_i + h(v_0)_j}\right] \tag{2.50}$$

where v_0 is the characteristic electronic frequency in the unexcited state. However, $h(v_0)$ is approximately equal to the first ionization potential I_i, and thus the induction energy can be represented by

$$u_{\alpha\alpha} = \frac{\alpha_1\alpha_2}{r^6}\left[\frac{I_i I_j}{I_i + I_j}\right] \tag{2.51}$$

Combinations of these energy interactions also occur. Therefore, a charge-dipole interaction is given by the following non-averaged expression:

$$u_{q\mu} = \frac{q_1\mu_2}{r^2}\cos\theta_2 \tag{2.52}$$

Induction forces between a charge and a polarizable electron cloud are expressed as

$$u_{\alpha q} = \frac{q_1^2\alpha_2}{r^4} \tag{2.53}$$

and the potential between a dipole and a polarizable electric cloud field is given by

$$u_{\mu\alpha} = \frac{\mu_1^2\alpha_2}{2r^6}\left(3\cos\theta_1 + 1\right) \tag{2.54}$$

The energy between two molecules can be found by adding all the electrostatic and charge-dipole interactions along with the dispersion and induction interactions.

The last energy contribution involves the orbital exponent (ξ) which determines the spatial extent of the wavefunction. This factor is used to minimize the system energy. The treatment of this energy contribution is developed in Hart, J. R. & Rappé, A. K. (1992) and Engkvist, O., Åstrand, P. & Karlström, G. (2000).

2.4 AIM Theory

During modern times, group contribution methods have been widely used to predict chemical properties. These group contribution methods yield properties that otherwise would be difficult to find in a variety of different physical and chemical conditions. In the field of thermodynamic property prediction, several methods have been proposed, and their results have been satisfactory. However, some difficulties and the disadvantages already mentioned indicate a need to find better methods that don't require extensive data on related systems and that adjust better to a wider variety of substances.

As was mentioned in the beginning of this chapter, the purpose of this research is to evaluate the use of AIM theory to calculate parameters for use in the group contribution models discussed in the previous sections.

AIM theory was created by Professor Richard F.W. Bader at McMaster University (Theory of Atoms in Molecules., 1995), and employs the molecule structure hypothesis in which a functional grouping of atoms have an additive and characteristic set of properties. The AIMPAK and AIM2000 software (AIMPAK, 1982; AIM2000, 1998) and related calculation methods allow the computation of these functional group properties.

The theory of atoms in molecules is based on the generalization of quantum mechanics to a subsystem of a total system, and this subsystem is bounded by surfaces with zero flux density. (Bader, R. F. W. & Becker, P., 1988). (Bader, R. F. W. & Bayles, D., 2000).

Energy and structural properties such as charge, dipole moment, polarizability, volume and surface area are obtained by AIM theory. Thus, the electron density describes the electronic charge of the atom to be studied; the dipole moment vector is given by this displacement of the negative and positive charges. The total polarizability of a molecule for AIM theory is the sum of atomic contributions, and is determined by the polarization of the atoms and by the transfer of charge between them, as caused by an externally applied field (Bader, R. F. W. & Laiding, K.E., 1990).

As for the structural parameters, the volume of the atom is measured by the intersection of an envelope of the charge density and the atomic surface of zero flux. The atomic surface is the space within which the integrations take place (Bader, R. F. W., et al. 1987).

The method to calculate these properties have been detailed by Arturo (2005). Basically, this process required that three main stages be followed.

The first stage determines the ground-state geometry of a molecule and the wavefunction by applying a rotational conformer search with multiple geometry optimizations through the Gaussian 98W package (Gaussian 98W, 1998). The initial guess is performed at a very low level and basis set using HF/6-31G method. Then, a MP2(full)/6-31++G** method that reflects a intermediate theoretical level and a moderately sized basis set is executed. The following step is to calculate the single point energy of the group at a high theory level and a large basis set (MP2(full)/AUG-cc-pvDZ). Finally, in order to calculate the polarizability, the single point energy calculations are performed three more times –one each for an electrical field applied in each direction- to determine the response of the electron density.

The second stage is to determine the functional groups to be calculated for each molecule. Arturo's work classified eight groups which are CH3, CH2, CH, C, H, N, O and F. Once the atoms are assembled into functional groups, the estimation of the properties applying AIM software –PROAIMV- (Biegler-König & Bader. 1982, Biegler-König, 2001; Biegler-König et al. 2001) will give way to the last set of calculations.

The third stage determines the energies, partial charges, volumes, and dipole moments in the ground state. Then, the software must calculate the partial charges and dipole moments under three electrical fields and different critical bond points than those used in the beginning. Subsequently, the exposed surface area, the average distance to the exposed surface area and the volume of the group are calculated using a Monte Carlo routine in which the critical points of the group and the wavefunction of the molecule are needed. Finally, the properties are estimated and tabulated.

As mentioned before, this routine calculation is applied just once on each substance treated which is an advantage over other group contribution methods. However, the processing time depends on the size of the molecule. As a result, this research will work with relatively small molecules, but it is expected that in the future faster computers will solve this limitation.

CHAPTER 3

IMPLEMENTATION

In order to study the performance of the Knox model using parameters determined from AIM properties, it was necessary, to assemble a vapor-liquid-equilibrium (VLE) database; assemble a database of the molecular and group properties of the compounds that were going to be used; create the algorithm for the Knox model and code it; apply a non linear regression utilizing the empirical database, and, finally, find the best approach to obtain the most accurate results possible with the nine global parameters. This chapter will explain each step that was followed.

3.1 Experimental Database

The first step was to select the compounds and type of data that were to be studied. Because of time limitations, no large molecules were selected, as well as no cyclic compounds due to numerical complications related to their structure. Additionally, in order to assure applicability to a wide range of compounds, molecules were selected from several different chemical groups, as indicated in Table 3.1.

Table 3.1 Chemical Categories to be Studied

Alkanes	Carboxyl Acids
Alkenes	Nitriles
Alcohols	Nitroalkanes
Ethers	Ketones
Amine	Esters
Amides	Inorganics

Once the list of compounds was narrowed, the second step was to choose the type of data that was going to be used. For this research, the data type chosen was Vapor-Liquid- Equilibrium (VLE). Binary and ternary mixtures at both high and low pressures as well as azeotropic systems were included.

The database structure was designed based on five tables that would give the most effective approach to run the model, the regression, and, finally, to analyze the results. These five tables are as follows:

1. compound properties table
2. groups AIM properties table
3. vapor pressure table
4. data table
5. references table

3.1.1 Compound Properties Table

To identify the molecule this work uses a Compound Identity Number (CID) as well as the name of the molecule. The compound properties that are reported in the tables are the critical properties, acentric factor, molecular weight, molecular dipole moment, liquid volume at a reference temperature, ITSM (a code used to classify the compound into one of six different groups according to their chemical structure and used when applying the Tsonopoulos correlation (Poling et al. 2001; Tsonopoulos & Dymond, 1997)). Finally, the CAS Registry Number (CAS_No) (CAS Registry Number, 2005). The compound properties were taken from different sources (Poling et al. 2001; Chemistry WebBook, 2003; CHERIC, 2005; Yaws, 2005). The structure of the compound properties table is shown in Table 3.2.

Table 3.2 Compound Properties Table Structure

Field Name	*Type of Field*	*Type of number*	*Description/Additional information*	*Symbol*	*Units*
CID	Text		*PGL Number*		
Name	Text		*Compound Name*		
Groups_Number	Number	Integer	*Number of Groups*	*GN*	
PC	Number	Double	*Critical Pressure*	P_C	Bar
TC	Number	Double	*Critical Temperature*	T_C	K
VC	Number	Double	*Critical Volume*	V_C	$\frac{cc}{mol}$
MW	Number	Double	*Molecular Weight*	*MW*	
Omega	Number	Double	*Acentric Factor*	ω	
DP	Number	Double	*Molecular Dipole Moment*	μ_M	
VLIQ	Number	Double	*Liquid Volume at Tref*	V_{LIQR}	$\frac{cc}{mol}$
VLIQR	Number	Double	*Tref(Reference Temperature)*	T_{LIQR}	K
ITSM	Number	Integer	*for Tsonopoulos correlation*		
System_ Numbers	Number	Integer	*Number of Systems tha use this compoundt*		
CAS_No	Text				
Chemical Group	Text				
Comments	Text				

3.1.2 Group AIM Properties Table

The group AIM properties table reports the different energy contributions per group. The values of these properties are taken from Arturo (2005). The structure for this table is given by Table 3.3 and contains the CID, the degeneracy, or multiplicity of the groups, the charge (q) for the group, its dipole moment (μ), polarizability (α), volume (V), surface area (A), and distance from the nuclei (r_{avg}), and the orbital exponent. The information to identify the type of group is displayed in the field group_name, and, finally, to recognize the molecule the name of the compound is also reported.

Table 3.3 Group AIM Properties Table Structure

Field Name	*Type of Field*	*Type of number*	*Description/Additional information*	*Symbol*	*Units*
CID	Text		*PGL Number*		
degeneracy	Number	Integer	*multiplicity of groups*	ν_{ik}	Atomic units
Q	Number	Double	*Charge of the group (Z-N)*	q	Atomic units
Mu	Number	Double	*Magnitude Dipole Moment*	μ	Atomic units
Aa	Number	Double	*Polarizability*	α	Atomic units
V	Number	Double	*Volume of the group*	V	Atomic units
A	Number	Double	*Exposed Surface Area*	A	Atomic units
Ravg	Number	Double	*Distance from center to exposed Surface Area*	r_{avg}	Atomic units
xiSTO	Number	Double	*Orbital exponent*	ξ	Atomic units
Compound Name	Text				
GroupName	Text		*e.g. methyl*		

3.1.3 Vapor Pressure Table

The program will calculate the vapor pressure using the different correlations taken from the literature (Poling et al. 2001; Chemistry WebBook; 2003, CHERIC, 2005). Depending on the working temperature, the program will apply different equations and report it in the experimental data table. The vapor pressure table is presented in Table **3.4**.

Table 3.4 Vapor Pressure Table Structure

Field Name	*Type of Field*	*Type of number*	*Description/Additional information*	*Symbol*	*Units*
CID	Text		*PGL Number*		
VP_{eqn}	Number	Integer	*Specifies Equation to be used for VP*		
VP1	Number	Double	*Vapor Pressure Constants*	*VP1*	
VP2	Number	Double	*Vapor Pressure Constants*	*VP2*	
VP3	Number	Double	*Vapor Pressure Constants*	*VP3*	
VP4	Number	Double	*Vapor Pressure Constants*	*VP4*	
VP5	Number	Double	*Vapor Pressure Constants*	*VP5*	
VP6	Number	Double	*Vapor Pressure Constants*	*VP6*	
VP7	Number	Double	*Vapor Pressure Constants*	*VP7*	
VP8	Number	Double	*Vapor Pressure Constants*	*VP8*	
Tmin	Number	Double	*Minimum Temperature for the equation*		K
Tmax	Number	Double	*Maximum Temperature for the equation*		K
Pmin	Number	Double	*Minimum Pressure for the equation*		Bar
Pmax	Number	Double	*Maximum Pressure for the equation*		Bar

3.1.4 Empirical Data and References Tables

All of the data for all the systems have been put together in a single table to allow the regression to use all of the datapoints for the various systems, so that the global parameters will adjust better to all kinds of systems. The table was made assuming that all systems have three compounds; if it is a binary system, the third component column is empty. The composition is reported just for the first component if it is a binary system, and if it is a ternary system a second composition will be specified. The number of components is also given in this table.

Temperature and pressure are reported as in the original article and converted to the units used by the program. The program calculates the vapor pressure according to the appropriate correlation. The structure of the experimental data table is reported in

Table 3.5. An additional field is added in this table to report the article by the reference number. This number leads to another table that presents all the information about the source article. Table 3.6 shows the structure of this last table of the data base.

Table 3.5 Experimental Data Table Structure

Field Name	*Type of Field*	*Number*	*Description/Additional information*	*Symbol*	*Units*
CID1	Text				
Name1	Text				
CID2	Text				
Name2	Text				
CID3	Text				
Name3	Text				
T	Number	Double	*Temperature of the System*	T	K
P	Number	Double	*Pressure of the system*	P	KPa
X1	Number	Double	*composition Compound1*	X_1	
X2	Number	Double	*If a binary system, this field should be empty. Always an X must be calculated (i.e. binary: X2 = 1-X1, ternary: X3 = 1-X1-X2)*	X_2	
PSAT1	Number	Double	*If not given in the article, the field is empty and then has to be calculated using Vapor_Pressure Constants in the Vapor Pressue table*	P_1^{SAT}	KPa
PSAT2				P_2^{SAT}	KPa
PSAT3				P_3^{SAT}	KPa
Torig	Number	Double	*Temperature given in its original units*		
TUnits			*Units of the original Temperature*		
Porig	Number	Double	*Pressure given in its original units*		
PUnits			*Units of the original Pressure*		
CompoundsNo.	Number	Integer	*Number of compounds involved.*	*NC*	
ReferenceNo.	Number	Integer	*Number of the reference*		
VPeqn1	Number	Integer	*Equation to be used to calculate PSAT1*	*VPeqn1*	
VPeqn2	Number	Integer	*Equation to be used to calculate PSAT2*	*VPeqn2*	
VPeqn3	Number	Integer	*Equation to be used to calculate PSAT3*	*VPeqn3*	

Table 3.6 References Table Structure

Field Name	*Type of Field*	*Type of number*	*Description/Additional information*
ReferenceNumber	Text		
Reference	Text		
Title	Text		
Authors	Text		
Year	Text		
Publication	Text		
Volume	Number		
Pages	Text		
SystemsNumber	Number	Integer	*number of systems in the article*

These five tables will interact. This and the procedure to find the pressure and the nine global parameters will be explained in the next section where the code is detailed.

3.2 Code Description

The code is divided into three main parts. The first reads the tables, uploads the information to the computers memory and calculates the properties required for the models such as vapor pressures of the pure systems, liquid molar volumes, and the second virial coefficients. The second calculates the structural parameters with the conditions and properties given in the tables, based on the Knox model and the AIM properties. Finally, the third part computes the pressure according to the Knox model by applying the approach described in Chapter 2. The programming language was VBA (Visual Basic for Applications) through Microsoft Excel Macros. The structure of the program is detailed as follows.

3.2.1 Read Database

The steps to read the database are as follows:

1. Read the experimental data table row by row
2. Read the number of compounds
3. For each compound, read its properties from the compounds properties table
4. From the Group AIM Properties Table read the AIM properties
5. Calculate the liquid molar volumes with the following formula (Poling et al. 2001):

$$XV_{LIQ} = \left(1 - \frac{T}{Tc(i)}\right)^{2/7} - \left(1 - \frac{\mathrm{T_{LIQR}\,(I)}}{Tc(i)}\right)^{2/7} \tag{3.1}$$

$$V_{LIQ}(i) = V_{LIQR}(i) + (0.29056 - 0.8775 * \omega(i))^{XV_{LIQ}}$$

6. The program will estimate the vapor pressures P_{SAT} from the vapor pressure constants using the appropriate correlation according to the working temperature and the ranges reported in the sources. The equations applied are as follows:

   a) Vapor Pressure Equation 1 (Poling et al. 2001):

$$P_{(i)}^{SAT} = 10^{VP1(i) - {}^{VP2(i)}\!/_{T} + VP3(i) - 273.15} \tag{3.2}$$

   b) Vapor Pressure Equation 2 (Poling et al. 2001):

$$X_{VP} = \frac{T - VP5(i) - 273.15}{VP4(i)}$$

$$VP_{\log} = \frac{VP1_{(i)} - VP2_{(i)}}{T + VP3_{(i)} - 273.15} + 0.43439 * \left(X_{VP}\right)^{VP6(i)}$$

$$+ VP7_{(i)} * \left(X_{VP}\right)^{8} + VP8_{(i)} * \left(X_{VP}\right)^{12}$$

$$P_{(i)}^{SAT} = 10^{VP_{\log}} \tag{3.3}$$

c) Vapor Pressure Equation 3 (Poling et al. 2001):

$$X_{VP} = 1 - T / VP(i)$$

$$Y_{VP} = VP2(i) * X_{VP}$$

$$+ VP3(i) * X_{VP} * \sqrt{X_{VP}} + VP4(i) * X_{VP}{}^{2} * \sqrt{X_{VP}} + VP5(i) * X_{VP}{}^{5}$$

$$P_{(i)}^{SAT} = e^{\ln(VP6(i)) + \frac{VP1(i)}{T} * Y_{VP}} \tag{3.4}$$

d) Vapor Pressure Equation 4 (CHERIC, 2005):

$$P_{(i)}^{SAT} = VP1(i) * Ln(T) + \frac{VP2}{T} + VP3 + VP4 * T^{2} \tag{3.5}$$

e) Vapor Pressure Equation 5 (Chemistry WebBook, 2003):

$$PS_{(i)}^{SAT} = 10^{VP1(i) - VP2(i) / T + VP3(i)} \tag{3.6}$$

f) Vapor Pressure Equation 6 (Yaws, Carl L., 2003):

$$X_{VP} = A + \frac{B}{T} + C * \log_{10}(T) + D * T + E * T^{2}$$

$$PS_{(i)}^{SAT} = \frac{10^{X_{VP}}}{760} \tag{3.7}$$

7. Calculate the virial coefficient for each component by applying the Tsonopoulos correlation (Poling et al. 2001; Tsonopoulos & Dymond,1997). For a pure component the second virial coefficient is calculated by applying equation (3.8)

$$BVIR(i,i) = \frac{(F0 + W_{(i)} * F1 + TSA_{(i)} * F2 + TSB_{(i)} * F3) * 83.14 * T_{C(i)}}{P_{C(i)}} \tag{3.8}$$

where $TSA_{(i)}$ and $TSB_{(i)}$ depend on the type of substance treated.

Table 3.7 Calculations of $TSA_{(i)}$ and $TSB_{(i)}$ for the Second Virial Coefficient*

Type Number (ITSM)	***Type of Substance***	***$TSA_{(i)}$***	***$TSB_{(i)}$***
1	Simple, normal (nonpolars)	$TSA_{(i)} = 0$	$TSB_{(i)} = 0$
2	Ketones, Aldehydes, Alkyl Nitriles, Ethers, Carboxylic acid, Esters.	$TSA_{(i)} = -2.14*10^{-4} * \mu_{M,r} - 4.308*10^{-21} * (\mu_{M,r})^8$	$TSB_{(i)} = 0$
3	Alkyl halides, Mercaptans, Sulfides, Disulfides	$TSA_{(i)} = -2.1188*10^{-4} * (\mu_{M,r})^4 - 7.831*10^{-21} * (\mu_{M,r})^8$	
4	1-Alkanols	$TSA_{(i)} = 0.0878$	$TSB_{(i)} = 0.00908 + 0.0006957 * \mu_{M,r}$
5	Methanol	$TSA_{(i)} = 0.0878$	$TSB_{(i)} = 0.0525$
6	Water	$TSA_{(i)} = -0.0109$	$TSB_{(i)} = 0$

*Tsonopoulos C., & Dymond, J.,(1997)

Where $\mu_{M,r}$ is the molecular reduced dipole moment and T_r is the reduced temperature, expressed by equation (3.9) and (3.10) respectively.

$$\mu_{M,r} = 100000 * \mu_{M,r(i)} * \mu_{M,r(i)} * \frac{P_{C(i)} / 1.01325}{T_{C(i)}^{2}} \tag{3.9}$$

$$T_r = \frac{T}{T_{c(i)}} \tag{3.10}$$

Finally *F0*, *F1*, *F2* and *F3* are given by the following formulas

$$F0 = 0.1445 - \frac{0.33}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \tag{3.11}$$

$$F1 = 0.637 - \frac{0.331}{TR^2} - \frac{0.423}{TR^3} - \frac{0.008}{TR^8} \tag{3.12}$$

$$F2 = \frac{1.0}{TR^6} \tag{3.13}$$

$$F3 = -\frac{1.0}{TR^8} \tag{3.14}$$

The approach for the second virial coefficient for the mixture is slightly different. The pseudo critical temperature for the unlike pair of molecules is calculated by Equation (3.15) where TK_{IJ} also depends on the type of the pair of substances. Using the type shown in Table 3.7 , TK_{IJ} can be obtained with **Table 3.8**.

$$T_{c_{ij}} = \left(T_{C(i)} + T_{C(j)}\right)^{1/2} * (1 - TK_{ij}) \tag{3.15}$$

Table 3.8 Calculation of *TKIJ*

Type pair	**TKIJ**
5-6, 6-5	$TK_{IJ} = 0$
1-2, 2-1, 1-3, 3-1, 2-4, 4-2, 2-5, 5-2, 3-4, 4-3, 3-5, 5-3, 4-6, 6-4	$TK_{IJ} = 0.1$
1-4, 4-1, 1-5, 5-1	$TK_{IJ} = 0.15$
2-6, 6-2, 3-6, 6-3	$TK_{IJ} = 0.35$
1-6, 6-1	$TK_{IJ} = 036114 - \frac{2.135}{V_c^{0.5}}$
Other pairs don't mention above	$TK_{IJ} = 1 - \left(\frac{2 * \left(V_{c(i)} * V_{c(j)} \right)^{1/6}}{V_{c(i)}^{1/3} * V_{c(j)}^{1/3}} \right)^3$

Finally, B_V for a pair of compounds is computed with

$$B_V(i, j) = \left(F0 + W(i) + F1 + TSAIJ * F2 + TSBIJ * F3 \right) * RPT \tag{3.16}$$

where F0, F1, F2 and F3 use Equations (3.11) to (3.14), and TSAIJ and TSBIJ are given by

$$TSAIJ = 0.5 * \left(TSA_{(i)} + TSA_{(j)} \right) \tag{3.17}$$

$$TSBIJ = 0.5 * \left(TSB_{(i)} + TSB_{(j)} \right) \tag{3.18}$$

And RTP equation is as follows:

$$RTP = 83.14 * \frac{(Vc(i)^{1/3} + Vc(j)^{1/3})}{4 * \left(\frac{Pc(i) * Vc(i)}{Tc(i)} + \frac{Pc(j) * Vc(j)}{Tc(j)} \right)} \tag{3.19}$$

The steps from 1 to 4 will be shown in

Figure 3.1, and steps 5 to 7 in Figure 3.2.

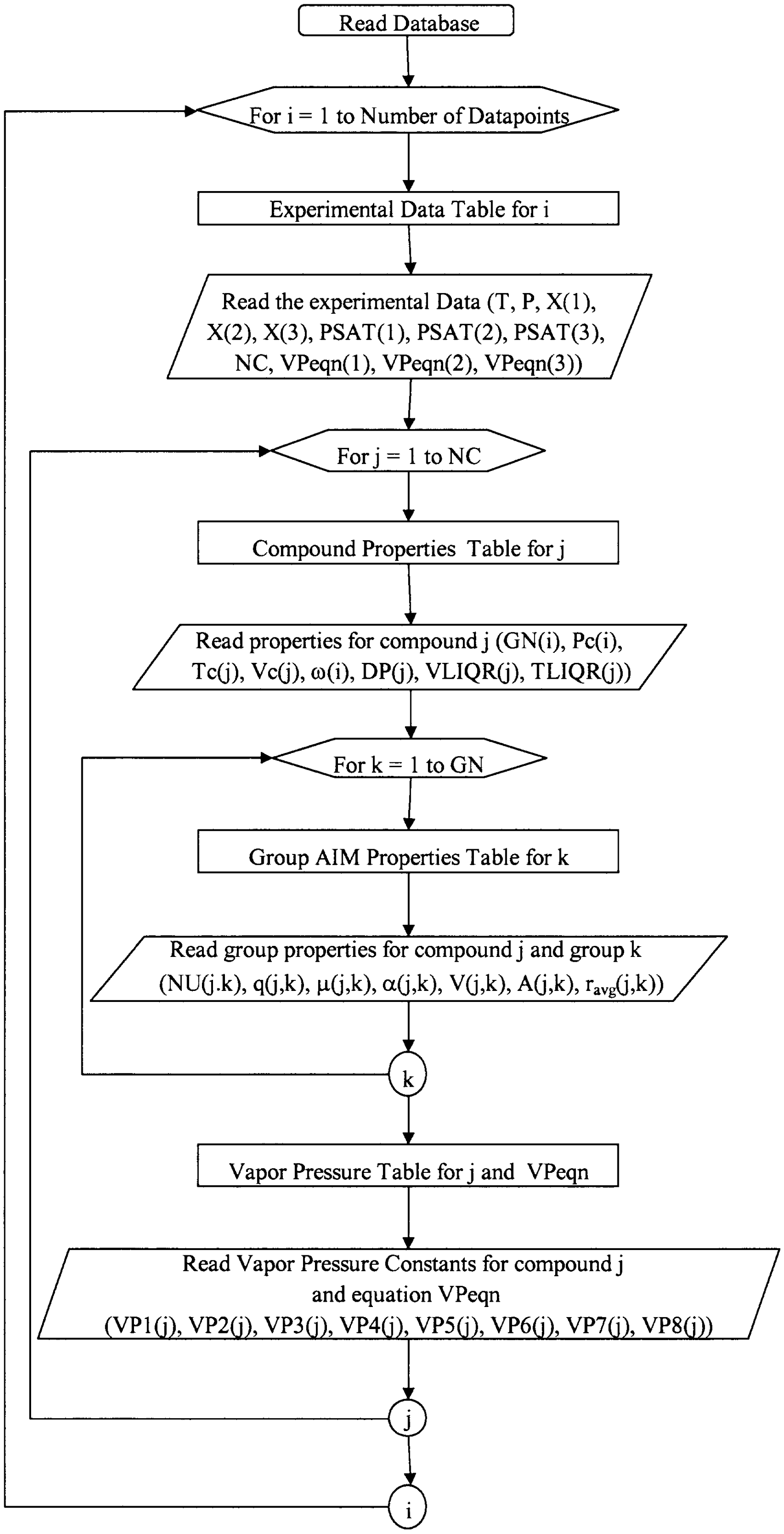


Figure 3.1 Read database.

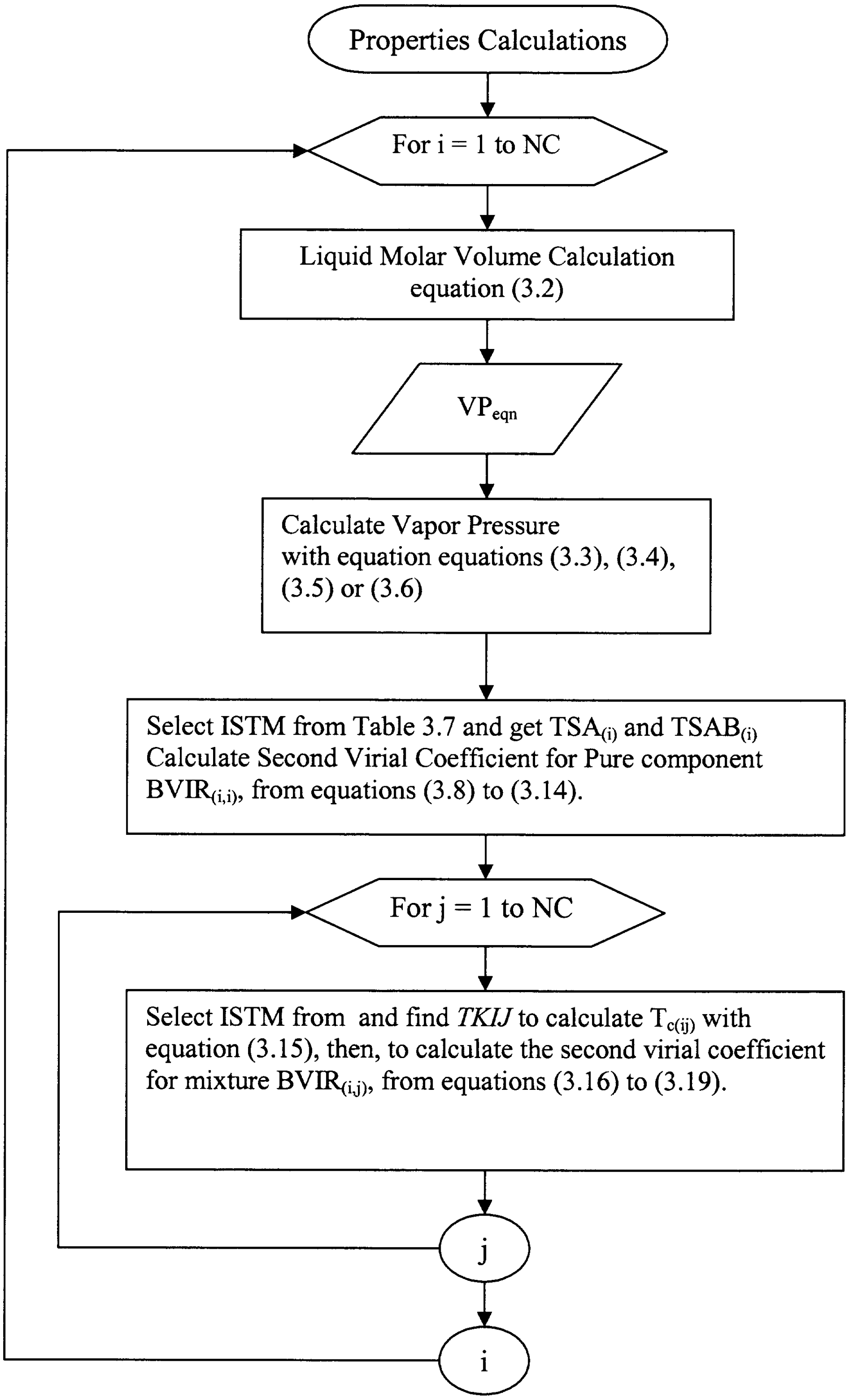
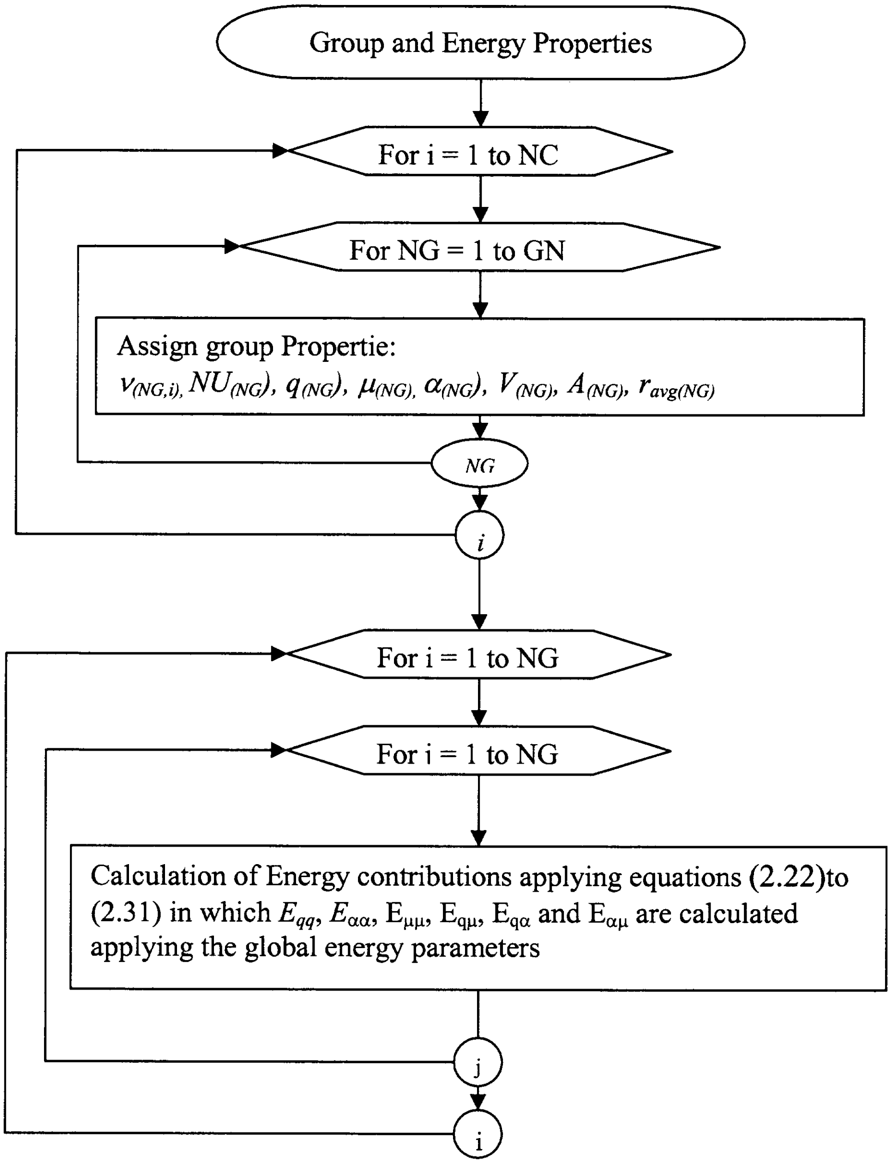


Figure 3.2 Calculation of liquid molar volume and vapor pressure for component *i* and second virial coefficient.

3.2.2 Apply the AIM Properties to Knox Model

The second part of the code utilizes the AIM properties to evaluate the group parameters that are needed for the Knox Model. The basic steps are described as follows:

1. The first step is to get the AIM properties for each of the groups in the system, and then, with these properties, the energies are calculated using the global parameter values that are being fit (Figure 3.3)
2. The next step calculates the group quantities Z_k, and C_{ij} with the properties previously obtained. This step is shown in Figure 3.4.
3. The last step in this section is the calculation of the structural parameters v_i, and z_i required for Knox Model, and this step is also described in Figure 3.4.



/Figure 3.3 Group properties and calculation of group energies.

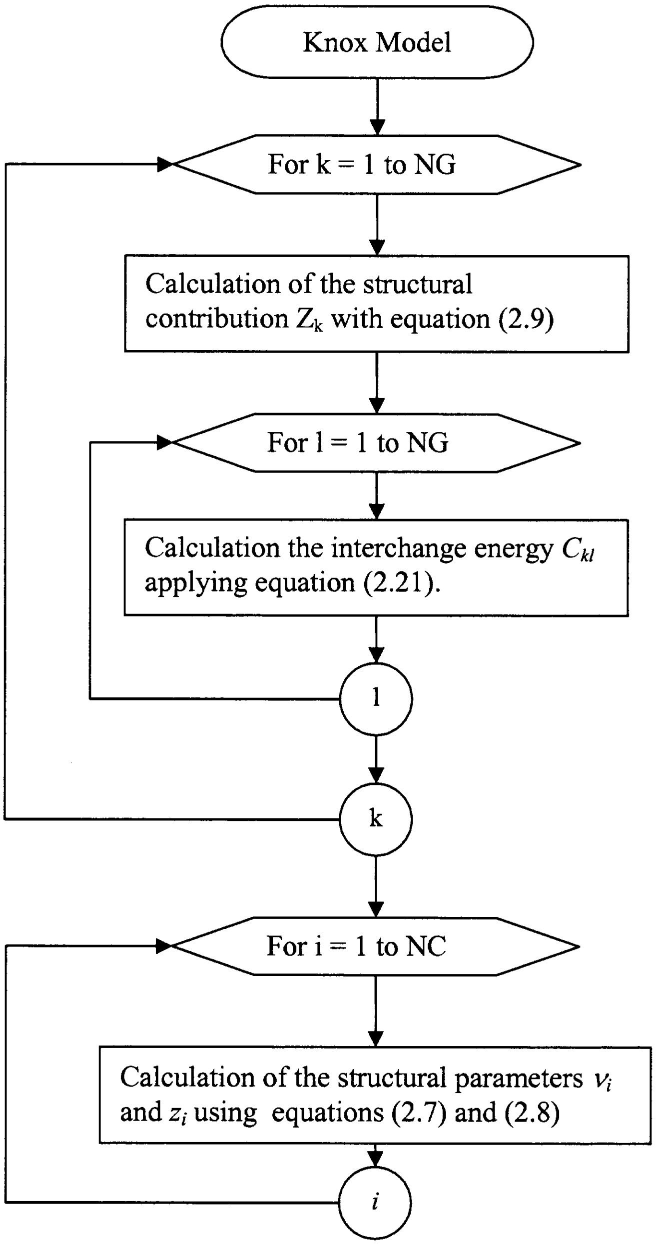


Figure 3.4 Calculation of the structural parameters and interchange energy for Knox model.

3.2.3 Pressure Calculation According to Knox Model

The pressure calculation requires the iteration mentioned in Chapter 2, in which the group compositions y_{ki} are obtained. This iteration is called XSOLVE and is shown in Figure 3.5. Finally, applying all the previous calculations **Figure 3.6** shows the steps to follow to calculate the pressure, for one datapoint.

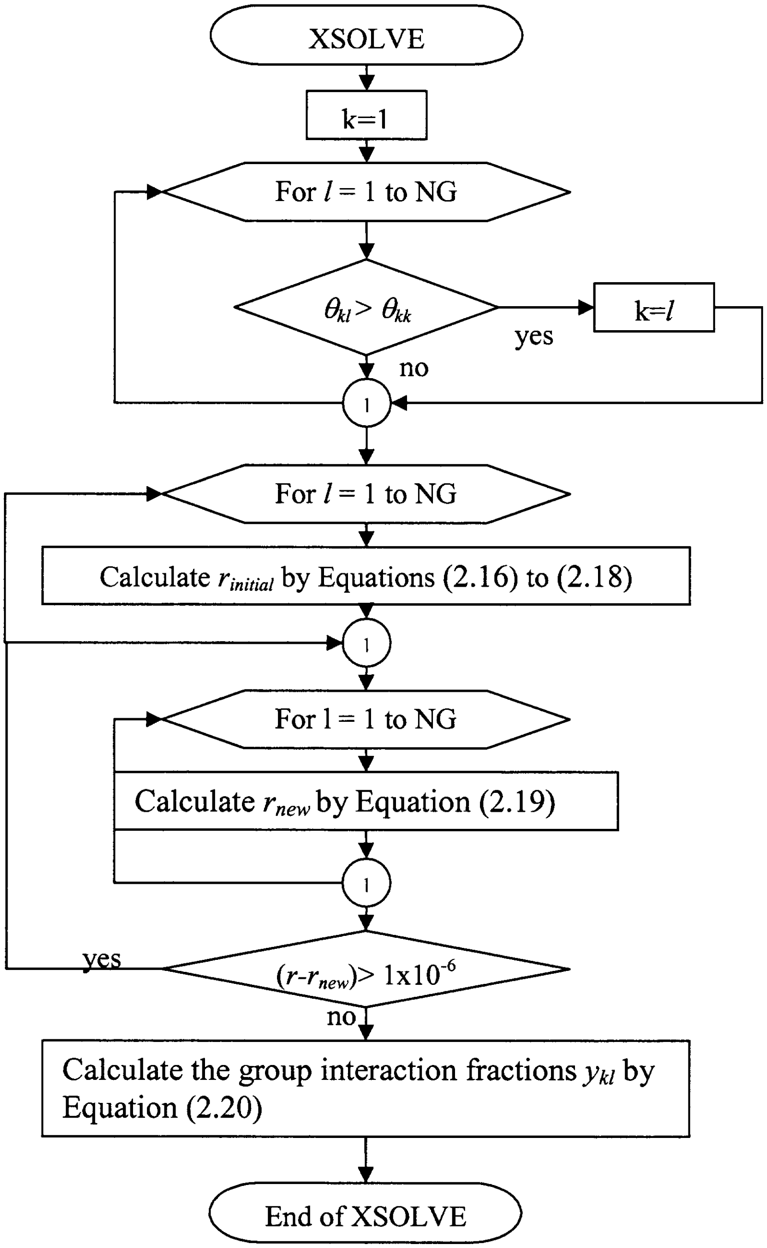


Figure 3.5 XSOLVE subroutine to calculate the group interaction fraction y_{kl}.

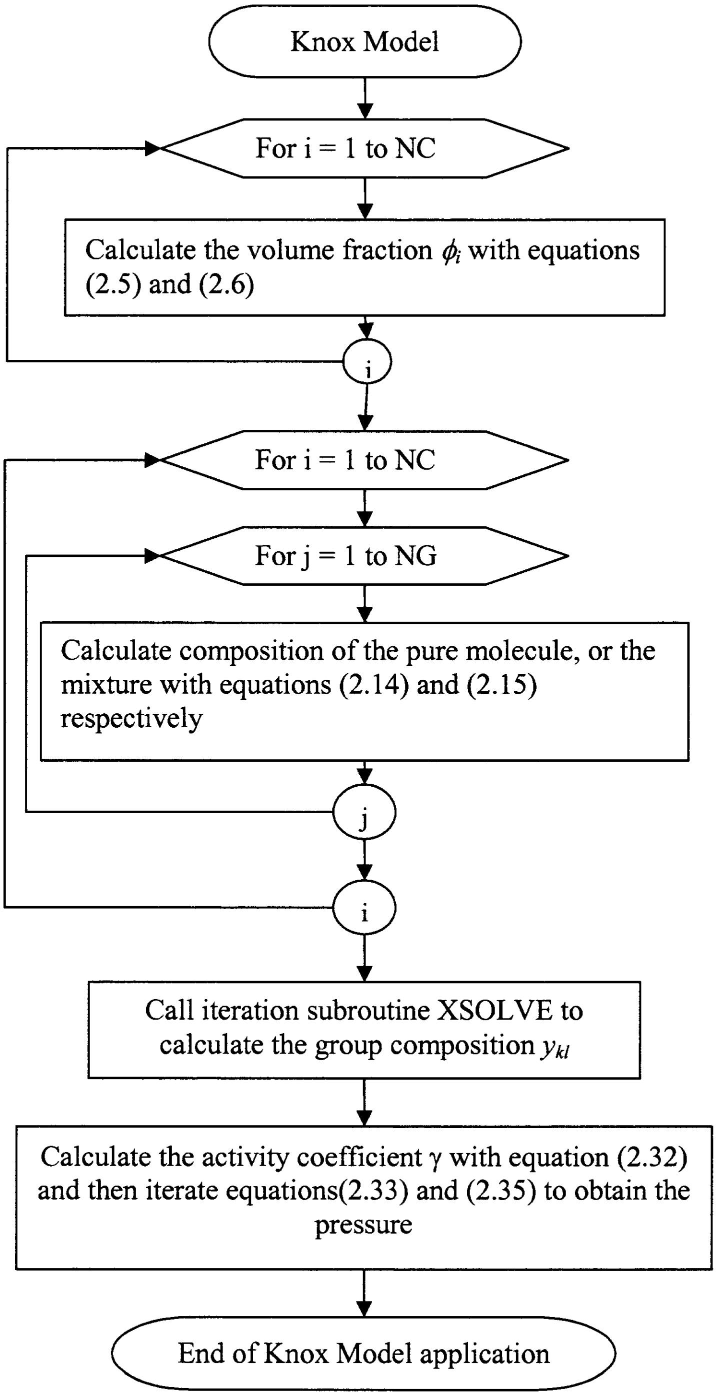


Figure 3.6 Calculation of pressure through the Knox model.

3.2.4 Estimation of the Global Parameters through Regression

The main process to estimate the global parameters involves nonlinear regression (Knox, 1982) that is done using Barker's method for the pressure calculation for all the experimental datapoints. The initial guesses for the energy parameters are related to the Boltzmann's constant and are shown in Table 3.9 as well as the equation.

Table 3.9 Initial Energy Parameter Values

Initial parameter	*Applied to Energy*	*Parameter Limits*	*Applied Equation*
$P_{Aini} = 1/k_b$	E_{qq}	*From 0 to* ∞	(3.20)
$P_{Bini} = 1/k_b$	$E_{q\mu}$	*From 0 to* ∞	(3.21)
$P_{Cini} = 2/k_b$	$E_{\mu\mu}$	*From 0 to* ∞	(3.22)
$P_{Dini} = -1/2k_b$	$E_{\alpha q}$	*From -* ∞ *to 0*	(3.23)
$P_{Fini} = -2/k_b$	$E_{\alpha\mu}$	*From -* ∞ *to 0*	(3.24)
$P_{Gini} = -3/8k_b$	$E_{\alpha\alpha}$	*From -* ∞ *to 0*	(3.25)
$P_{Hini} = -2/k_b$	$E_{\alpha\mu q}$	*From -* ∞ *to* ∞	(3.26)
$P_{Jini} = 1/k_b$	E_{rep}	*From 0 to* ∞	(3.27)

A deeper explanation of the physical basis for these expressions for the initial parameters can be found in Hirschfelder, J. O., et al. (1964).

The regression first obtains the initial parameters and their restrictions. With the initial values, it then reads each datapoint and calculates its pressure by applying the Knox model using parameters based on the AIM properties, calculates the deviations from the experimental data and, then adjusts the parameters. This process is repeated several times. Once the deviations don't change significantly, the regression stops and reports the new parameters and the new results. The entire code is displayed in Appendix A.

CHAPTER 4

RESULTS

4.1 Database Used to Fit the Global Parameters

The experimental data that werecollected to fit the global parameters is summarized in Table 4.1. Table 4.2 presents each system with its number of datapoints, ranges of pressure and temperature, and reference number.

Additionally, a summary organized by chemical categories is provided in Appendix B. The first two tables in the appendix report the number of datapoints and number of systems, their maximum and minimum temperature and pressure, as well as the number of isothermal and isobaric systems, all organized by chemical category. The other two tables summarize the same information but for the mixtures organized by combinations of chemical categories. Appendix C reports the reference for the articles that were used to generate the database used in the calculations.

Table 4.1 Systems Summary

Number of Articles	38
Total Number of Systems	97
Number of Datapoints	1848
Number of Isobaric Systems	23
Number of Isothermals Systems	73
Binary Systems	87
Ternary Systems	10
Max Temperature	493.15
Min Temperature	283.15
Max Pressure	4145
Min Pressure	2.3

Table 4.2 Systems Summary

S	*C1*	*C2*	*C3*	*R*	*DP*	*Tmax (K)*	*Tmin (K)*	*Pmax (KPa)*	*Pmin (KPa)*
1	1-propanol	1-pentanol		1	19	408.68	370.85	101.30	101.30
2	2-propanol	1-propanol		2	11	298.15	298.15	5.71	2.81
3	propanone	methanol		3	18	293.15	293.15	24.77	13.00
4	Hexane	ethanol		4	14	473.15	473.15	3479.00	1811.00
5	pentane	ethanol		5	26	422.60	422.60	1968.00	974.80
6	pentane	ethanol		5	0	465.40	465.40	4145.00	974.80
7	methanol	methyl acetate		7	19	334.45	334.45	99.80	99.00
8	ethyl acetate	1-butanol		8	31	388.80	339.60	70.50	70.50
9	ethyl acetate	1-butanol		8	0		-	94.00	70.50
10	1butanamine	hexane		13	180	283.15	283.15	10.51	5.80
11	1butanamine	hexane		13	0	293.15	293.15	16.87	5.80
12	1butanamine	hexane		13	0	303.15	303.15	26.10	5.80
13	1butanamine	hexane		13	0	313.15	313.15	38.85	5.80
14	1butanamine	hexane		13	0	323.15	323.15	56.40	5.80
15	1butanamine	hexane		13	0	333.15	333.15	79.70	5.80
16	1butanamine	hexane		13	0	343.15	343.15	109.88	5.80
17	1butanamine	hexane		13	0	353.15	353.15	148.75	5.80
18	1butanamine	hexane		13	0	373.15	373.15	256.42	5.80
19	dimethyl ether	ethanol		17	43	332.65	332.65	1253.00	382.00
20	dimethyl ether	ethanol		17	0	353.35	353.35	1772.00	382.00
21	dimethyl ether	ethanol		17	0	373.15	373.15	3160.00	382.00
22	dimethyl ether	ethanol	water	17	29	333.55	333.55	1344.66	273.00
23	dimethyl ether	ethanol	water	17	0	353.45	353.45	2023.00	273.00
24	dimethyl ether	ethanol	water	17	0	373.55	373.55	2541.00	273.00
25	dimethyl ether	methanol		18	13	353.15	353.15	2240.00	190.00
26	propane	2-butanol		20	24	328.10	328.10	1917.00	1010.00
27	propane	2-butanol		20	0	348.10	348.10	2860.00	1010.00
28	propane	2-butanol	2-propanol	20	6	328.10	328.10	2624.00	1585.00
29	dimethyl ether	2-propanol		21	29	323.35	323.35	961.00	129.00
30	dimethyl ether	2-propanol		21	0	348.85	348.85	1930.00	129.00
31	dimethyl ether	2-propanol		21	0	373.15	373.15	2621.00	129.00

Table 4.2 Systems Summary (Continued)

S	*C1*	*C2*	*C3*	*R*	*DP*	*Tmax (K)*	*Tmin (K)*	*Pmax (KPa)*	*Pmin (KPa)*
32	1-butene	2methyl-2propanol		24	23	326.14	326.14	646.48	27.49
33	1-butene	ethanol		24	23	326.14	326.14	644.77	34.36
34	1-butene	2-propanol		24	23	326.13	326.13	652.64	27.49
35	1-butene	2-butanol		24	23	326.16	326.16	644.32	12.68
36	butane	dimethyl ether		25	11	293.15	293.15	512.50	207.50
37	ethanol	butane		25	15	293.15	293.15	207.50	5.80
38	ethanol	dimethyl ether		25	16	293.15	293.15	512.50	5.80
39	water	dimethyl ether		25	16	293.15	293.15	514.19	2.30
40	butanone	2methyl-2butanol		29	26	375.11	352.76	101.30	101.30
41	2-propanol	3-pentanone (diethyl ketone)		29	25	374.80	355.39	101.30	101.30
42	nitroethane	methanol		30	20	387.16	337.58	101.30	101.30
43	nitroethane	ethanol		30	22	387.16	351.17	101.30	101.30
44	nitroethane	1-propanol		30	21	387.16	367.78	101.30	101.30
45	nitroethane	2-propanol		30	23	387.16	354.86	101.30	101.30
46	nitroethane	2-butanol		30	21	387.16	370.31	101.30	101.30
47	nitroethane	2methyl-2propanol		30	21	387.16	355.47	101.30	101.30
48	Hexane	1-propanol		31	27	483.15	483.15	2771.00	2088.00
49	Hexane	1-propanol		31	0	493.15	493.15	3215.00	2088.00
50	n-ethylethanmine (dietyl amine)	propanone		32	13	323.15	323.15	96.71	84.67
51	n-ethylethanmine (dietyl amine)	ethanenitrile		32	12	323.15	323.15	85.86	38.96
52	propene	dimethyl ether		33	23	313.10	313.10	1647.30	891.60
53	ethanenitrile	propanenitrile		34	55	313.15	313.15	22.65	12.66
54	ethanenitrile	propanenitrile		34	0	323.15	323.15	33.80	12.66
55	ethanenitrile	propanenitrile		34	0	333.15	333.15	49.15	12.66
56	1-propanol	1-butanol		36	30	353.15	353.15	50.86	21.90
57	1-propanol	1-butanol		36	0	363.15	363.15	76.89	21.90
58	1-propanol	1-butanol		36	0	373.15	373.15	114.05	21.90
59	propanenitrile	pentane		38	11	313.15	313.15	117.79	12.55
60	propanenitrile	hexane		38	12	313.15	313.15	45.12	12.55

Table 4.2 Systems Summary (Continued)

S	*C1*	*C2*	*C3*	*REF*	*DP*	*Tmax (K)*	*Tmin (K)*	*Pmax (KPa)*	*Pmin (KPa)*
61	Methyl acetate	ethyl acetate		39	27	353.15	353.15	203.20	121.50
62	Methyl acetate	ethyl acetate		39	0	363.15	363.15	272.10	121.50
63	Methyl acetate	ethyl acetate		39	0	373.17	373.17	356.10	121.50
64	ethyl acetate	2methyl-2butanol		44	23	373.47	350.45	101.32	101.32
65	isobutanol	3methyl-1butanol		44	28	403.80	381.10	101.32	101.32
66	methanol	propanone		53	32	346.95	329.75	99.80	99.80
67	methanol	3methyl-1butanol		54	18		-	101.30	101.30
68	vinyl ethanoate	3methyl-1butanol		54	16	404.20	345.80	101.30	101.30
69	Methyl acetate	1-hexene		60	24	323.15	323.15	93.13	64.67
70	ethanoic acid (acetic acid)	ethyl acetate		66	26	323.20	323.20	38.11	7.61
71	ethanoic acid (acetic acid)	ethyl acetate		66	0	343.20	343.20	79.71	7.61
72	n-ethylethanmine (dietyl amine)	ethyl acetate		68	30	297.98	297.98	31.39	12.57
73	n-ethylethanmine (dietyl amine)	ethyl acetate		68	0	348.09	348.09	189.63	12.57
74	methanol	water		69	52	323.15	323.15	47.33	29.12
75	methanol	water		69	0	328.15	328.15	59.21	29.12
76	methanol	water		69	0	333.15	333.15	72.83	29.12
77	ethanol	water		69	107	323.15	323.15	29.57	20.33
78	ethanol	water		69	0	328.15	328.15	37.44	20.33
79	ethanol	water		69	0	333.15	333.15	47.06	20.33
80	1-pentene	methyl acetate		70	57	323.15	323.15	193.54	79.43
81	2methyl-2propanol	isobutanol		75	15	379.40	353.80	94.90	94.90
82	ethyl acetate	nitromethane		76	21	374.38	350.28	101.30	101.30
83	Propyl ethanoate	nitromethane		76	21	374.69	371.30	101.30	101.30
84	methyl propionate	nitromethane		76	21	374.38	352.71	101.30	101.30
85	ethyl propanoate	nitromethane		76	21	374.38	369.84	101.30	101.30

Table 4.2 Systems Summary (Continued)

S	*C1*	*C2*	*C2*	*REF*	*DP*	*Tmax (K)*	*Tmin (K)*	*Pmax (KPa)*	*Pmin (KPa)*
86	pentane	hexane		77	38	298.70	298.70	69.96	20.69
87	pentane	hexane		77	0	303.70	303.70	83.82	20.69
88	pentane	hexane		77	0	308.70	308.70	100.63	20.69
89	Water	methanoic acid	ethanoic acid	101	67	383.95	374.24	101.30	101.30
90	propanone	2-propanol	water	102	45	362.51	333.26	200.10	76.26
91	1-pentanol	1-propanol	water	103	34	392.80	362.30	101.30	101.30
92	methanol	water		105	39	308.15	308.15	28.00	5.62
93	methanol	water		105	0	323.15	323.15	55.64	5.62
94	methanol	water		105	0	338.15	338.15	103.30	5.62
95	methanol	ethanol	water	106	112	323.15	323.15	44.98	20.92
96	methanol	ethanol	water	106	0	328.15	328.15	59.84	20.92
97	methanol	ethanol	water	106	0	333.15	333.15	75.47	20.92

4.2 Process to Fit the Parameters

After some trials, it was found that fitting several parameters at the same time, would not give adequate results. Therefore, different fitting parameter processes were tested to evaluate the one that would lead to the best calculations. As a result, a new fitting process was established, and is described as follows. The first three parameters to be fitted were the parameter for the structural contribution P_K, the parameter for the Coulomb energy, P_A, and the charge-dipole moment energy parameter, P_B. The other parameters were not involved in the calculation process at this stage (i.e. they were kept constant with a zero value). Subsequently, one energy parameter was fitted at a time along with the structural parameter P_K, keeping the others constant. In consequence, for the next step, the values obtained for P_A and P_B were kept constant and the energy parameter to be fitted was the charge-dipole moment-polarizability parameter P_H. Once P_H was obtained, it was fixed along with P_A and P_B, and the repulsion energy parameter P_J was calculated. The polarizability-dipole moment parameter P_G, polarizability-charge parameter P_D, dipole moment parameter P_C, and polarizability parameter, P_G, were fitted in that order, following the same method as before. When all the parameters have been calculated, a last fit is done with all the parameters.

Table 4.3 shows the nine steps fitting process with the values of the parameters for each from 1 to 8. The final parameters were obtained after fitting all the parameters in Step9 and are reported in Table 4.4.

Table 4.3 Fitting Parameter Values

	Energy Contribution	***Step 1***	***Step 2***	***Step 3***	***Step 4***	***Step 5***	***Step 6***	***Step 7***	***Step 8***
P_K		**0.220**	**0.220**	**0.220**	**0.184**	**0.230**	**0.232**	**0.228**	**0.172**
P_A	E_{qq}	**0.000**	0.000	0.000	0.000	0.000	0.000	0.000	0.000
P_B	E_{qm}	**9.707**	9.707	9.707	9.707	9.707	9.707	9.707	9.707
P_C	E_{mm}	0	0	0	0	0	0	**0.013**	0.013
P_D	E_{aq}	0	0	0	0	0	**-0.604**	-0.604	-0.604
P_F	E_{am}	0	0	0	0	**-1.04E+06**	-1.04E+06	-1.04E+06	-1.04E+06
P_G	E_{aa}	0	0	0	0	0	0	0	**-4.94E+05**
P_H	E_{qma}	0	0	**-2.99E+05**	-2.99E+05	-2.99E+05	-2.99E+05	-2.99E+05	-2.99E+05
P_F	E_{rep}	0	0	0	**4.67E-03**	4.67E-03	4.67E-03	4.67E-03	4.67E-03

Table 4.4 Final Parameter Values

Parameter	*Energy Contribution*	*Final Values*
P_K		0.1721
P_A	E_{qq}	1.70E-03
P_B	E_{qm}	9.7105
P_C	E_{mm}	5.92E-08
P_D	E_{aq}	-0.5833
P_F	E_{am}	-1.04E+06
P_G	E_{aa}	-4.94E+05
P_H	E_{qma}	-2.99E+05
P_F	E_{rep}	2.96E-03

4.3 Results

Selected systems have been plotted to understand how the model predicts the behavior of the different categories of chemical mixtures. The summary of these systems is presented in Table 4.5. In addition to the experimental and calculated results, some figures present calculations using the UNIFAC model. These results were obtained from Kim (2005).

Table 4.5 Report of Figures for Chemical Categories Mixtures

Chemical Category Mixture	*System*	*Figure*
ALKANE-ALCOHOL	hexane + ethanol	Figure 4.3
ALKENE-ALCOHOL	1butene + 2butanol	Figure 4.4
ALCOHOL-ALCOHOL	2methyl-2propanol + isobutanol	Figure 4.5
ETHER-ALCOHOL	dimethyl ether + methanol	Figure 4.1
KETONE-ALCOHOL	butanone + 2methyl-2butanol	Figure 4.6
ESTER-ALCOHOL	vinyl ethanoate + 2methyl-2butanol	Figure 4.7
NITRO-ALCOHOL	nitroethane + methanol	Figure 4.8
ALCOHOL-WATER	ethanol + water	Figure 4.2
ALKANE-ETHER	butane + dimethyl ether	Figure 4.9
ALKENE-ESTER	1pentene + methyl acetate	Figure 4.10
ALKENE-ETHER	propene + dimethyl ether	Figure 4.11
AMINE-ALKANE	1butanamine + hexane	Figure 4.12
AMINE-ESTER	n-ethylethanmine + ethyl acetate	Figure 4.13
AMINE-KETONE	n-ethylethanmine + propanone	Figure 4.14
AMINE-NITRILE	dietyl amine + ethanenitrile	Figure 4.15
CARBOXYLIC ACID -ESTER	Acetic acid + ethyl acetate	Figure 4.16
ESTER-ESTER	methyl acetate + ethyl acetate	Figure 4.17
WATER-ETHER	Water + dimethyl ether	Figure 4.18
NITRILE-ALKANE	propanenitrile + pentane	Figure 4.19
NITRILE-NITRILE	ethanenitrile + propanenitrile	Figure 4.20
ESTER-NITRO	ethyl acetate + nitromethane	Figure 4.21

From the figures it is possible to see that the model studied in this research can predict most of the behavior of both isothermal and isobaric systems with very accurate results. Isothermal systems, such as ethanol-water, 1pentene - methyl acetate, 1butanamine - hexane, ethanenitrile – propanenitrile, acetic acid - ethyl acetate, n-ethylethanmine - ethyl acetate or n-ethylethanmine – propanone, are predicted with almost no error. For instances, in systems like hexane – ethanol or 1butene - 2butanol, the model predicts the behavior of the isothermal, with only some minor error that are seen from the graphs. Among all the isothermals presented below, propanenitrile – pentane and dietyl amine + ethanenitrile are the only systems that are not predicted well by the calculations. It is important to highlight that the water - dimethyl ether system (Figure 4.18) presents a Liquid- Liquid- Equilibrium (LLE) phase that is remarkably predicted by the Knox model.

The isobaric systems presented in the graphs, show very precise results. Having, for example, the 2methyl-2propanol + isobutanol system, the predictions of the model show a very low error, moreover, taking into account that the two molecules are isomers.

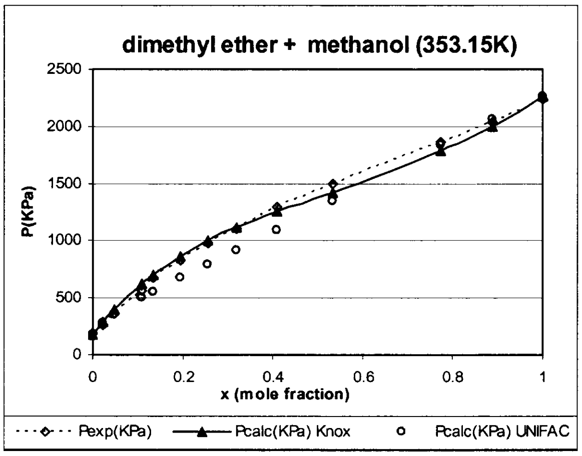


Figure 4.1 Dimethyl ether + methanol system at 353.15 K

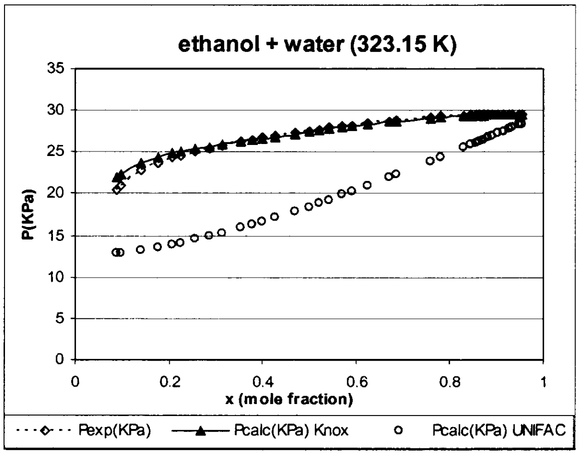


Figure 4.2 Ethanol + water system at 323.15 K

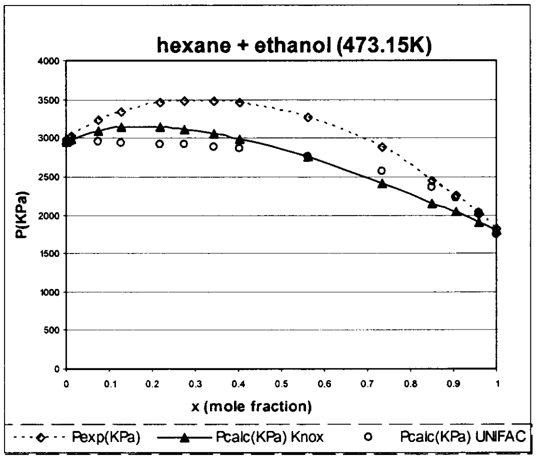


Figure 4.3 Hexane + ethanol system at 473.15

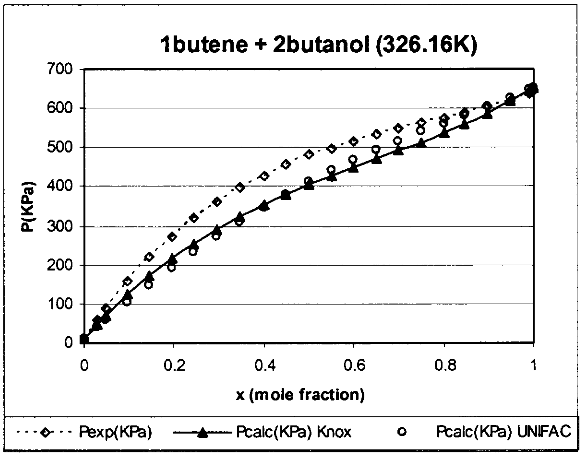


Figure 4.4 1-Butene + 2-Butanol system at 326.16

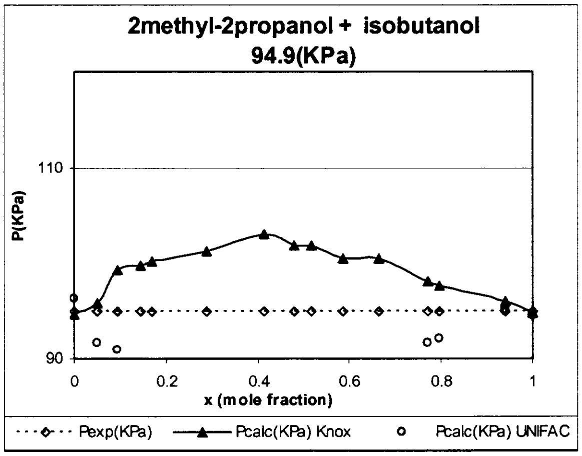


Figure 4.5 2methyl -2propanol + isobutanol system at 94.9 KPa

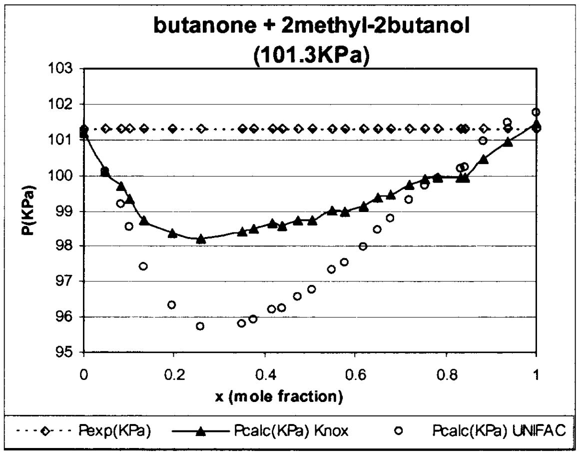


Figure 4.6 Butanone + 2methyl-2butanol at 101.3 KPa

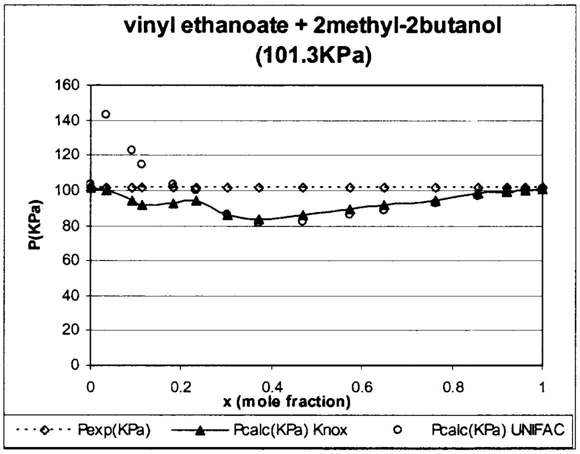


Figure 4.7 Vinyl Ethanoate + 2methyl-2butanol

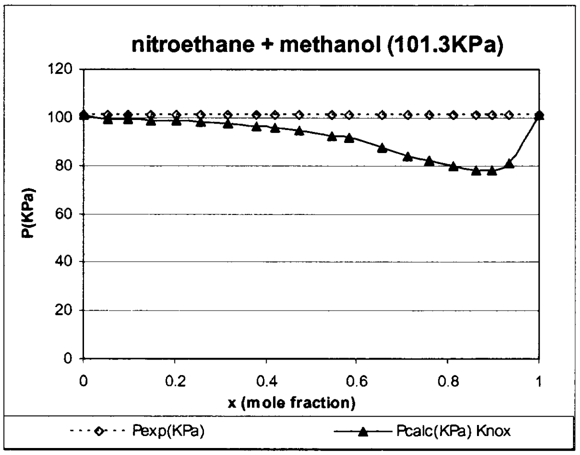


Figure 4.8 Nitroethane + methanol at 101.3 KPa

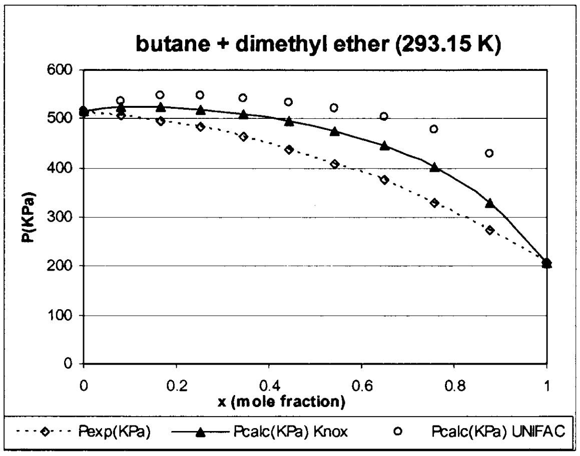


Figure 4.9 Butane + dimethyl ether system at 293.15 K

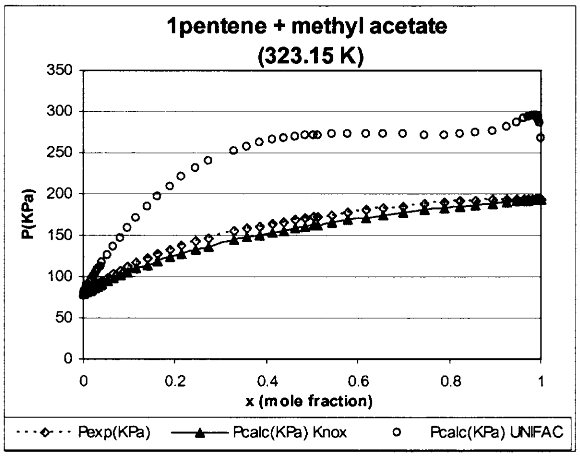


Figure 4.10 1Pentene + methyl acetate system at 323.15 K

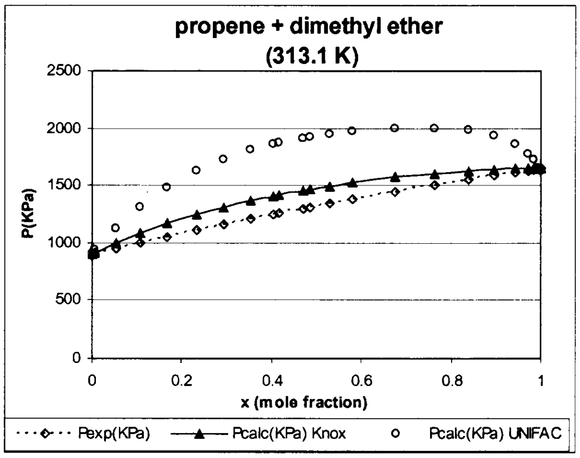


Figure 4.11 propene + dimethyl ether system at 313.1 K

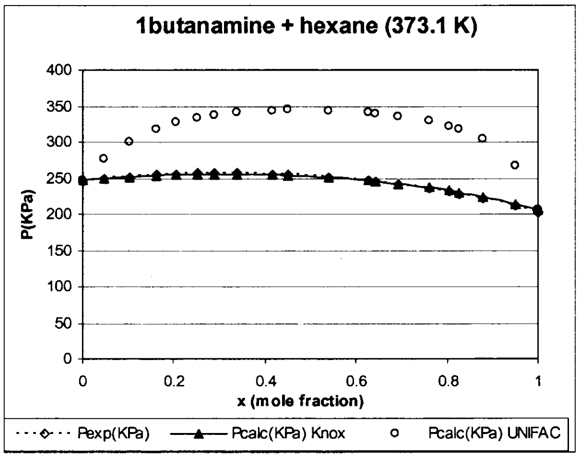


Figure 4.12 1butanamine + hexane system at 373.1 K

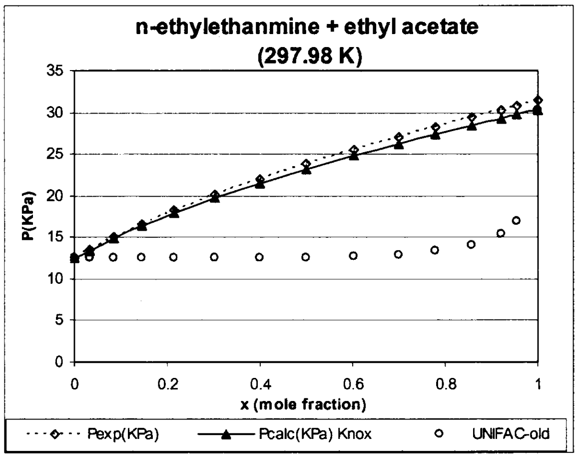


Figure 4.13 n-Ethylethanmine + ethyl acetate system at 297.98 K

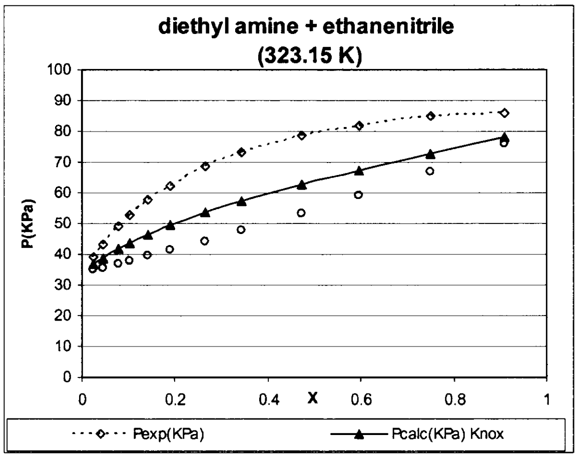


Figure 4.14 n-Ethylethanmine + propanone system at 323.15 K

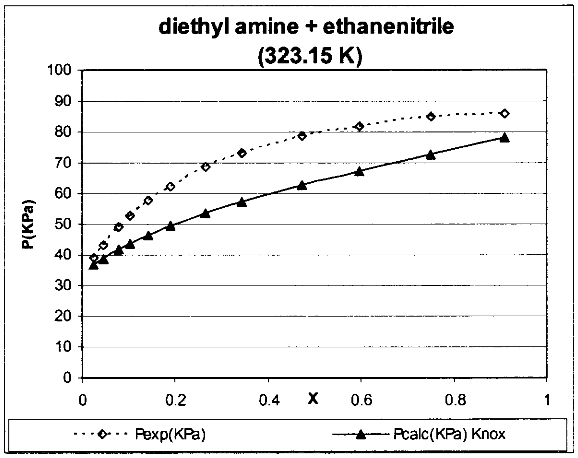


Figure 4.15 diethyl amine + ethanenitrile system at 323.15 K

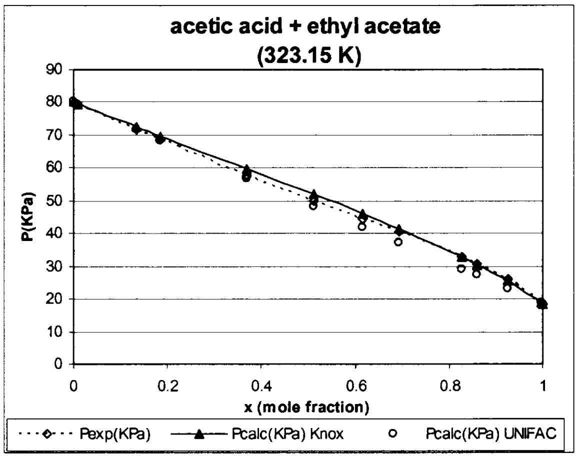


Figure 4.16 Acetic acid + ethyl acetate system at 323.15 K

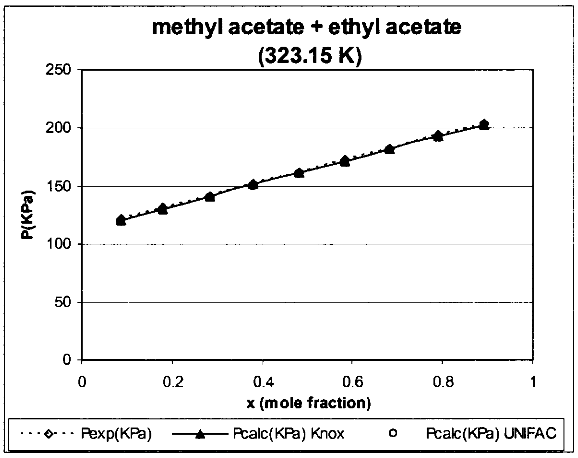


Figure 4.17 Methyl actetate + ethyl acetate system at 323.15 K

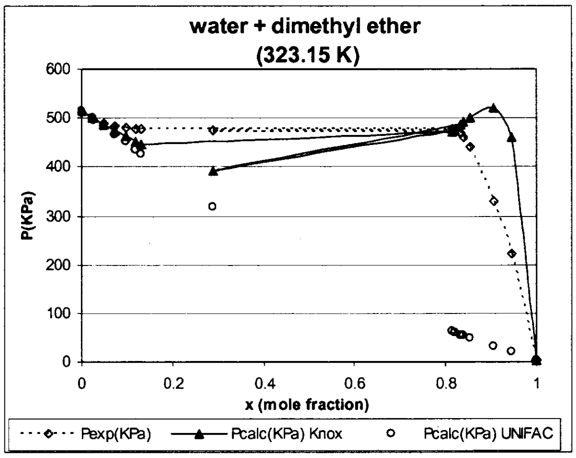


Figure 4.18 Water + dimethyl ether at 323.15 K

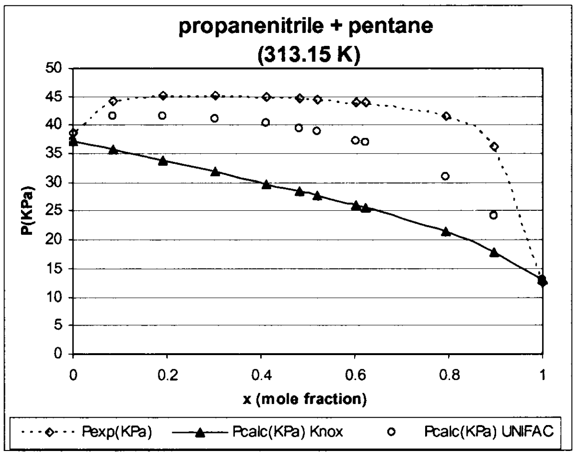


Figure 4.19 Propanenitrile + pentane system at 313.15 K

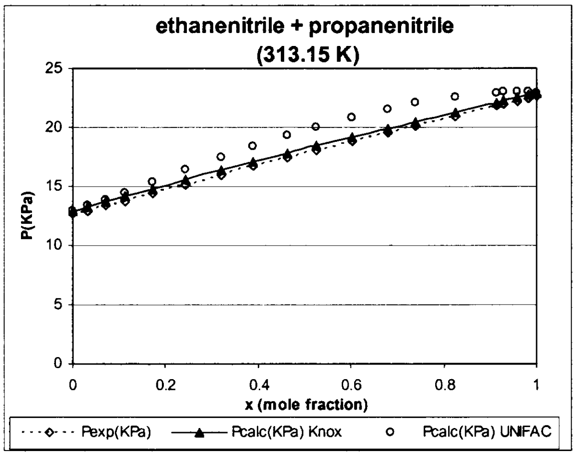


Figure 4.20 Ethanenitrile + propanenitrile system at 313.15 K

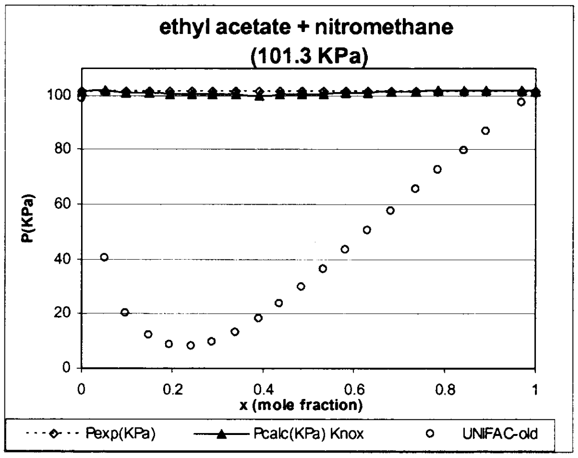


Figure 4.21 Ethyl acetate + nitromethane system at 101.3 KPa

Comparing this research with a parallel study with the UNIFAC model and AIM properties (Kim, 2005), the figures show that, in general, the predictions for the model studied in this research are more accurate. With the exception of a couple of systems, such as, 2methyl -2propanol + isobutanol and hexane + ethanol, the Knox model better predicts the behavior of the systems, and has a better precision.

Additional to the graphs, Table 4.6 reports the average error for each system sorted by their chemical categories mixtures. Thus, the results show that alcohol-ester systems present low average errors as well as alcohol-water mixtures. Furthermore, alkane-alkane, amine-alkane, ester-alkane, alkene-ether, alkene-ester, amine-ketone, carboxylic acids-ester, ester-ester, ester-nitro, amine-ketone, amine-nitrile and nitrile-nitrile systems are very well predicted by the model.

Except for mixtures such as methanol - 3methyl1butanol, ethanol-dimethyl ether or methanol- propanone, the systems with alcohol-alcohol, ether-alcohol and alcohol – ketone mixtures show only small or insignificant errors. Unfortunately, alkane-alcohol, nitro –alcohol, nitriles-alkanes as well as alkene-alcohol present some deviations and some of them have average errors above 20%. Some explanations for these deviations can be that the types of molecules that present problems were not well represented in the database or that these molecules are not well described by the method proposed.

For the ternary systems, such as methanol-ethanol-water and dimethyl ether-ethanol-water, the results show very good predictions. The table also reports an average error around 10 % for propanone-2butanol-2propanol as well as for the 1pentanol - 1propanol-water mixture and above 20% for the two ternary systems remaining

Table 4.6 Average Errors Reported by System

S	*C1*	*C2*	*C3*	*C1-C2-C3*	*AVG*
1	1-propanol	1-pentanol		ALCOHOL-ALCOHOL	-0.04%
2	2-propanol	1-propanol		ALCOHOL-ALCOHOL	2.34%
56	1-propanol	1-butanol		ALCOHOL-ALCOHOL	-0.12%
57	1-propanol	1-butanol		ALCOHOL-ALCOHOL	-0.43%
58	1-propanol	1-butanol		ALCOHOL-ALCOHOL	-0.87%
65	isobutanol	3methyl-1butanol		ALCOHOL-ALCOHOL	-0.78%
67	methanol	3methyl-1butanol		ALCOHOL-ALCOHOL	44.44%
81	2methyl-2propanol	isobutanol		ALCOHOL-ALCOHOL	4.33%
37	ethanol	butane		ALCOHOL-ALKANE	-31.57%
4	hexane	ethanol		ALKANE-ALCOHOL	-8.60%
5	pentane	ethanol		ALKANE-ALCOHOL	-18.05%
6	pentane	ethanol		ALKANE-ALCOHOL	-12.49%
26	propane	2-butanol		ALKANE-ALCOHOL	-10.05%
27	propane	2-butanol		ALKANE-ALCOHOL	-9.52%
48	hexane	1-propanol		ALKANE-ALCOHOL	-11.61%
49	hexane	1-propanol		ALKANE-ALCOHOL	-7.05%
7	methanol	methyl acetate		ALCOHOL-ESTER	5.72%
8	ethyl acetate	1-butanol		ESTER-ALCOHOL	-1.30%
9	ethyl acetate	1-butanol		ESTER-ALCOHOL	-1.32%
64	ethyl acetate	2methyl-2butanol		ESTER-ALCOHOL	3.88%
68	vinyl ethanoate	3methyl-1butanol		ESTER-ALCOHOL	-7.39%
38	ethanol	dimethyl ether		ALCOHOL-ETHER	-16.15%
19	dimethyl ether	ethanol		ETHER-ALCOHOL	-11.05%
20	dimethyl ether	ethanol		ETHER-ALCOHOL	-9.12%
21	dimethyl ether	ethanol		ETHER-ALCOHOL	-6.70%
25	dimethyl ether	methanol		ETHER-ALCOHOL	0.08%
29	dimethyl ether	2-propanol		ETHER-ALCOHOL	-7.05%
30	dimethyl ether	2-propanol		ETHER-ALCOHOL	-3.57%
31	dimethyl ether	2-propanol		ETHER-ALCOHOL	-5.44%
74	methanol	water		ALCOHOL-INORGANIC	-6.18%
75	methanol	water		ALCOHOL-INORGANIC	-6.38%
76	methanol	water		ALCOHOL-INORGANIC	-6.86%

Table 4.6 Average Errors Reported by System (Continued)

S	*C1*	*C2*	*C3*	*C1-C2-C3*	*AVG*
77	ethanol	water		ALCOHOL-INORGANIC	0.36%
78	ethanol	water		ALCOHOL-INORGANIC	-0.22%
79	ethanol	water		ALCOHOL-INORGANIC	-0.21%
92	methanol	water		ALCOHOL-INORGANIC	-3.36%
93	methanol	water		ALCOHOL-INORGANIC	-4.38%
94	methanol	water		ALCOHOL-INORGANIC	-5.29%
41	2-propanol	3-pentanone (diethyl ketone)		ALCOHOL-KETONE	-5.48%
66	methanol	propanone		ALCOHOL-KETONE	37.07%
3	propanone	methanol		KETONE-ALCOHOL	38.86%
40	butanone	2methyl-2butanol		KETONE-ALCOHOL	-1.83%
42	nitroethane	methanol		NITRO-ALCOHOL	-9.45%
43	nitroethane	ethanol		NITRO-ALCOHOL	-20.58%
44	nitroethane	1-propanol		NITRO-ALCOHOL	-14.45%
45	nitroethane	2-propanol		NITRO-ALCOHOL	-16.71%
46	nitroethane	2-butanol		NITRO-ALCOHOL	-11.20%
47	nitroethane	2methyl-2propanol		NITRO-ALCOHOL	-11.68%
32	1-butene	2methyl-2propanol		ALKENE-ALCOHOL	-17.23%
33	1-butene	ethanol		ALKENE-ALCOHOL	-20.76%
34	1-butene	2-propanol		ALKENE-ALCOHOL	-18.91%
35	1-butene	2-butanol		ALKENE-ALCOHOL	-10.21%
10	1butanamine	hexane		AMINE-ALKANE	-7.69%
11	1butanamine	hexane		AMINE-ALKANE	-7.09%
12	1butanamine	hexane		AMINE-ALKANE	-5.45%
13	1butanamine	hexane		AMINE-ALKANE	-4.21%
14	1butanamine	hexane		AMINE-ALKANE	-4.45%
15	1butanamine	hexane		AMINE-ALKANE	-3.63%
16	1butanamine	hexane		AMINE-ALKANE	-2.53%
17	1butanamine	hexane		AMINE-ALKANE	-1.80%
18	1butanamine	hexane		AMINE-ALKANE	0.23%
86	pentane	hexane		ALKANE-ALKANE	-3.54%
87	pentane	hexane		ALKANE-ALKANE	-3.39%
88	pentane	hexane		ALKANE-ALKANE	-5.30%

Table 4.6 Average Errors Reported by System (Continued)

S	*C1*	*C2*	*C4*	***C1-C2-C3***	*AVG*
36	butane	dimethyl ether		ALKANE-ETHER	10.06%
59	propanenitrile	pentane		NITRILE-ALKANE	-29.15%
60	propanenitrile	hexane		NITRILE-ALKANE	-32.29%
80	1-pentene	methyl acetate		ALKENE-ESTER	-3.41%
69	methyl acetate	1-hexene		ESTER-ALKENE	0.04%
52	propene	dimethyl ether		ALKENE-ETHER	7.00%
72	n-ethylethanmine (dietyl amine)	ethyl acetate		AMINE-ESTER	-2.53%
73	n-ethylethanmine (dietyl amine)	ethyl acetate		AMINE-ESTER	-1.08%
50	n-ethylethanmine (dietyl amine)	propanone		AMINE-KETONE	-3.33%
51	n-ethylethanmine (dietyl amine)	ethanenitrile		AMINE-NITRILE	-16.57%
70	ethanoic acid (acetic acid)	ethyl acetate		CARBOXYLIC ACID-ESTER	1.35%
71	ethanoic acid (acetic acid)	ethyl acetate		CARBOXYLIC ACID-ESTER	1.49%
61	methyl acetate	ethyl acetate		ESTER-ESTER	-0.41%
62	methyl acetate	ethyl acetate		ESTER-ESTER	-0.63%
63	methyl acetate	ethyl acetate		ESTER-ESTER	-0.43%
82	ethyl acetate	nitromethane		ESTER-NITRO	-3.59%
83	propyl ethanoate	nitromethane		ESTER-NITRO	-0.31%
84	methyl propionate	nitromethane		ESTER-NITRO	-2.93%
85	ethyl propanoate	nitromethane		ESTER-NITRO	-2.38%
39	water	dimethyl ether		INORGANIC-ETHER	5.33%
53	ethanenitrile	propanenitrile		NITRILE-NITRILE	1.92%
54	ethanenitrile	propanenitrile		NITRILE-NITRILE	1.66%
55	ethanenitrile	propanenitrile		NITRILE-NITRILE	1.43%

Table 4.6 Average Errors Reported by System (Continued)

S	*C1*	*C2*	*C3*	***C1-C2-C3***	*AVG*
91	1-pentanol	1-propanol	water	ALCOHOL-ALCOHOL-INORGANIC	-9.95%
89	Water	methanoic acid (formic acid)	ethanoic acid (acetic acid)	INORGANIC-CARBOXYLIC ACID-CARBOXYLIC ACID	23.39%
90	propanone	2-propanol	water	KETONE-ALCOHOL-INORGANIC	37.93%
28	propane	2-butanol	2-propanol	ALKANE-ALCOHOL-ALCOHOL	-11.61%
95	methanol	ethanol	water	ALCOHOL-ALCOHOL-INORGANIC	5.24%
96	methanol	ethanol	water	ALCOHOL-ALCOHOL-INORGANIC	4.47%
97	methanol	ethanol	water	ALCOHOL-ALCOHOL-INORGANIC	3.61%
22	dimethyl ether	ethanol	water	ETHER-ALCOHOL-INORGANIC	-6.18%
23	dimethyl ether	ethanol	water	ETHER-ALCOHOL-INORGANIC	-6.38%
24	dimethyl ether	ethanol	water	ETHER-ALCOHOL-INORGANIC	-6.86%

CHAPTER 5

CONCLUSIONS

The results introduced in Chapter 4 demonstrate that using the Knox model with the new group contribution method based on AIM theory is able to predict with accuracy VLE for many systems. Both binary and ternary mixtures have been evaluated and have shown that the model can predict the behavior of the system for several types of mixtures. Moreover, the model has proved to work well with systems that for different reasons have presented trouble in the past, such as isomers or polar mixtures, giving very small errors. When comparing the Knox model with UNIFAC, applying the same method for evaluation of the group contribution parameters, the results show better behavior predictions and more precise results.

A few systems presented significant errors. One of the reasons could be that when doing the fitting process, the database did not have sufficient representation of those types of molecules. Another cause may be that the molecular behavior of those systems is not well described by the method proposed in this research. Therefore, a deeper study on such systems can be done to improve the reliability of the model. Work by Arturo (2005) suggests that a new version of the model that also tracks next-connected atoms, would be even more successful.

The database built in this work required an extensive searching effort, which, once more, demonstrates the need for of a dependable method to predict such thermodynamic properties. For this reason, more research should be done not only to perfect the prediction of the systems, but to expand the number of molecules studied in this work. Some limitations, such as the size of the molecule will soon be overcome with faster computer technology. A remarkable result obtained by this research was the prediction of a liquid-liquid equilibrium system, inviting a deeper study in this subject.

To conclude, the method presented by this research is able to accurately predict thermodynamic properties for the most of the systems studied. A further study that involves more systems and new molecules can be done, to expand the use of the Knox model and the AIM-group contribution method.

APPENDIX A

CODE

Appendix A displays the actual code that was used to evaluate the Knox Model using AIM groups properties.

A.1 Read Database Code

```
Function UploadDB(RowD As Long) As Integer

  Dim XX As Double

  Sheets("ExperimentalDataTable").Select
  Tup(RowD) = CDbl(Val(Cells(RowD + 2, 7).Value))

  XX = 0
  NCup(RowD) = CInt(Cells(RowD + 2, 18).Value)

  For I = 1 To NCup(RowD)
    'Composition
    If I <> NCup(RowD) Then
      XIup(I, RowD) = CDbl(Cells(RowD + 2, 8 + I).Value)
      XX = XX + XIup(I, RowD)
    Else
      XIup(I, RowD) = Abs(1 - XX)
    End If

    'VP equation
    IVPup(I, RowD) = CInt(Cells(RowD + 2, 19 + I).Value)
      'Integer noting vapor pressure correlation equation

  Next I


  For I = 1 To NCup(RowD)
    Sheets("ExperimentalDataTable").Select

    CIDup(I, RowD) = CInt(Val(Cells(RowD + 2, 1 + 2 * (I - 1)).Value)) 'CID per component

    'Compounds
    Sheets("CompoundPropertiesTable").Select
    Cells(2, 17).Value = CIDup(I, RowD)
    TCup(I, RowD) = CDbl(Cells(6, 17).Value)          'Critical Temperature per Compound

    NGIup(I, RowD) = CInt(Cells(4, 17).Value)         'Number of Groups per Compound
```

```
    PCup(I, RowD) = CDbl(Cells(5, 17).Value)          'Critical Pressure per Compound
    VCup(I, RowD) = CDbl(Cells(7, 17).Value)          'Critical Volume per Compound
    Wup(I, RowD) = CDbl(Cells(9, 17).Value)           'Acentric Factor per Compound
    DPup(I, RowD) = CDbl(Cells(10, 17).Value)         'Dipole Moment
            'Liquid volume at a reference temperature in cc/mol
    VLIQRup(I, RowD) = CDbl(Cells(11, 17).Value)
            'Average radius for each type of group
    TLIQRup(I, RowD) = CDbl(Val(Cells(12, 17).Value))
            'Integer noting compound "class" for Tsonopoulos
    ITSMup(I, RowD) = CInt(Cells(13, 17).Value)

    'Groups

    Sheets("GroupAIMPropertiesTable").Select
    For J = 1 To NGIup(I, RowD)
      Cells(2, 22).Value = CIDup(I, RowD)
      Cells(2, 24).Value = J
       'Number of groups of each type in each molecule
      NGQup(I, J, RowD) = CInt(Cells(5, 22).Value)
      IGCLup(I, J, RowD) = CDbl(Cells(3, 22).Value)       'Group class for each group type
      GQup(I, J, RowD) = CDbl(Cells(7, 22).Value)         'Group charge for each group type
      GMUup(I, J, RowD) = CDbl(Cells(10, 22).Value)       'Group dipole for each group type
       'Group polarizability for each group type
      GALup(I, J, RowD) = CDbl(Cells(11, 22).Value)
       'Group volume for each type of group
       GVup(I, J, RowD) = CDbl(Cells(12, 22).Value)
       'Group area for each type of group
      GAup(I, J, RowD) = CDbl(Cells(13, 22).Value)
       'Average radius for each type of group
      GRup(I, J, RowD) = CDbl(Cells(14, 22).Value)
      GEup(I, J, RowD) = CDbl(Cells(8, 22).Value)
      GLup(I, J, RowD) = CDbl(Cells(9, 22).Value)
      GXiup(I, J, RowD) = CDbl(Cells(15, 22).Value)
    Next J

  Next I

  UploadDB = True

  Call VaporPressure(RowD)
  Call LiquidMolarVolume(RowD)


End Function

Sub LiquidMolarVolume(RowD As Long)
  Dim XX As Double

  For I = 1 To NCup(RowD)
    XX = (1 - Tup(RowD) / TCup(I, RowD)) ^ (2 / 7) - (1 - TLIQRup(I, RowD) / TCup(I,
RowD)) ^ (2 / 7)
```

```
    VLIQup(I, RowD) = VLIQRup(I, RowD) * (0.29056 - 0.08775 * Wup(I, RowD)) ^ XX

  Next I

End Sub

Sub VaporPressure(RowD As Long)

  Dim XX As Double
  Dim PSX As Double

   For I = 1 To NCup(RowD)
    Sheets("VaporPressureTable").Select
    Cells(2, 21).Value = CIDup(I, RowD)
    Cells(2, 23).Value = IVPup(I, RowD)
    VP1up(I, RowD) = CDbl(Cells(3, 21).Value)      'Vapor Pressure Correlation Constant 1 per
Compound
    VP2up(I, RowD) = CDbl(Cells(4, 21).Value)      'Vapor Pressure Correlation Constant 2 per
Compound
    VP3up(I, RowD) = CDbl(Cells(5, 21).Value)      'Vapor Pressure Correlation Constant 3 per
Compound
    VP4up(I, RowD) = CDbl(Cells(6, 21).Value)      'Vapor Pressure Correlation Constant 4 per
Compound
    VP5up(I, RowD) = CDbl(Cells(7, 21).Value)      'Vapor Pressure Correlation Constant 5 per
Compound
    VP6up(I, RowD) = CDbl(Cells(8, 21).Value)      'Vapor Pressure Correlation Constant 6 per
Compound
    VP7up(I, RowD) = CDbl(Cells(9, 21).Value)      'Vapor Pressure Correlation Constant 7 per
Compound
    VP8up(I, RowD) = CDbl(Cells(10, 21).Value)     'Vapor Pressure Correlation Constant 8 per
Compound

    Select Case IVPup(I, RowD)

      Case 1
        '**** eqn 1 PGL
        PSATup(I, RowD) = 10 ^ (VP1up(I, RowD) - VP2up(I, RowD) / (Tup(RowD) +
VP3up(I, RowD) - 273.15))

      Case 2
        '**** eqn 2 PGL
        XX = (Tup(RowD) - VP5up(I, RowD) - 273.15) / (VP4up(I, RowD))
        PSX = (VP1up(I, RowD) - VP2up(I, RowD)) / (T - VP3up(I, RowD) - 273.15)
        PSX = PSX + 0.43429 * XX ^ VP6up(I, RowD)
        PSX = PSX + VP7up(I, RowD) * XX ^ 8
        PSX = PSX + VP7up(I, RowD) * XX ^ 12
        PSATup(I, RowD) = 10 ^ (PSX)


      Case 3
        '**** eqn 3 PGL
```

```
        XX = 1 - Tup(RowD) / VP1up(I, RowD)
        PSX = VP2up(I, RowD) * XX
        PSX = PSX + VP3up(I, RowD) * XX * Sqr(XX)
        PSX = PSX + VP4up(I, RowD) * XX ^ 2 * Sqr(XX)
        PSX = PSX + VP5up(I, RowD) * XX ^ 5
        PSATup(I, RowD) = Exp(Log(VP6up(I, RowD)) + PSX * VP1up(I, RowD) /
Tup(RowD))


      Case 4
        '**** eqn CHERIC
        PSX = VP1up(I, RowD) * Log(Tup(RowD))
        PSX = PSX + VP2up(I, RowD) / (Tup(RowD))
        PSX = PSX + VP3up(I, RowD)
        PSX = PSX + VP4up(I, RowD) * (Tup(RowD)) ^ 2
        PSATup(I, RowD) = Exp(PSX) / 100

      Case 5

      Case 6


      Case 7
        '**** eqn webbook
        PSATup(I, RowD) = 10 ^ (VP1up(I, RowD) - (VP2up(I, RowD) / (Tup(RowD) +
VP3up(I, RowD))))

      Case 8
        '**** from an article
        PSATup(I, RowD) = (Exp(VP1up(I, RowD) - (VP2up(I, RowD) / (Tup(RowD) +
VP3up(I, RowD))))) / 100

      Case 9
        '**** just for water from PGL modification of eqn 3
        XX = 1 - Tup(RowD) / VP1up(I, RowD)
        PSX = VP2up(I, RowD) * XX
        PSX = PSX + VP3up(I, RowD) * XX * Sqr(XX)
        PSX = PSX + VP4up(I, RowD) * XX ^ 3
        PSX = PSX + VP5up(I, RowD) * XX ^ 6
        PSATup(I, RowD) = Exp(Log(VP6up(I, RowD)) + PSX * VP1up(I, RowD) /
Tup(RowD))

      Case 10
        '**** eqn Yaws
        PSX = VP1up(I, RowD) + VP2up(I, RowD) / Tup(RowD) + VP3up(I, RowD) *
Log(Tup(RowD)) / Log(10#) + VP4up(I, RowD) * Tup(RowD) + VP5up(I, RowD) *
Tup(RowD) ^ 2
        PSATup(I, RowD) = (10 ^ (PSX)) / 760 'convert to bars


      Case Else
```

```
        End Select
        Sheets("ExperimentalDataTable").Select

        Cells(RowD + 2, 10 + I).Value = PSATup(I, RowD)

    Next I


End Sub


Function VirialCoefficient(T As Double, NC As Integer, TC, PC, VC, DP, W, ITSM)

    Dim TSA(3) As Double
    Dim TSB(3) As Double
    Dim DPR As Double
    Dim TR As Double
    Dim F0 As Double, F1 As Double, F2 As Double, F3 As Double
    ReDim BVIRs(3, 3) As Double


    'For Virial Coefficient between two compounds
    Dim ij As Integer                  'to determine couple of types
    Dim TSAIJ As Double, TSBIJ As Double
    Dim TKIJ As Double
    Dim TCIJ As Double
    Dim RPT As Double


    '**** Calculation of Virial Coefficient for Pure Component
    For I = 1 To NC
        DPR = 100000 * DP(I) ^ 2 * (PC(I) / 1.01325) / TC(I) ^ 2

        Select Case ITSM(I)
            Case 1
                TSA(I) = 0
                TSB(I) = 0
            Case 2
                TSA(I) = -2.14 * 10 ^ -4 * DPR - 4.308 * 10 ^ -21 * DPR ^ 8
                TSB(I) = 0
            Case 3
                TSA(I) = -2.188 * 10 ^ -4 * DPR ^ 4 - 7.831 - 10 ^ -21 * DPR ^ 8
                TSB(I) = 0
            Case 4
                TSA(I) = 0.0878
                TSB(I) = 0.00908 + 0.0006957 * DPR
            Case 5
                TSA(I) = 0.0878
                TSB(I) = 0.0525
            Case 6
```

```
            TSA(I) = 0.0279
            TSB(I) = 0.0229
        Case Else

    End Select
    TR = T / TC(I)
    F0 = 0.1445 - 0.33 / TR - 0.1385 / TR ^ 2 - 0.0121 / TR ^ 3 - 0.000607 / TR ^ 8
    F1 = 0.0637 - 0.331 / TR ^ 2 - 0.423 / TR ^ 3 - 0.008 / TR ^ 8
    F2 = 1# / TR ^ 6
    F3 = -1# / TR ^ 8

    BVIRs(I, I) = (F0 + W(I) * F1 + TSA(I) * F2 + TSB(I) * F3) * 83.14 * TC(I) / PC(I)

Next I


'**** Calculation of Virial Coefficient for two compounds
For I = 1 To NC
    For J = 1 To NC
        If I <> J Then
            TSAIJ = 0
            TSBIJ = 0
            If ITSM(I) = 1 Or ITSM(J) = 1 Then
            Else
                TSAIJ = 0.5 * (TSA(I) + TSA(J))
                TSBIJ = 0.5 * (TSB(I) + TSB(J))
            End If
            ij = ITSM(I) * 10 + ITSM(J)
            Select Case ij
                Case 56, 65
                    TKIJ = 0
                Case 12, 21, 13, 31, 24, 42, 25, 52, 34, 43, 35, 53, 46, 64
                    TKIJ = 0.1
                Case 14, 41, 15, 51
                    TKIJ = 0.15
                Case 26, 62, 36, 63
                    TKIJ = 0.35
                Case 16
                    TKIJ = 0.6114 - 2.7135 / VC(I) ^ 0.5
                 Case 61
                    TKIJ = 0.6114 - 2.7135 / VC(J) ^ 0.5
                Case Else
                    TKIJ = 1 - ((2 * (VC(I) * VC(J)) ^ (1 / 6) / (VC(I) ^ (1 / 3) + VC(J) ^ (1 / 3))) ^ 3)
            End Select

            TCIJ = (TC(I) * TC(J)) ^ (1 / 2) * (1 - TKIJ)
            TR = T / TCIJ

            RPT = 83.14 * ((VC(I) ^ (1 / 3) + VC(J) ^ (1 / 3)) ^ 3 / (4 * (PC(I) * VC(I) / TC(I) +
PC(J) * VC(J) / TC(J))))
```

```
            F0 = 0.1445 - 0.33 / TR - 0.1385 / TR ^ 2 - 0.0121 / TR ^ 3 - 0.000607 / TR ^ 8
            F1 = 0.0637 - 0.331 / TR ^ 2 - 0.423 / TR ^ 3 - 0.008 / TR ^ 8
            F2 = 1# / TR ^ 6
            F3 = -1# / TR ^ 8

            BVIRs(I, J) = (F0 + W(I) * F1 + TSAIJ * F2 + TSBIJ * F3) * RPT

        End If
      Next J
    Next I

    VirialCoefficient = BVIRs

End Function
```

A.2 Group Contributions Calculations Code

```
Function PressureCalculation(B, RowD As Long) As Double

    'Initial Properties
    Dim T As Double                 'Temperature of the system

    'Compounds
    'Initial Data
    Dim NC As Integer               'Number of Components
    ReDim XI(3) As Double           'Composition
    ReDim CID(3) As Integer         'Component ID
    ReDim NGI(3) As Integer         'Number of Groups per Compound
    ReDim TC(3) As Double           'Critical Temperature per Compound
    ReDim PC(3) As Double           'Critical Pressure per Compound
    ReDim VC(3) As Double           'Critical Volume per Compound
    ReDim W(3) As Double            'Acentric Factors per Compound
    ReDim VLIQR(3) As Double        'Liquid volume at a reference temperature in cc/mol
    ReDim TLIQR(3) As Double        'Reference temperature for liquid molar volume in K
    ReDim DP(3) As Double           'Dipole Moment
    ReDim ITSM(3) As Integer        'For Virial Coefficient Calculations

    'Groups
    ReDim NU(50, 3) As Long         'multiplicity of groups (degeneracy)
    ReDim NGQ(3, 50) As Integer     'Number of groups of each type in each molecule
    ReDim IGCL(3, 50) As Integer    'Group class for each group type
    ReDim GQ(3, 50) As Double       'Group charge for each group type
    ReDim GMU(3, 50) As Double      'Group dipole for each group type
    ReDim GAL(3, 50) As Double      'Group polarizability for each group type
    ReDim GV(3, 50) As Double       'Group volume for each type of group
    ReDim GA(3, 50) As Double       'Group area for each type of group
```

```
ReDim GR(3, 50) As Double      'Average radius for each type of group
ReDim GE(3, 50) As Double
ReDim GL(3, 50) As Double
ReDim GXi(3, 50) As Double
Dim NG As Integer              'Number of groups in a System compound
ReDim GQUANT(50) As Double     '
ReDim VG(50) As Double         'Group volume for each type of group
ReDim AG(50) As Double         'Group area for each type of group
ReDim RG(50) As Double         'Average radius for each type of group
ReDim ICG(50) As Double        'Group class for each group type
ReDim QG(50) As Double         'Group charge for each group type
ReDim DG(50) As Double         'Group dipole for each group type
ReDim PG(50) As Double         'Group polarizability for each group type
ReDim EG(50) As Double         '
ReDim LG(50) As Double         '
ReDim XiG(50) As Double        'Group Orbital Exponent
ReDim XG(50) As Double         'Group Composition

'Calculations
ReDim PSAT(3) As Double        'Vapor Pressure
ReDim BVIR(3, 3) As Double     'Virial Coefficient
ReDim DEL(3, 3) As Double      'Virial Coefficient
ReDim VLIQ(3) As Double        'Liquid molar volume
ReDim EJK(50, 50) As Double    'Group Energies

'Final Results

Dim HERT As Double
Dim PCALCs As Double

'*** Select Model
Model = "Knox"
'Model = "UNIFAC"


'**** Molecular Quantities
T = Tup(RowD)

NC = NCup(RowD)

'**** Composition
For I = 1 To NC
   XI(I) = XIup(I, RowD)
Next I

For I = 1 To NC

   CID(I) = CIDup(I, RowD)   'Compound ID
   '**** Compounds
   NGI(I) = NGIup(I, RowD)    'Number of Groups per Compound
   TC(I) = TCup(I, RowD)      'Critical Temperature per Compound
```

```
   PC(I) = PCup(I, RowD)      'Critical Pressure per Compound
   VC(I) = VCup(I, RowD)      'Critical Volume per Compound
   W(I) = Wup(I, RowD)       'Acentric Factor per Compound
   DP(I) = DPup(I, RowD)      'Dipole Moment per Compound
   ITSM(I) = ITSMup(I, RowD)   'Integer noting compound "class" for Tsonopoulos

   '**** Groups
   For J = 1 To NGIup(I, RowD)
      NGQ(I, J) = NGQup(I, J, RowD)      'Number of groups of each
      IGCL(I, J) = IGCLup(I, J, RowD)     'Group class for each group type
      GQ(I, J) = GQup(I, J, RowD)         'Group charge for each group type
      GMU(I, J) = GMUup(I, J, RowD)     'Group dipole for each group type
      GAL(I, J) = GALup(I, J, RowD)      'Group polarizability for each group type
      GV(I, J) = GVup(I, J, RowD)         'Group volume for each type of group
      GA(I, J) = GAup(I, J, RowD)         'Group area for each type of group
      GR(I, J) = GRup(I, J, RowD)          'Average radius for each type of group
      GE(I, J) = GEup(I, J, RowD)
      GL(I, J) = GLup(I, J, RowD)
      GXi(I, J) = GXiup(I, J, RowD)         'Group Orbital Exponential
   Next J

   If VLIQup(I, RowD) > VCup(I, RowD) Then
      VLIQ(I) = VCup(I, RowD)
   Else
      VLIQ(I) = VLIQup(I, RowD)
   End If
   PSAT(I) = PSATup(I, RowD)

Next I

'*** Second Virial Coefficient and detla
BVIR = VirialCoefficient(T, NC, TC, PC, VC, DP, W, ITSM)

For I = 1 To NC
   For J = 1 To NC
      DEL(I, J) = 2# * BVIR(I, J) - BVIR(I, I) - BVIR(J, J)
   Next J
Next I

'**** Call GroupProperties
Dim XX As Double
NG = 0
For I = 1 To NC
   For J = 1 To NGI(I)
      NG = NG + 1
      NU(NG, I) = NGQ(I, J)                 'multiplicity of groups (degeneracy)
      GQUANT(NG) = XI(I) * NGQ(I, J)
      XX = XX + GQUANT(NG)
      VG(NG) = GV(I, J)                    'Group volume for each type of group
      AG(NG) = GA(I, J)                    'Group area for each type of group
      RG(NG) = GR(I, J)                    'Average radius for each type of group
```

```
        ICG(NG) = IGCL(I, J)                    'Group class for each group type
        QG(NG) = GQ(I, J)                        'Group charge for each group type
        DG(NG) = GMU(I, J)                      'Group dipole for each group type
        PG(NG) = GAL(I, J)                       ‘Group polarizability for each group
        EG(NG) = GE(I, J)
        LG(NG) = GL(I, J)
        XiG(NG) = GXi(I, J)                     'Group exponential orbital
      Next J
    Next I

    For J = 1 To NG
      XG(J) = GQUANT(J) / XX                        'Group composition
    Next J


    '*** Calculation of Energies
EJK = GroupEnergies(B, RowD, RG, QG, DG, PG, NG, T, XiG)

    '*** Models to Calculate Pressure
PCALCs = Models(B, RowD, T, AG, VG, EJK, NU, PSAT, DEL, VLIQ, BVIR, XI, NG,
NC)

   PressureCalculation = PCALCs


End Function


Function GroupEnergies(BPAR, RowD As Long, RG, QG, DG, PG, NG As Integer, T As
Double, XiG)

    Dim RAD As Double
    Dim Eqq As Double
    Dim Equ As Double
    Dim Euu As Double
    Dim Eaq As Double
    Dim Eau As Double
    Dim Eaa As Double
    Dim Equa As Double
    Dim Erep As Double
    Dim Ro As Double

    Dim BNo As Integer

    ReDim PAR(10) As Double
    ReDim EJKs(50, 50) As Double

    BNo = 2
    For I = 2 To 9

      If CountB(I) = 1 Then
```

```
            PAR(I) = BPAR(BNo)
            BNo = BNo + 1
        Else
            PAR(I) = StickB(I)
        End If

    Next I

    For J = 1 To NG
        For k = 1 To NG
            RAD = RG(J) + RG(k)

            '**** positive correlation constants
            Eqq = PAR(2) * QG(J) * QG(k) / RAD
            Equ = PAR(3) * (QG(J) * DG(k) + QG(k) * DG(J)) / RAD ^ 2
            Euu = PAR(4) * (DG(k) * DG(J)) / RAD ^ 3

            Ro = (XiG(J) + XiG(k)) * RAD / 2
            Erep = PAR(9) * (Exp(-Ro) * (1 + Ro + (1 / 3) * Ro ^ 2)) ^ 2

            '**** negative correlation constants
            Eaq = (QG(J) ^ 2 * PG(k) + QG(k) ^ 2 * PG(J)) / RAD ^ 4
            Eaq = Eaq * PAR(5)
            Eau = PAR(6) * (DG(J) ^ 2 * PG(k) + DG(k) ^ 2 * PG(J)) / RAD ^ 6
            Eaa = PAR(7) * PG(J) * PG(k) / RAD ^ 6
            Equa = PAR(8) * (QG(J) * DG(J) * PG(k) + QG(k) * DG(k) * PG(J)) / RAD ^ 5

            EJKs(J, k) = Eqq + Equ + Euu + Eaq + Eau + Eaa + Erep + Equa

        Next k
    Next J

    GroupEnergies = EJKs

End Function
```

A.3 Pressure Calculations Code

```
Function Models(BPAR, RowD As Long, T As Double, AG, VG, EJK, NU, PSAT, DEL,
VLIQ, BVIR, XI, NG As Integer, NC As Integer)

    '**** For Knox Model
    ReDim ZK(50) As Double       'structural Contribution
    ReDim ZI(3) As Double        'degeneracy * area(ZK)
    ReDim VI(3) As Double        'degeneracy * v
    ReDim YKI(50, 3)             'for local groups fractions
    ReDim C(50, 50) As Double    'energies over NGs
    ReDim DEKL(50, 50) As Double

    '**** pure component group and local group fractions
```

```
ReDim XKL(50, 50) As Double          'results from XSOLVE
ReDim XKLI(50, 50, 50) As Double
ReDim YK(50) As Double
Dim SUM1 As Double
Dim SUM2 As Double
Dim SUM3 As Double
Dim SUM4 As Double
Dim SUM5 As Double
Dim SUM6 As Double
Dim SUM7 As Double

'**** For UNIFAC Model
ReDim ULGKI(50, 3) As Double
ReDim DLGKI(50, 3) As Double
ReDim ULGK(50) As Double
ReDim DLGK(50) As Double
ReDim QK(50) As Double               'area over NG
ReDim RK(50) As Double               'volume over NG
ReDim AKL(50, 50) As Double          'energies over NGs
ReDim PSIKL(50, 50) As Double        'exp energies /T over NGs
ReDim RI(3) As Double                'degeneracy * area(ZK)
ReDim QI(3) As Double                'degeneracy * volume (RK)
ReDim EL(3) As Double                'RI, QI
Dim Z As Double


'**** mixture properties
ReDim PHI(3) As Double
ReDim YI(3) As Double
ReDim ELNGM(3) As Double

'**** Calculate equilibrium total pressure
ReDim GAMMA(3) As Double
ReDim PSIMP(3) As Double
Dim SUM As Double
ReDim YV(3) As Double
Dim MaxIT As Long
Dim NIT As Long
Dim PTEST As Double
Dim SUMYYD As Double
ReDim FUG(3) As Double

'Calculated Pressure
Dim PCALC As Double


'*** Calculation of Knox Z's or UNIFAC R's and Q's


For J = 1 To NG
   Select Case Model
```

```
        Case "Knox"
            ZK(J) = BPAR(1) * AG(J)
        Case "UNIFAC"
            QK(J) = BPAR(1) * AG(J)
            RK(J) = VG(J)
        Case Else

    End Select
Next J

For k = 1 To NG
    For L = 1 To NG
        Select Case Model
            Case "Knox"
                DEKL(k, L) = EJK(k, L) + EJK(k, L) - EJK(L, L) - EJK(k, k)
                C(k, L) = Exp(-DEKL(k, L) / T)
            Case "UNIFAC"
                AKL(k, L) = EJK(k, L) - EJK(L, L)
                PSIKL(k, L) = Exp(-1# * AKL(k, L) / T)
            Case Else

        End Select
    Next L
Next k

'**** Calculation of molecular structural parameters
For I = 1 To NC
    'Knox
    ZI(I) = 0#
    VI(I) = 0#

    'UNIFAC
    RI(I) = 0#
    QI(I) = 0#

    For k = 1 To NG
        Select Case Model
            Case "Knox"
                ZI(I) = ZI(I) + NU(k, I) * ZK(k)
                VI(I) = VI(I) + NU(k, I) * VG(k)
            Case "UNIFAC"
                RI(I) = RI(I) + NU(k, I) * RK(k)
                QI(I) = QI(I) + NU(k, I) * QK(k)
            Case Else
        End Select

    Next k

    If Model = "UNIFAC" Then
        Z = 10
        EL(I) = (Z / 2#) * (RI(I) - QI(I)) - (RI(I) - 1#)
```

```
   End If

Next I

'**** calculation of pure component group and local group fractions
Select Case Model
   Case "Knox"

      For I = 1 To NC
         For k = 1 To NG
            YK(k) = NU(k, I) * ZK(k) / ZI(I)
         Next k

         XKL = XSOLVE(YK, C, NG)

         For k = 1 To NG
            YKI(k, I) = YK(k)

            For L = 1 To NG
               XKLI(k, L, I) = XKL(k, L)
            Next L

         Next k

      Next I


   Case "UNIFAC"
      For I = 1 To NC
         For k = 1 To NG
            YK(k) = NU(k, I) * QK(k) / QI(I)
         Next k

         For k = 1 To NG

            SUM1 = 0#
            SUM2 = 0#
            SUM4 = 0#
            SUM5 = 0#
            SUM7 = 0#

            For m = 1 To NG
               SUM1 = SUM1 + YK(m) * PSIKL(m, k)
               SUM4 = SUM4 + YK(m) * PSIKL(m, k) * AKL(m, k) / T
               SUM3 = 0#
               SUM6 = 0#

               For n = 1 To NG
                  SUM3 = SUM3 + YK(n) * PSIKL(n, m)
                  SUM6 = SUM6 + YK(n) * PSIKL(n, m) * AKL(n, m) / T
               Next n
```

```
                SUM2 = SUM2 + YK(m) * PSIKL(k, m) / SUM3
                SUM5 = SUM5 + YK(m) * PSIKL(k, m) * AKL(k, m) / (T * SUM3)
                SUM7 = SUM7 + YK(m) * PSIKL(k, m) * SUM6 / (SUM3 * SUM3)

            Next m
            ULGKI(k, l) = QK(k) * (1# - SUM2 - Log(SUM1))
            DLGKI(k, l) = QK(k) * (SUM4 / SUM1 + SUM5 - SUM7)
        Next k
    Next l

  Case Else

End Select

'**** calculation of mixture properties
Select Case Model
  'by Guggenheim Analogy Group (GAG) model
  Case "Knox"
    SUM1 = 0#
    SUM2 = 0#
    For l = 1 To NC
      SUM1 = SUM1 + VI(l) * XI(l)
      SUM2 = SUM2 + ZI(l) * XI(l)
    Next l

    For l = 1 To NC
      PHI(l) = VI(l) * XI(l) / SUM1
      YI(l) = ZI(l) * XI(l) / SUM2
    Next l

    For k = 1 To NG
       SUM3 = 0#
       For l = 1 To NC
         SUM3 = SUM3 + XI(l) * NU(k, l)
       Next l
       YK(k) = ZK(k) * SUM3 / SUM2
    Next k

    XKL = XSOLVE(YK, C, NG)

    For l = 1 To NC
      If XI(l) = 0# Then
        ELNGM(l) = 0#
      Else
        ELNGM(l) = Log(PHI(l) / XI(l)) + (1# - PHI(l) / XI(l))
        ELNGM(l) = ELNGM(l) - (ZI(l) / 2#)  *
                        (Log(PHI(l) / YI(l)) - PHI(l) / YI(l) + 1#)
        For k = 1 To NG
          If NU(k, l) <> 0 Then
            ELNGM(l) = ELNGM(l) - (ZK(k) * NU(k, l) / 2#) *
                            Log(XKLI(k, k, l) / YKI(k, l))
```

```
               ELNGM(I) = ELNGM(I) + (ZK(k) * NU(k, I) / 2#) *
                                Log(XKL(k, k) / YK(k))
            End If
         Next k
      End If
   Next I
   HERT = 0#
   For I = 1 To NC
      For k = 1 To NG
         For L = 1 To NG
            HERT = HERT + (ZK(k) * XI(I) * NU(k, I) / 2#) * (Log(C(k, L))) *
                     (XKLI(k, L, I) - XKL(k, L))
         Next L
      Next k
   Next I


Case "UNIFAC"
   SUM1 = 0#
   SUM2 = 0#
   SUM3 = 0#
   For J = 1 To NC
      SUM1 = SUM1 + XI(J) * RI(J)
      SUM2 = SUM2 + XI(J) * QI(J)
      SUM3 = SUM3 + XI(J) * EL(J)
   Next J

   For I = 1 To NC
      PHI(I) = XI(I) * RI(I) / SUM1
      YI(I) = XI(I) * QI(I) / SUM2
      ELNGM(I) = Log(RI(I) / SUM1) + (Z * QI(I) / 2#)
                     Log(QI(I) * SUM1 / (RI(I) * SUM2)) +
                     EL(I) - SUM3 * RI(I) / SUM1
   Next I

   For k = 1 To NG
      SUM1 = 0#
      For I = 1 To NC
         SUM1 = SUM1 + NU(k, I) * QK(k) * XI(I)
      Next I
      YK(k) = SUM1 / SUM2
   Next k

   For k = 1 To NG
      SUM1 = 0#
      SUM2 = 0#
      SUM4 = 0#
      SUM5 = 0#
      SUM7 = 0#
      For m = 1 To NG
         SUM1 = SUM1 + YK(m) * PSIKL(m, k)
```

```
            SUM4 = SUM4 + YK(m) * PSIKL(m, k) * AKL(m, k) / T
            SUM3 = 0#
            SUM6 = 0#
               For n = 1 To NG
                  SUM3 = SUM3 + YK(n) * PSIKL(n, m)
                  SUM6 = SUM6 + YK(n) * PSIKL(n, m) * AKL(n, m) / T
               Next n
            SUM2 = SUM2 + YK(m) * PSIKL(k, m) / SUM3
            SUM5 = SUM5 + YK(m) * PSIKL(k, m) * AKL(k, m) / (T * SUM3)
            SUM7 = SUM7 + YK(m) * PSIKL(k, m) * SUM6 / (SUM3 * SUM3)
         Next m
         ULGK(k) = QK(k) * (1# - SUM2 - Log(SUM1))
         DLGK(k) = QK(k) * (SUM4 / SUM1 + SUM5 - SUM7)
      Next k

      For I = 1 To NC
         For k = 1 To NG
            ELNGM(I) = ELNGM(I) + NU(k, I) * (ULGK(k) - ULGKI(k, I))
         Next k
      Next I
      HERT = 0#
      For I = 1 To NC
         For k = 1 To NG
            HERT = HERT + XI(I) * NU(k, I) * (DLGK(k) - DLGKI(k, I))
         Next k
      Next I

   Case Else

End Select


'**** Calculate equilibrium total pressure
PCALC = 0#

For I = 1 To NC
   GAMMA(I) = Exp(ELNGM(I))
   PSIMP(I) = XI(I) * GAMMA(I) * PSAT(I)
   PCALC = PCALC + PSIMP(I)
Next I

SUM = 0#
For I = 1 To NC
   YV(I) = PSIMP(I) / PCALC
   SUM = SUM + YV(I)
Next I

'**** Start Fugacity Iteration
TOLP = 0.001
MaxIT = 10
NIT = 1
```

```
5  PTEST = PCALC
   PCALC = 0#

   For I = 1 To NC
      SUMYYD = 0#
      For J = 1 To NC
         For k = 1 To NC
            SUMYYD = SUMYYD + YV(J) * YV(k) * (2# * DEL(J, I) - DEL(J, k)) / 2#
         Next k
      Next J
      FUG(I) = Exp(((VLIQ(I) - BVIR(I, I)) *
               (PTEST - PSAT(I)) - SUMYYD * PTEST) / (83.14 * T))
      PCALC = PCALC + PSIMP(I) * FUG(I)
   Next I

   SUM = 0#
   For I = 1 To NC
      YV(I) = PSIMP(I) * FUG(I) / PCALC
     SUM = SUM + YV(I)
   Next I
   NIT = NIT + 1

   If NIT - MaxIT <= 0 Then

      If (Abs(PCALC - PTEST) / PTEST) > TOLP Then
         GoTo 5
      End If
    End If

   PCALC = PCALC * 100     'convert from bar to KPa

   Models = PCALC

End Function
```

A.4 Regression Code

```
Function RegressionSOLVE(RowD As Long, NParm As Integer, B, RIT As Long,
RMaxIT As Long)

   'Counter for the iterations
   Dim NoLoop As Long

   'Convergence points
   Dim Conv1 As Double
   Dim Conv2 As Double
   Dim Conv3 As Double
   Dim POIN01 As Double
   Dim POI001 As Double

   'SQR totals
```

```
Dim SUMSQ As Double

'Results and datapoints
ReDim Zs(1000000) As Double
ReDim Zls(1000000) As Double
Dim ZZ As Double

'calculated parameters
ReDim Bl(10) As Double

Dim DLT As Double

'parameters
Dim NParm1 As Integer

'for the loops
Dim J1 As Integer, J2 As Integer
Dim J3 As Integer, J4 As Integer
Dim J As Long, I As Integer
'Dim L As Integer

'partial Derivatives
Dim PDERIV(10, 1000000) As Double

'Regression Variables
ReDim WORK(10) As Double
ReDim SCALES(10) As Double
ReDim GRAD(10) As Double
ReDim DIAG(10) As Double
'ReDim NORMAL(10, 10) As Double
Dim RATIO As Double

'for the angle
Dim CANGLE As Double
Dim SCALEF As Double

'Convergence Test
Dim DIFF As Double

'Convergence
CONV(4) = 10
CONV(5) = 0.01
CONV(3) = 0.01
CONV(1) = 0.00001
CONV(2) = 0.00001

Conv1 = CONV(1)
Conv2 = CONV(2)
Conv3 = Conv1 '+ 1

If CONV(4) < 0 Then CONV(4) = 10
```

```
NUFAC = CONV(4)
If CONV(5) < 0 Then CONV(5) = 0.01
LAMBDA = CONV(5)

POIN01 = CONV(3)
POI001 = POIN01 / 10#

If CONV(1) < 0# Then CONV(1) = 0.00001
If CONV(2) < 0# Then CONV(2) = 0.00001
Conv1 = CONV(1)
Conv2 = CONV(2)
Conv3 = Conv1 + 1

NParm1 = NParm + 1

NData = RowD

'Compute the sum of SQRS (SUMSQ) for the first set of values
SUMSQ = 0#
For RowD = 1 To NData

   Zs(RowD) = PressureCalculation(B, RowD)
      SUMSQ = SUMSQ + (Ys(RowD) - Zs(RowD)) ^ 2

Next RowD

If dbg = True Then
   End
End If

If SUMSQ = 0 Then
   MsgBox ("ERROR SUMSQ = 0")
   RegressionSOLVE = BI
   Exit Function
End If

'Initialize Normal(j, i)
For I = 1 To NParm1
   For J = 1 To NParm1
      NORMAL(J, I) = 0
   Next J
Next I

'Calculate the partial Derivatives with respect
'to the parameter values for each set of data points
'store in PDERIV

For J = 1 To NParm

   DLT = POIN01 * Abs(B(J))
```

```
    If DLT = 0 Then DLT = POI001
    B(J) = B(J) + DLT

    For RowD = 1 To NData

        ZZ = PressureCalculation(B, RowD)
        PDERIV(J, RowD) = (ZZ - Zs(RowD)) / DLT

    Next RowD

    B(J) = B(J) - DLT

Next J

For J1 = 1 To NData
    For J2 = 1 To NParm
        WORK(J2) = PDERIV(J2, J1)
    Next J2
    WORK(NParm1) = Ys(J1) - Zs(J1)
    For J3 = 1 To NParm1
        For J4 = J3 To NParm1
            NORMAL(J4, J3) = NORMAL(J4, J3) + WORK(J3) * WORK(J4)
        Next J4
    Next J3

Next J1

'Start the procedure to estimate the parameters
LAMBDA = LAMBDA / NUFAC
For J1 = 1 To NParm
    J2 = J1 + 1
    For J3 = J2 To NParm1
        NORMAL(J1, J3) = NORMAL(J3, J1)
    Next J3
    DIAG(J1) = NORMAL(J1, J1)
Next J1
DIAG(NParm1) = NORMAL(NParm1, NParm1)

'This loop sees if new estimates have reduced the residual
'sum of squares. If not and the angle is less than 30 degrees,
'add only 1/2 off the correction previously used and recompute
'the residual sum of squares.
'If the angle exceeds 30 degrees, multiply lambda by NUFAC
'and solve normal equations again,
'then recompute the residual sum of squares

'these two variables are just to assure that for the
'first loop SCALEF = 1
'and the NORMAL is first calculated

CANGLE = 0.8
```

```
    NoLoop = 0
    SUMSQR = SUMSQ * Conv3 + 1

    Do While SUMSQR / SUMSQ >= Conv3
       NoLoop = NoLoop + 1
       If NoLoop > 20 Then
          MsgBox "Number of loops exceeded"
          End

       End If

       If CANGLE > 0.866 Then
10           SCALEF = SCALEF / 2#
       Else
          If NoLoop <> 1 Then
             LAMBDA = LAMBDA * NUFAC
             For J1 = 1 To NParm
                J2 = J1 + 1
                For J3 = J2 To NParm1
                   NORMAL(J3, J1) = NORMAL(J1, J3)
                Next J3
                NORMAL(J1, J1) = DIAG(J1)
             Next J1
             NORMAL(NParm1, NParm1) = DIAG(NParm1)
          End If

          SCALES = CalculateSCALE(NParm)
          GRAD = CalculateGRAD(NParm, NParm1, SCALES)

          'first loop to calculate NORMAL
          RATIO = CalculateRATIO(NParm, NParm1, LAMBDA)

          'second loop
          WORK = CalculateWORK(NParm, NParm1)
          'angle

          CANGLE = CalculateANGLE(NParm, WORK, GRAD)

          'Initialize a scale factor SCALEF,

          SCALEF = 1# '(point 380)

       End If

       'Calculate new parameters with SCALEF

       For J = 1 To NParm
          BI(J) = B(J) + SCALEF * WORK(J) / SCALES(J)

          If BI(J) < BMIN(J) Then
             GoTo 10
```

```
        End If
        If BI(J) > BMAX(J) Then
           GoTo 10
        End If
     Next J

     SUMSQR = 0#
     For J = 1 To NData
        ZIs(J) = PressureCalculation(BI, J)
        SUMSQR = SUMSQR + (Ys(J) - ZIs(J)) ^ 2
     Next J


  Loop

  'Once the new estimates have been found
  'which reduce the residual sum of squares
  'and these estimates are in BI(),
  'the corresponding residuals and the
  'residual sum of squares
  'are in ZIs()and SUMSQR respectively
  'perform the converge test

  For J = 1 To NData
     Zs(J) = ZIs(J)
  Next J

  'ERROR2 will contain the number of parameters
  'that fail the convergence test. ERROR will be set
  'to -5, if ERROR2 is greater than 0

  For J = 1 To NParm
     DIFF = Abs(BI(J) - B(J))
     B(J) = BI(J)
     If DIFF / (1 * 10 ^ -2) > Conv2 Then
        ERROR2 = ERROR2 + 1
     End If

  Next J
  DIFF = Abs(SUMSQR - SUMSQ)
  SUMSQ = SUMSQR

  RowD = NData
  If SUMSQ <> 0 Then
     ERROR = 0
     If DIFF / SUMSQ > Conv1 Then ERROR = -1
     If ERROR2 > 0 Then ERROR = -5
        RegressionSOLVE = BI
        Exit Function
     End
```

```
   Else
      ERROR = 0
      MsgBox ("FIN " & ERROR)
      RegressionSOLVE = BI
      RowD = NData
      Exit Function
   End If

End Function
Function CalculateSCALE(NParm As Integer)

   'Scale the Matrix and save the gradient vector
   'for future in computing the angle between the gradient
   'and the GAUSS - NEWTON - MARQUARDT  vector

   ReDim SCLS(10) As Double
   For J = 1 To NParm
      SCLS(J) = Sqr(NORMAL(J, J))
   Next J
   CalculateSCALE = SCLS

End Function
Function CalculateANGLE(NParm As Integer, WORK, GRAD) As Double

   'Compute the cosine of the angle between
   'the gradient vector GRAD() and the correction vector WORK()

   'to be used in the event the angle between the vectors
   'is greater than 30 degrees
   '(cosine of the angle less than 0.866)

   Dim SA As Double, SB As Double, SC As Double
   Dim CNGL As Double

   Dim J As Integer

   SA = 0
   SB = 0
   SC = 0

   For J = 1 To NParm
      SA = SA + WORK(J) * GRAD(J)
      SB = SB + WORK(J) ^ 2
      SC = SC + GRAD(J) ^ 2
   Next J

   CNGL = Abs(SA / (Sqr(SB * SC)))

   CalculateANGLE = CNGL

End Function
```

```
Function CalculateGRAD(NParm As Integer, NParm1 As Integer, SCALES)

   Dim J2 As Integer, J1 As Integer
   ReDim GRD(10) As Double

   For J1 = 1 To NParm
      For J2 = J1 To NParm
         NORMAL(J2, J1) = NORMAL(J2, J1) / (SCALES(J1) * SCALES(J2))
      Next J2
      NORMAL(NParm1, J1) = NORMAL(NParm1, J1) / SCALES(J1)
      GRD(J1) = NORMAL(NParm1, J1)
   Next J1

   'Normal Equations now Scaled.
   'the GRAS() vector contains the Gradient vector

   CalculateGRAD = GRD

End Function
Function CalculateRATIO(NParm As Integer, NParm1 As Integer, LAMBDA As Double)

   Dim J1 As Integer, J2 As Integer
   Dim I As Integer, J As Integer

   Dim RATIOs As Double

   For J1 = 1 To NParm
      NORMAL(J1, J1) = NORMAL(J1, J1) + LAMBDA
   Next J1

   For I = 1 To NParm
      J1 = I + 1
      For J2 = 1 To I
         If NORMAL(J2, J2) < 0# Then
            'Singular Matrix was encountered
            'generate error code -2 and terminate

            ERROR2 = I
            ERROR = -2
            MsgBox ("NORMAL <0 ")
            CalculateRATIO = -1
            Exit Function
         Else
            RATIOs = NORMAL(J1, J2) / NORMAL(J2, J2)
            For J = J1 To NParm1
               NORMAL(J, J1) = NORMAL(J, J1) - RATIOs * NORMAL(J, J2)
            Next J
            NORMAL(J1, J2) = RATIOs
         End If
      Next J2
   Next I
```

```
   CalculateRATIO = RATIOs

End Function
Function CalculateWORK(NParm As Integer, NParm1 As Integer)

   Dim J2 As Integer, J3 As Integer, J4 As Integer
   Dim J As Integer, I As Integer
   Dim L As Integer

   ReDim WRK(10) As Double

   WRK(NParm) = NORMAL(NParm1, NParm)
   If NParm > 1 Then
      J2 = NParm - 1
      I = J2
      J = NParm1
      For J3 = 2 To NParm
         WRK(J2) = NORMAL(J, I)
         L = NParm
         For J4 = 2 To J3
            J = J - 1
            WRK(J2) = WRK(J2) - WRK(L) * NORMAL(J, I)
            L = L - 1
         Next J4
         J2 = J2 - 1
         J = NParm1
         I = I - 1
      Next J3
   End If

   'Correction Vector is stored in WORK()

   CalculateWORK = WRK

End Function
```

APPENDIX B

SYSTEMS SUMMARY

This appendix presents a summary of the database used to perform the calculations for the model. The summary includes the number of systems and datapoints organized by chemical categories and their mixtures. It also reports their range of temperature and pressure as well as the number of isothermal and isobaric systems.

Table B.1 Chemical Group Systems

Compound	Systems	Datapoint
ALKANE	27	402
ALKENE	7	196
ALCOHOL	63	1104
ETHER	14	180
ALDEHYDE	0	0
KETONE	6	159
CARBOXYLIC ACID	4	160
ESTER	21	364
AMINE	13	235
AMIDE	0	0
NITRILE	9	145
NITRO	10	212
FLUORIDE	0	0
INORGANIC	12	316
DIAMINE	0	0
TRIAMINE	0	0
WATER	12	0

Table B.2 Chemical Group Summary

Compound	*Isobaric*	*Isothermal*	*Tmax (K)*	*Tmin (K)*	*Pmax (KPa)*	*Pmin (KPa)*
ALKANE	0	27	493.15	293.15	4145.00	20.69
ALKENE	0	7	326.18	313.10	1647.30	12.68
ALCOHOL	21	41	408.68	293.15	512.50	2.81
ETHER	0	14	373.55	323.35	3160.00	129.00
ALDEHYDE	0	0	0.00	0.00	0.00	0.00
KETONE	3	2	375.11	293.15	200.10	13.00
CARBOXYLIC ACID	2	2	343.20	323.20	79.71	7.61
ESTER	8	13	404.20	323.15	356.10	64.67
AMINE	0	13	373.15	283.15	256.42	5.80
AMIDE	0	0	0.00	0.00	0.00	0.00
NITRILE	0	9	333.15	313.15	117.79	12.55
NITRO	10	0	387.16	337.58	101.30	101.30
FLUORIDE	0	0	0.00	0.00	0.00	0.00
INORGANIC	1	10	383.95	293.15	514.19	2.30
DIAMINE	0	0	0.00	0.00	0.00	0.00
TRIAMINE	0	0	0.00	0.00	0.00	0.00
WATER	0	0	0.00	0.00	0.00	0.00

Table B.3 Mixture Systems

C1	*C2*	*C3*	*Systems*	*Datapoints*	*Isobaric*	*Isothermal*
ALKANE	**ALKANE**		3	38	0	3
ALCOHOL	**ALKANE**		8	106	0	8
ALKENE	**ALCOHOL**		4	92	0	4
ALCOHOL	**ALCOHOL**		8	121	4	4
ETHER	**ALCOHOL**		8	101	0	8
KETONE	**ALCOHOL**		4	101	3	1
ESTER	**ALCOHOL**		5	89	4	1
NITRO	**ALCOHOL**		6	128	6	0
ALCOHOL	**INORGANIC**		9	198	0	9
ALKANE	**ETHER**		1	11	0	1
ALKENE	**ESTER**		2	81	0	2
ALKENE	**ETHER**		1	23	0	1
AMINE	**ALKANE**		9	180	0	9
AMINE	**ESTER**		2	30	0	2
AMINE	**KETONE**		1	13	0	1
AMINE	**NITRILE**		1	12	0	1
CARBOXYLIC ACID	**ESTER**		2	26	0	2
ESTER	**ESTER**		3	27	0	3
INORGANIC	**ETHER**		1	16	0	1
NITRILE	**ALKANE**		2	23	0	2
NITRILE	**NITRILE**		3	55	0	3
ESTER	**NITRO**		4	84	4	0
INORGANIC	**CARBOXYLIC ACID**	**CARBOXYLIC ACID**	1	67	1	0
ETHER	**ALCOHOL**	**INORGANIC**	3	29	0	3
KETONE	**ALCOHOL**	**INORGANIC**	1	45	0	0
ALCOHOL	**ALCOHOL**	**INORGANIC**	4	146	1	3
ALKANE	**ALCOHOL**	**ALCOHOL**	1	6	0	1
TOTAL			**97**	**1848**	**23**	**73**

Table B.4 Mixture Summary

C1	*C2*	*C3*	*Tmax (K)*	*Tmin (K)*	*Pmax (KPa)*	*Pmin (KPa)*
ALKANE	**ALKANE**		493.15	283.15	4145	2.3
ALCOHOL	**ALKANE**		308.7	293.15	207.50	5.80
ALKENE	**ALCOHOL**		493.15	328.1	4145.00	974.80
ALCOHOL	**ALCOHOL**		326.16	326.13	652.64	12.68
ETHER	**ALCOHOL**		408.68	298.15	3160.00	2.81
KETONE	**ALCOHOL**		375.11	293.15	512.50	5.80
ESTER	**ALCOHOL**		404.2	669.35	101.32	170.30
NITRO	**ALCOHOL**		334.45	334.45	99.80	99.00
ALCOHOL	**INORGANIC**		387.16	337.58	101.30	101.30
ALKANE	**ETHER**		338.15	308.15	103.30	5.62
ALKENE	**ESTER**		323.15	293.15	512.50	79.43
ALKENE	**ETHER**		323.15	323.15	93.13	64.67
AMINE	**ALKANE**		313.1	313.1	1647.30	891.60
AMINE	**ESTER**		373.15	283.15	256.42	5.80
AMINE	**KETONE**		348.09	297.98	189.63	12.57
AMINE	**NITRILE**		323.15	323.15	96.71	84.67
CARBOXYLIC ACID	**ESTER**		323.15	323.15	85.86	38.96
ESTER	**ESTER**		343.2	323.2	79.71	7.61
INORGANIC	**ETHER**		373.17	353.15	356.10	121.50
NITRILE	**ALKANE**		293.15	293.15	514.19	2.30
NITRILE	**NITRILE**		313.15	313.15	117.79	12.55
ESTER	**NITRO**		333.15	313.15	49.15	12.66
INORGANIC	**CARBOXYLIC ACID**	**CARBOXYLIC ACID**	374.69	350.28	101.30	101.30
ETHER	**ALCOHOL**	**INORGANIC**	383.95	374.24	101.30	101.30
KETONE	**ALCOHOL**	**INORGANIC**	373.55	333.55	2541.00	273.00
ALCOHOL	**ALCOHOL**	**INORGANIC**	362.51	333.26	200.10	76.26
ALKANE	**ALCOHOL**	**ALCOHOL**	392.8	323.15	101.30	20.92
TOTAL			**493.15**	**283.15**	**4145.00**	**2.3**

APPENDIX C

REFERENCES FOR THE DATABASE ARTICLES

The database used in this research is the compilation of a set of VLE articles. The references for these articles are shown in Table C.1.

Table C.1 Reference Table.

Ref.	*Title*	*Authors*	*Year*	*Volume*	*Pages*	*Publication*	*Systems*
1	Isobaric vapour–liquid equilibria data for the binary system 1-propanol + 1-pentanol and isobaric vapour–liquid–liquid equilibria data for the ternary system water + 1-propanol + 1-pentanol at 101.3 kPa	Juan Carlos Asensi, J.C., Molto, J., Olaya, M.M., Ruiz & F. Gomis, V.	2002	46	675-678	Journal of Chemical and Engineering Data	3
2	Vapor-Liquid Equilibrium of Propan-2-ol + Propan-1-ol + Sodium Iodide at 298.15 K	Yamamoto, H. & Shibata,J.	1999	203	237–252	Fluid Phase Equilibria	5
3	Vapour-liquid equilibria. X. The ternary system cyclohexane-methanol-acetone at 293.15 and 303.15 K	Oracz, P., Góral, M., Wilczek-Vera, G. & Warycha, S.	1996	45	887-892	Journal of Chemical and Engineering Data	4
4	Isothermal vapor–liquid equilibria for the system ethanol and n-hexane in the near critical region	Jungha, S., Jongcheon, Lee. & Hwayong, Kim.,	2001	163	99–108	Fluid Phase Equilibria	2
5	Isothermal vapor–liquid equilibria for ethanol and n-pentane system at the near critical region	Jungha, S., Jongcheon, Lee. & Hwayong, Kim.,	2000	175	139–152	Fluid Phase Equilibria	6
7	Isobaric vapor-liquid equilibria of the methanol, methyl acetate and methyl acrylate system at atmospheric pressure	Chein-Hsiun, Tu., Yuh-Shen, Wu. & Tzu-Ling Liu	1997	220	41-46	Fluid Phase Equilibria	2
8	Isobaric vapor-liquid equilibria of the system ethyl acetate/n-butanol at 70.5 and 94.0 kPa	Darwish., NA. & Al-Khateib., A.A.,	1996	200	329–336	Fluid Phase Equilibria	2
13	The association of normal and tertiary butylamine in mixtures with n-hexane according to isothermal vapour pressure measurements	Wolff, H.,Landeck H., Frerichs, H.P. & Wolff, E.,	1995	49	38-42	Journal of Chemical and Engineering Data	1
17	High-Pressure Vapor-Liquid Equilibrium for Dimethyl Ether + Ethanol and Dimethyl Ether + Ethanol + Water	Elbaccouch,M.M & Elliott, J.R.,	2000	49	11-17	Journal of Chemical and Engineering Data	3
18	High-Pressure Vapor-Liquid Equilibria in the Systems Nitrogen + Dimethyl Ether, Methanol + Dimethyl Ether, Carbon Dioxide + Dimethyl Ether + Methanol, and Nitrogen + Dimethyl Ether + Methanol	Teodorescu, M. & Rasmussen, P.,	2001	46	675-678	Journal of Chemical and Engineering Data	3
20	High-Pressure Vapor-Liquid Equilibria for Propane + 2-Butanol, Propylene + 2-Butanol, and Propane + 2-Butanol + 2-Propanol	Gros, H.P., Zabaloy, M.S. & Brignole, E.A.,	1996	41	237–252	Journal of Chemical and Engineering Data	1
21	High-Pressure Vapor-Liquid Equilibrium for Dimethyl Ether + 2-Propanol and Dimethyl Ether + 2-Propanol + Water	Elbaccouch, M.M. & Elliott, J.R. Jr.,	2001	46	887-892	Journal of Chemical and Engineering Data	3
24	Vapour–liquid equilibrium for the 1-butene + methanol, + ethanol, + 2-propanol, + 2-butanol and + 2-methyl-2-propanol systems at 326 K	Laakkonen, M., Pokki, JP., Uusi-Kyyny,P. & Aittamaa, J.,	2003	203	99–108	Journal of Chemical and Engineering Data	3

Table C.1 Reference Table (Continued)

Ref.	*Title*	*Authors*	*Year*	*Volume*	*Pages*	*Publication*	*Systems*
25	Vapor-Liquid Equilibria in Quaternary Mixtures of Dimethyl Ether n-Butane + Ethanol + Water	Dahlhoff, G. & Pfennig, A.,	2000	45	887-892	Journal of Chemical and Engineering Data	4
29	Vapor–liquid equilibria of the binary mixtures 2-butanone+t-pentanol, t-pentanol+butyl acetate and 2-propanol+diethyl ketone at 101.3 kPa	Wen, TY., Tang , M. & Chen, Y.P.	1999	163	99–108	Fluid Phase Equilibria	2
30	Vapor–liquid equilibria for binary mixtures of nitroethane with aliphatic alcohols (C1–C4) at 101.3 kPa	Tu, C.-H., Wang,W.-F., Hsian,H.-Y. & Chou, Y.-T.,	2000	175	139–152	Fluid Phase Equilibria	6
31	Vapor–liquid equilibria for the system 1-propanol + n-hexane near the critical region	Oha, B.C., Kima, Y., Shin, H.G. & Kima, H.,	2004	220	41-46	Fluid Phase Equilibria	2
32	Vapor–liquid equilibria and excess molar volumes of diethylamine(1) + acetone(2) and diethylamine(1) + acetonitrile(2) binary systems	Chaudhari, S.K.,	2002	200	329–336	Fluid Phase Equilibria	2
33	Vapor-Liquid Equilibrium and Excess Systems Propane + Dimethyl Ether and at Temperatures from (298 to 323) K	Horstmann, S., Birke,G. & Fischer, Kai.,	2004	49	38-42	Journal of Chemical and Engineering Data	1
34	Vapor-Liquid Equilibrium for Acetonitrile + Propanenitrile and 1-Pentanamine + 1-Methoxy-2-propanol	Antosik, M., Gałka,M. & Malanowski.S.K.,	2004	49	11-17	Journal of Chemical and Engineering Data	3
36	Isothermal and isobaric vapor + liquid equilibria of N,N-dimethylformamide + n-propanol + n-butanol	Wang,C., Li,H., Zhu,L. & Shijun Han	2001	189	119–127	Fluid Phase Equilibria	3
38	Phase equilibria for binary n-alkanenitrile-n-alkane mixtures. III. Vapour-liquid phase equilibria for propanenitrile with C5-C8 n-alkanes	McLure a, I.A., Arriaga-Colina, J.L. & Armitage, D.A.,	1997	127	237-249	Fluid Phase Equilibria	2
39	Isothermal vapor-liquid equilibria for mixtures of methyl tert-butyl ether, methyl acetate, and ethyl acetate	Lee,M.J., Hsiao, C.C. & Lin, H.M.,	1997	137	193-207	Fluid Phase Equilibria	3
44	Vapor-Liquid Equilibria of the Systems Ethyl Ethanoate 2-Methyl-2-butanol, 2-Methyl-1-propanol + 3-Methyl-Cyclohexanol + Benzyl Alcohol at 101.32 Kpa	Senol, A.,	1998	43	763-769	Journal of Chemical and Engineering Data	2
53	Vapor-liquid equilibria of the ternary system methanol + acetone + methyl vinyl ketone at atmospheric pressure	Tu, C.H., Wu, Y.S. & Liu, T.L.,	1997	131	181-188	Fluid Phase Equilibria	1
54	Isobaric vapor-liquid equilibria of 3-methyl-1-butanol with methanol and vinyl acetate at 101.3 KPa	Resa, J.M.,Gonzalez, C., Moradillo,B. & Ruiz,A.,	1997	132	205-213	Fluid Phase Equilibria	2

Table C.1 Reference Table (Continued)

Ref.	*Title*	*Authors*	*Year*	*Volume*	*Pages*	*Publication*	*Systems*
25	Vapor-Liquid Equilibria in Quaternary Mixtures of Dimethyl Ether n-Butane + Ethanol + Water	Dahlhoff, G. & Pfennig, A.,	2000	45	887-892	Journal of Chemical and Engineering Data	4
29	Vapor–liquid equilibria of the binary mixtures 2-butanone+t-pentanol, t-pentanol+butyl acetate and 2-propanol+diethyl ketone at 101.3 kPa	Wen, TY., Tang , M. & Chen, Y.P.	1999	163	99–108	Fluid Phase Equilibria	2
30	Vapor–liquid equilibria for binary mixtures of nitroethane with aliphatic alcohols (C1–C4) at 101.3 kPa	Tu, C.-H., Wang,W.-F., Hsian,H.-Y. & Chou, Y.-T.,	2000	175	139–152	Fluid Phase Equilibria	6
31	Vapor–liquid equilibria for the system 1-propanol + n-hexane near the critical region	Oha, B.C., Kima, Y., Shin, H.G. & Kima, H.,	2004	220	41-46	Fluid Phase Equilibria	2
32	Vapor–liquid equilibria and excess molar volumes of diethylamine(1) + acetone(2) and diethylamine(1) + acetonitrile(2) binary systems	Chaudhari, S.K.,	2002	200	329–336	Fluid Phase Equilibria	2
33	Vapor-Liquid Equilibrium and Excess Systems Propane + Dimethyl Ether and at Temperatures from (298 to 323) K	Horstmann, S., Birke,G. & Fischer, Kai.,	2004	49	38-42	Journal of Chemical and Engineering Data	1
34	Vapor-Liquid Equilibrium for Acetonitrile + Propanenitrile and 1-Pentanamine + 1-Methoxy-2-propanol	Antosik, M., Gałka,M. & Malanowski.S.K.,	2004	49	11-17	Journal of Chemical and Engineering Data	3
36	Isothermal and isobaric vapor + liquid equilibria of N,N-dimethylformamide + n-propanol + n-butanol	Wang,C., Li,H., Zhu,L. & Shijun Han	2001	189	119–127	Fluid Phase Equilibria	3
38	Phase equilibria for binary n-alkanenitrile-n-alkane mixtures. III. Vapour-liquid phase equilibria for propanenitrile with C5-C8 n-alkanes	McLure a, I.A., Arriaga-Colina, J.L. & Armitage, D.A.,	1997	127	237-249	Fluid Phase Equilibria	2
39	Isothermal vapor-liquid equilibria for mixtures of methyl tert-butyl ether, methyl acetate, and ethyl acetate	Lee,M.J., Hsiao, C.C. & Lin, H.M.,	1997	137	193-207	Fluid Phase Equilibria	3
44	Vapor-Liquid Equilibria of the Systems Ethyl Ethanoate 2-Methyl-2-butanol, 2-Methyl-1-propanol + 3-Methyl-Cyclohexanol + Benzyl Alcohol at 101.32 Kpa	Senol, A.,	1998	43	763-769	Journal of Chemical and Engineering Data	2
53	Vapor-liquid equilibria of the ternary system methanol + acetone + methyl vinyl ketone at atmospheric pressure	Tu, C.H., Wu, Y.S. & Liu, T.L.,	1997	131	181-188	Fluid Phase Equilibria	1
54	Isobaric vapor-liquid equilibria of 3-methyl-1-butanol with methanol and vinyl acetate at 101.3 KPa	Resa, J.M.,Gonzalez, C., Moradillo,B. & Ruiz,A.,	1997	132	205-213	Fluid Phase Equilibria	2

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