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ABSTRACT

EVALUATION OF UNIFAC GROUP INTERACTION PARAMETERS USING PROPERTIES BASED ON QUANTUM MECHANICAL CALCULATIONS

**by
Hansan Kim**

Current group-contribution methods such as ASOG and UNIFAC are widely used for approximate estimation of mixture behavior but unable to distinguish between isomers. Atoms in Molecules (AIM) theory can solve these problems by using quantum mechanics and computational chemistry to compute atomic contributions to molecular properties and to intermolecular interactions. Rigorously defined properties available through AIM theory and new functional group definitions are used for the UNIFAC model to predict the behavior of various mixtures. Results are presented for various mixtures with nine regressed global parameters to optimize model's predictive capability. The results are also compared to analogous results for the Knox model.

**EVALUATION OF UNIFAC GROUP INTERACTION PARAMETERS USING
PROPERTIES BASED ON QUANTUM MECHANICAL CALCULATIONS**

**by
Hansan Kim**

**A Thesis
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New Jersey Institute of Technology
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Master of Science in Chemical Engineering**

Otto H. York Department of Chemical Engineering

May 2005

APPROVAL PAGE

**EVALUATION OF UNIFAC GROUP INTERACTION PARAMETERS USING
PROPERTIES BASED ON QUANTUM MECHANICAL CALCULATIONS**

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...standing with a bag on my hand in Terminal 4.

To my loved family

사랑하는 우리 부모님과 서야 에게...

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CHAPTER 1

BACKGROUND

The challenges of the prediction of phase behavior have been met with correlative methods of experimental data reduction and the description of systems using models of molecular interactions. One of these, a group contribution method is the a method for predicting the phase behavior. Current group contribution methods such as ASOG and UNIFAC are widely used for estimation of mixture behavior in industries but it still has problems: inability to distinguish between isomers, no consideration of the position of each group in the molecule on a physical basis, and need for specialized groups result in higher cost and more parameters.

To make up for these defects, quantum mechanics and computational chemistry are introduced for both thermodynamic properties and phase equilibria. In thermodynamics, these two methods can distinguish isomers, group position on physical basis and compute the atomic contribution to molecular properties and to intermolecular interactions. Presently, the most advanced concept of the group contribution methods is the theory of atoms in molecule (AIM).

Rigorously defined atoms and groups available through AIM (Atoms In Molecule) theory are used here to establish group contribution methods to estimate various mixtures. Computational chemistry and quantum mechanics provide an improvement to group contribution methods by introducing charges, dipole moment, polarizability, exposed surface area and volume of functional groups which are unique to the molecule in which it appears. With these quantities computed by *ab initio* quantum

orbital calculations, correlations based on physical chemistry yield the interaction energy between functional groups. Interaction energy calculation is a very important role in which are linked group contribution methods using activity coefficient.

In this work, properties calculated by *ab initio* computational methods using Gaussian 98, AIM 2000 and AIMPAC and correlation of functional groups were taken from Arturo (2005). Current group contribution models such as UNIFAC and Knox for the activity coefficient have energy interaction parameters that are regressed from experimental data. An *ab initio* quantum orbital calculation method based on AIM theory will compute the molecular interaction energies and then these energies will be used to obtain interaction parameters in prediction models. Hence, the prediction of phase equilibrium can be made for each activity coefficient model. The algorithm of interaction energy calculation is used for both the group interaction parameter (\mathbf{a}_{nm}) of UNIFAC and one parameter (C_{kl}) of Knox (Knox, 1987). In fact, this *key work* is intended to reduce the average error for estimation of phase equilibrium within residual molar Gibbs free energy.

The evaluation of eight group interaction parameters and one structural parameter from regression within experimental data collected in the literatures was made. In total, nine regressed *global parameters* are used for prediction of mixture behavior for each model. Identification of a new group is one of the most important steps in establishing group contribution methods. New group definitions are introduced and used for the calculation of group interaction energy in this work. The results will be presented for various mixtures with nine regressed *global parameters* to optimize the models' predictive capability.

CHAPTER 2

INTRODUCTION

2.1 Phase Equilibrium

A knowledge of phase equilibrium is fundamental to an understanding of separation processes in chemical engineering. A variety of experimental data and computational methods have been proposed and published to interpret this thermodynamic phase equilibrium behavior. In this chapter, the thermodynamic fundamentals of vapor-liquid equilibrium and the relation between the properties of real solutions and those of ideal solutions will be reviewed and their calculation will be described.

2.1.1 Fundamentals

The fundamental equations of phase equilibrium in an open system are written in terms of chemical potentials additionally described by [1]

$$\mu_i \equiv \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} = \left(\frac{\partial A}{\partial n_i} \right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (2.1)$$

where n_i , n_j are mole numbers, with n_j meaning that all mole numbers other than n_i are kept constant [2.1]. Other equivalent expressions for chemical potential in terms of H , A , G can be derived by the fundamental equation for the state function. Since the chemical potential, μ_i , is an intensive quantity, its value does not depend on the amount of material but temperature and pressure. For a closed homogeneous system, U is a function of S and V in extensive properties.

$$U = U(S,V) \quad (2.2)$$

However, in an open system, the mole numbers of components are also required for in the chemical potential [1].

$$U = U(S, V, n_1, n_2, \dots, n_m) \quad (2.3)$$

where m is the number of components. One of the important fundamental properties in this study is the Gibbs energy, from which is developed the activity coefficient. A variety of models for the calculation of the activity coefficient have been proposed in data reduction methods: NRTL [10], Wilson [10], UNIQUAC [10], and others.

The partial molar Gibbs energy can be the chemical potential μ_i by the definition of partial molar properties since it constrains pressure, temperature, and n_j . According to the definition of a partial molar property, μ_i is equivalent to the partial molar Gibbs energy.

$$\mu_i = \bar{g}_i = \left[\frac{\partial(G)}{\partial n_i} \right]_{T, P, n_j} \quad (2.4)$$

Using the definition for U and chemical potential as an open homogeneous system, the fundamental Equation in terms of U is

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (2.5)$$

By integration at constant temperature and composition, the Equation (2.5) gives

$$U = TS - PV + \sum_i \mu_i n_i \quad (2.6)$$

Differentiation of this equation gives

$$dU = TdS + SdT - PdV - VdP + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad (2.7)$$

By comparing Equation (2.5) with Equation (2.7), the Gibbs-Duhem Equation which is fundamental in thermodynamics of solutions is given by

$$SdT - VdP + \sum_i n_i d\mu_i = 0 \quad (2.8)$$

This equation at constant temperature and pressure becomes

$$\sum_i n_i d\mu_i = 0 \quad (2.9a)$$

$$\text{or} \quad \sum_i x_i d\mu_i = 0 \quad (2.9b)$$

2.1.2 Activity Coefficient in Terms of Excess Functions

A real solution does not behave like an ideal solution. However, all solutions of chemically stable nonelectrolytes behave as ideal dilute solutions in the limit of very large dilution [1]. In order to increase the accuracy of prediction for mixture behavior, the correction terms which distinguish the properties of real solutions with those of ideal solutions are defined in terms of excess functions.

Excess functions are thermodynamic properties of solutions in excess of those of an ideal solution at the standard state: same temperature, pressure, and composition. For phase equilibrium, the most useful partial excess property is the partial molar Gibbs energy that is directly related to the activity coefficient [1].

The excess Gibbs energy is defined by

$$G^E \equiv G - G^{id} \quad (2.10)$$

Using a similar approach as in Equation (2.10), the partial molar excess Gibbs energy by the definition of the partial property becomes

$$\bar{g}_i^E = \left(\frac{\partial G^E}{\partial n_i} \right)_{T,P,n_j} \quad (2.11)$$

By introducing the definition of fugacity [1], the partial molar Gibbs energy at constant temperature becomes

$$d\mu_i = d\bar{g}_i = RTd \ln \hat{f}_i \quad (2.12)$$

For phase equilibrium, the activity coefficient γ_i in liquid phase behavior is defined by introducing a fugacity coefficient.

$$\gamma_i = \frac{\hat{f}_i}{x_i f_i^o} \quad (2.13)$$

Substitution of Equation (2.13) in (2.12) then the partial molar excess Gibbs energy, by the definition, is

$$\bar{g}_i^E = RT \ln \gamma_i \quad (2.14)$$

From Euler's theorem, the excess Gibbs energy becomes

$$g^E = RT \sum_i x_i \ln \gamma_i \quad (2.15)$$

g^E/RT can be determined from known γ_i as a function of composition. Equation (2.15) is useful for the systems at low pressure. However, it has problems for the systems at high pressure. When the temperature exceeds the critical temperature, the standard state for the fugacity of the species is hypothetical, and the symmetrical normalization of the activity coefficient becomes ambiguous [20]. Hence, the Gibbs-Duhem Equation at high pressure is not negligible in the difference of the molar volume of the liquid mixture. Accordingly, the Gibbs-Duhem Equation at high pressure at constant temperature from Equation (2.8) becomes

$$\sum_i x_i d \ln \gamma_i = \frac{v^E}{RT} dP \quad (2.16)$$

2.2 Classic Group Contribution Method

Estimation of activity coefficients for a mixture is very important to the prediction of the behavior of vapor-liquid equilibrium when there is a lack of experimental data, fragmentary data, or no data at all [1]. The group contribution concept can provide the means of estimation for vapor-liquid equilibrium.

In group contribution methods, a molecule is divided into functional groups [1]. Molecule-molecule interactions are considered to be properly weighted sums of group-group interactions. The properties of each group are assumed to be independent of the rest of the molecule to which it is attached [2]. Therefore, the mixture is treated as a mixture of groups. This group is postulated and its quantitative contributions are regressed from experimental data. And then this group is tested by comparison with authentic experimental data on other systems as to whether it is acceptable or not. Finally, with this regressed data and the functional group contributions, it is possible to calculate molecule-molecule interactions [1], to calculate activity coefficients, and then to predict phase equilibrium where no data are available. Over the years, several methods of evaluating activity coefficients from group contribution models have been proposed: ASOG, UNIFAC, and Knox.

The ASOG (analytical solution of groups) method was developed by Derr and Deal (1969, 1973), and the parameters of ASOG were published by Kojima and Tochigi (1979) [3]. The UNIFAC (universal functional activity coefficient) method was developed by Fredenslund (1975) and the parameters of UNIFAC were published by Hansen et al. (1991), Gmehling et al. (1993) and Fredenslund and Sørensen (1994) [3]. The Knox method represents one-fluid theory and was developed by Knox (1987).

In this chapter, UNIFAC and Knox will be reviewed from the angles of capability, limitation and applications as published in the literature.

2.2.1 UNIFAC and Revisions

The UNIFAC (universal functional activity coefficient) group contribution method was developed based on the solution of group concepts, by Fredenslund, Jones and Prausnitz [4]. UNIFAC was described by Fredenslund et al in 1977 [1, 4] and it combined the UNIQUAC (universal quasi-chemical) model and the so-called analytical solution of groups concept [5]. UNIQUAC was derived from a statistical-mechanical basis by application of Guggenheim's quasi-chemical theory through introduction of the local area fraction as the primary concentration variable [6]. With other predictive methods, calculation of activity coefficients and estimation of vapor-liquid equilibrium in the UNIFAC model is determined by a reasonable combination of theoretical model and regression of experimental data collected in data banks.

Like many group contribution models, UNIFAC is based on the local composition concept. The UNIFAC method for estimation of activity coefficients [7] depends on the parameters: group volume parameters, R , group surface area parameters, Q , and binary group-interaction parameters, a .

In the UNIFAC model, the activity coefficient is determined in terms of a combinatorial part and a residual part according to the following equation:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2.17)$$

The combinatorial part of the UNIFAC model considers the shape and the size of the molecules in the mixture.

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i \left(\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) \quad (2.18)$$

Where the quantity J_i is given by

$$J_i = \frac{\phi_i}{x_i} \quad (2.19)$$

The molecule volume fraction ϕ_i and the molecule surface area fraction θ_i are given by respectively

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad (2.20)$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad (2.21)$$

The first three terms in Equation (2.18) are, in fact, the Flory-Huggins expression[1], and the last one is the Staverman-Guggenheim correction term [8]. In Equations (2.20) and (2.21), a relative molecular volume r_i and a relative molecule surface area q_i are given by

$$r_i = \sum_k v_k^{(i)} R_k \quad (2.22)$$

$$q_i = \sum_k v_k^{(i)} Q_k \quad (2.23)$$

In Equations (2.22) and (2.23), the quantity v_k^i is the number of subgroups of type k in a molecule of species i . The relative molecular volume r_i and the relative molecular surface area q_i are calculated from the subgroup parameters R_k and Q_k of the subgroups k respectively. Group parameters R_k and Q_k are obtained from the van der Waals group volumes and surface areas V_{wk} and A_{wk} given by Bondi [9, 11]

$$R_k = V_{wk} / 15.17 \quad (2.24)$$

$$Q_k = A_{wk} / (2.5 \times 10^9) \quad (2.25)$$

The normalization factors 15.17 and 2.5×10^9 are those given by Abrams and Prausnitz [6, 7]. Essentially, the combinatorial part represents the excess entropy of mixing due to differences in shape and size and the residual part represents the excess enthalpy of mixing resulting from differing interaction energies [2]. The residual part of the UNIFAC model considers the energetic interactions between the groups. The interaction between the molecules can be calculated from the group activity coefficients in both the mixture and the pure substances [9].

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (2.26)$$

where Γ_k is the group activity coefficient of group k in the mixture and $\Gamma_k^{(i)}$ is the group activity coefficient of group k in the pure substance i at the same conditions. The group activity coefficient Γ_k is calculated according to

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \quad (2.27)$$

where Θ_m is the area fraction of group m , and the sums are over all the different groups [7].

Θ_m is calculated in a similar manner to θ_i in the combinatorial part according to

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (2.28)$$

where X_m is the mole fraction of group m in the mixture.

$$X_m = \frac{\sum_j v_m^{(i)} x_j}{\sum_j \sum_n v_n^{(i)} x_j} \quad (2.29)$$

In Equation (2.27), the group interaction parameter Ψ_{nm} is a temperature-dependent parameter and is given by

$$\Psi_{nm} = \exp\left(-\frac{U_{nm} - U_{mm}}{RT}\right) = \exp\left(-\frac{a_{nm}}{T}\right) \quad (2.30)$$

where a_{nm} is a measure of the energy of interaction between group n and m and is assumed to be temperature-independent. The group interaction parameters a_{nm} (units of degree Kelvin) are not symmetric so that $a_{nm} \neq a_{mn}$ and thus must be obtained from a wide range of experimental phase equilibrium data [12]. This approach leads to satisfactory results of prediction for vapor-liquid equilibrium behavior in most cases [13], as does modified UNIFAC as well, which will be discussed later. An extensive table of UNIFAC group-interaction parameters has been published and revised in a series of articles. However, UNIFAC has the following limitations which are noted by Fredenslund and Sørensen (1994), as given by Sandler (1994) [19].

1. The UNIFAC method does not distinguish between isomers.
2. Since it is based on a $\gamma - \phi$ (i.e., combined method) approach, application is limited to moderate pressures, depending on the equation of state selected and on the influence of pressure on γ_i .
3. Temperatures are limited to the approximate range 275-425 K.
4. Noncondensable gases, polymers, and electrolytes are excluded.
5. UNIFAC parameters based on VLE data can not be used for LLE predictions.
6. "Proximity" effects are not accounted for; for example, --CH groups in alcohols and glycols do not have the same effect.

The original UNIFAC method reviewed so far was intended for the prediction of vapor-liquid equilibrium data in a limited temperature range from 275 to 425K [13] and hence the limitations of prediction of real phase behavior for mixtures. Predictions above 425K and below 275K can lead to poor results [13, 14]. Problems also can occur in enthalpies of mixing or solid-liquid equilibrium. Furthermore, the real phase equilibrium behavior in the dilute region of the compounds to be separated is not always in agreement with the experimental data because vapor-liquid data usually do not provide information about the dilute region (γ^∞) and the temperature dependence of the activity coefficients [8, 13, 14].

A Modified version of UNIFAC has been proposed to overcome limitations in original UNIFAC. Modified UNIFAC (Dortmund) [15, 16], though it still has some deficiencies, improves the results for asymmetric systems through a modified combinatorial portion and introduction of temperature-dependent parameters. [13, 14].

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \quad (2.31)$$

Figure 2.1 shows the improvement of the prediction for excess enthalpies by introducing modified UNIFAC (Dortmund) [17]. The original UNIFAC was not able to predict the enthalpy of mixing correctly. However, the use of modified UNIFAC (Dortmund) leads to much more satisfactory results. This reflects that the introduction of temperature-dependent parameters compensates the region in which original UNIFAC was not able to extrapolate.

Figure 2.2 shows that the modified UNIFAC describes much better than the original UNIFAC the temperature dependence of the activity coefficients at infinite dilution for the systems n-hexane + ethanol [17].

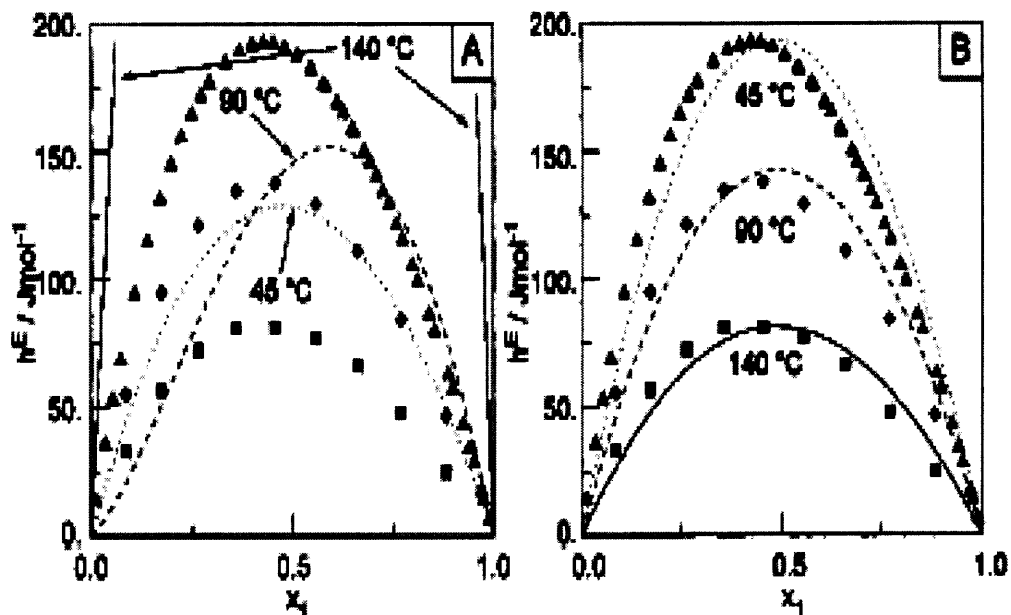


Figure 2.1 Excess enthalpies of the system hexane + cyclohexane (Symbols, experimental data; Solid line and dotted lines, predicted data; A, before revision; B, after revision).

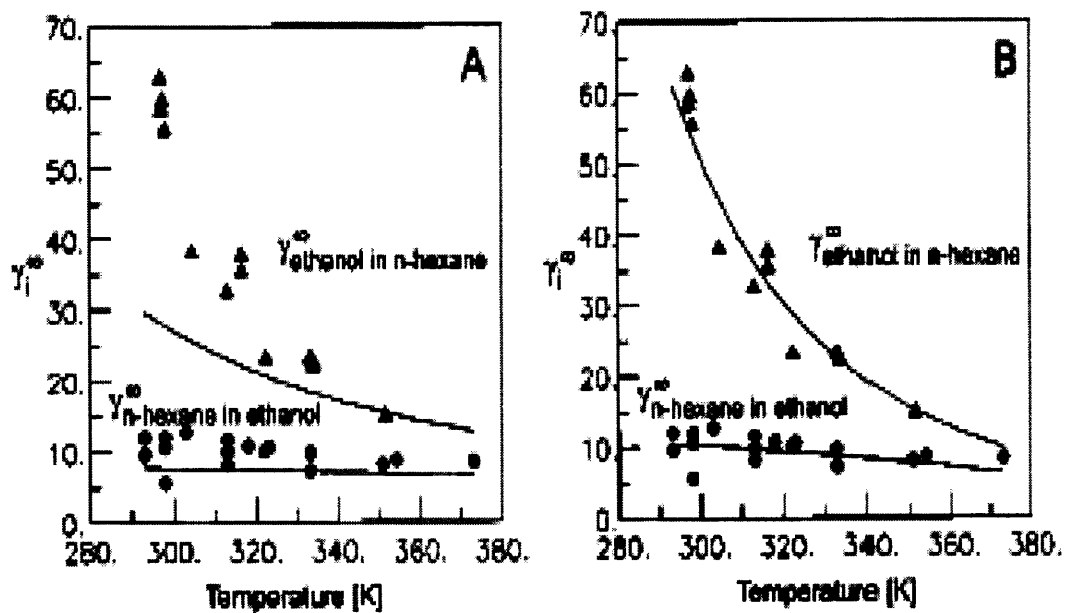


Figure 2.2 Activity coefficients of the system n-hexane + ethanol: (A) UNIFAC; (B) modified UNIFAC. (Symbols, experimental data; Solid line, predicted data)

2.2.2 The Knox Model

The Knox model (Knox, 1987) is based on the quasi-chemical expression with one interaction energy parameter in addition to the group structural parameters and the athermal Guggenheim Equation for mixtures. The most significant practical difference between the Knox and UNIFAC methods is the number of interaction energy parameters.

The assumptions of the Knox model are: (1) The volume per molecule and the energies of molecular translation, rotation, and vibration are unaffected by mixing. (2) Each interaction in the mixture can be characterized as a group-group interaction which is independent of temperature, pressure and composition. (3) The number of groups of type k in a molecule of type i is given as $v_k^{(i)}$. The number of groups of type k in the mixture M_k is given by

$$M_k = \sum_i N_i v_k^{(i)} \quad (2.32)$$

where N_i is the number of molecules of type i . (4) Each group of type k engages in a characteristic number Z_k of interactions with other groups.

The total number of pair interactions is

$$I = \sum_k \frac{Z_k M_k}{2} \quad (2.33)$$

The number of k - l interactions as randomly assigned, M_{kl} , is

$$M_{kl} = M_{lk} \quad (2.34)$$

$$\frac{Z_k M_k}{2} = \sum_l M_{kl} \quad (2.35)$$

The Helmholtz energy change of mixing is given by

$$\frac{\Delta A}{RT} = \frac{\Delta A^a}{RT} - \sum_i \sum_k \left(\frac{Z_k x_i v_k^{(i)}}{2} \right) \ln \left(\frac{\Theta_k}{\Theta_k^{(i)}} \right) + \sum_i \sum_k \left(\frac{Z_k x_i v_k^{(i)}}{2} \right) \ln \left(\frac{y_{kk}}{y_{kk}^{(i)}} \right) \quad (2.36)$$

From Equations (2.33) and (2.35), the local group composition of l -groups about k -groups y_{kl} and the group interaction fraction Θ_k are defined as

$$y_{kl} = \frac{M_{kl}}{\left(\frac{Z_k M_k}{2} \right)} \quad (2.37)$$

$$\Theta_k = \frac{\left(\frac{Z_k M_k}{2} \right)}{\sum_l \left(\frac{Z_l M_l}{2} \right)} = \frac{\sum_i \left(\frac{Z_k x_i v_k^{(i)}}{2} \right)}{\sum_i \sum_l \left(\frac{Z_l x_i v_l^{(i)}}{2} \right)} \quad (2.38)$$

The local group compositions are evaluated by the following equations [22].

$$\Theta_k y_{kl} = \Theta_l y_{lk} \quad (2.39)$$

$$1 = \sum_l y_{kl} \quad (2.40)$$

$$C_{kl} \equiv \frac{y_{kl} y_{lk}}{y_{kk} y_{ll}} = \exp \left(- \frac{2\varepsilon_{kl} - \varepsilon_{kk} - \varepsilon_{ll}}{kT} \right) \quad (2.41)$$

where C_{kl} is defined in relation to the interchange energy [23] and ε_{kl} the energy of k - l group-group interaction.

By assumption number one in Equation (2.40), the Gibbs energy change of mixing and the Helmholtz energy change of mixing are identical. The Guggenheim expression for the athermal Gibbs Energy change of mixing is

$$\frac{\Delta G^a}{RT} = \sum_i x_i \ln \phi_i + \sum_i \left(\frac{z_i x_i}{2} \right) \ln \left(\frac{\Theta_i}{\phi_i} \right) \quad (2.42)$$

where Θ_i represents the interaction fraction, ϕ_i the volume fraction of component i , z_i the relative molecular group surface area and v_i the relative molecular volume.

$$\phi_i = \frac{v_i x_i}{\sum_j v_j x_j} \quad (2.43)$$

$$\Theta_i = \frac{\left(\frac{z_i x_i}{2}\right)}{\sum_j \left(\frac{z_j x_j}{2}\right)} \quad (2.44)$$

$$z_i = \sum_k v_k^{(i)} Z_k \quad (2.45)$$

$$v_i = \sum_k v_k^{(i)} V_k \quad (2.46)$$

where Z_k and V_k are the group structure parameters, $v_k^{(i)}$ the number of groups of type k in a molecule of type i . The saturated liquid molar volume can be used for v_i instead of using Equation (2.46).

The excess Gibbs energy is obtained by combining Equations (2.36) and (2.41), then subtracting the ideal solution Gibbs energy of mixing.

$$\begin{aligned} \frac{G^E}{RT} = & \sum_i x_i \ln \frac{\phi_i}{x_i} + \sum_i \left(\frac{z_i x_i}{2}\right) \ln \frac{\Theta_i}{\phi_i} - \sum_i \sum_k \left(\frac{Z_k x_i v_k^{(i)}}{2}\right) \ln \frac{\Theta_k}{\Theta_k^{(i)}} \\ & + \sum_i \sum_k \left(\frac{Z_k x_i v_k^{(i)}}{2}\right) \ln \left(\frac{y_{kk}}{y_{kk}^{(i)}}\right) \end{aligned} \quad (2.47)$$

From the excess Gibbs energy the activity coefficient is obtained.

$$\begin{aligned} \ln \gamma_i = & \ln \frac{\phi_i}{x_i} + \left(1 - \frac{\phi_i}{x_i}\right) - \frac{z_i}{2} \left(1 - \frac{\phi_i}{\Theta_i} + \ln \frac{\phi_i}{\Theta_i}\right) - \sum_k \left(\frac{Z_k v_k^{(i)}}{2}\right) \ln \frac{\Theta_k}{\Theta_k^{(i)}} \\ & + \sum_k \left(\frac{Z_k v_k^{(i)}}{2}\right) \ln \frac{y_{kk}}{y_{kk}^{(i)}} \end{aligned} \quad (2.48)$$

The detailed numerical method for all equations described in this chapter is best described in reference [23].

CHAPTER 3

GLOBAL OPTIMIZATION APPROACH

3.1 Parameterization for Interaction Energy

The model of energy for group interactions implanted into UNIFAC and Knox in this study was developed by Steven G. Arturo in his dissertation (Auturo, 2005). Nine global parameters are used to develop this model: Eight energy interaction parameters and one structure parameter. The eight terms of interaction energies are designed under the following headings:

- Electrostatic forces between electric charges of magnitudes q_i and q_j .
- Induction forces between induced dipoles (μ_i and μ_j) and polarizabilities (α_i and α_j).
- Forces of repulsion between non-polar molecules from orbital exponent (ζ).
- All energies are independent of temperature and pressure in systems as required by the UNIFAC and Knox methods.

All values are AIM (Atoms In Molecule) properties from *ab initio* molecular orbital calculations. All the quantities are in atomic units and temperature is in Kelvin. Seven terms of interaction energies are from the combination of Equations (3.1) to (3.7) and one from the third, that is, Equation (3.8). The following terms are combinations of associated energies between groups.

$$E_{qq} = A \frac{q_i q_j}{r_i + r_j} \quad A = \frac{1}{k_B} \quad (3.1)$$

where E_{qq} is the energy between charges and r is averaged radius.

$$E_{q\mu} = B \frac{q_i \mu_j + q_j \mu_i}{(r_i + r_j)^2} \quad B = \frac{1}{k_B} \quad (3.2)$$

where $E_{q\mu}$ is the energy due to polarizability (α) and induced dipole (μ).

$$E_{\mu\mu} = C \frac{\mu_i \mu_j}{(r_i + r_j)^3} \quad C = \frac{2}{k_B} \quad (3.3)$$

where $E_{\mu\mu}$ is the energy due to induced dipoles (μ).

$$E_{\alpha q} = D \frac{q_i^2 \alpha_j + q_j^2 \alpha_i}{(r_i + r_j)^4} \quad D = -\frac{1}{2k_B} \quad (3.4)$$

where $E_{\alpha q}$ is the energy due to polarizability (α) and charge (q).

$$E_{\alpha\mu} = F \frac{\mu_i^2 \alpha_j + \mu_j^2 \alpha_i}{(r_i + r_j)^6} \quad F = -\frac{2}{k_B} \quad (3.5)$$

where $E_{\alpha\mu}$ is the energy due to polarizability (α) and induced dipole (μ).

$$E_{\alpha\alpha} = G \frac{\alpha_i \alpha_j}{(r_i + r_j)^6} \quad G = -\frac{3}{8k_B} \quad (3.6)$$

where $E_{\alpha\alpha}$ is the energy due to polarizabilities (α).

$$E_{q\mu\alpha} = H \frac{q_i \mu_i \alpha_j + q_j \mu_j \alpha_i}{(r_i + r_j)^5} \quad H = \pm \frac{2}{k_B} \quad (3.7)$$

where $E_{q\mu\alpha}$ is the energy due to charge (q), induced dipole (μ), and polarizability (α).

$$E_{rep} = J \left[\exp\left(-\rho_{ij} \left(1 + \rho_{ij} + \frac{1}{3}\rho_{ij}^2\right)\right) \right]^2 \quad J = \frac{1}{k_B} \quad (3.8)$$

$$\text{where, } \rho_{ij} = \frac{(\xi_i + \xi_j)(r_i + r_j)}{2}$$

where E_{rep} is the repulsion energy and ξ is the orbital exponent.

The total interaction energy between groups is obtained by summing all of the associated energy contributions.

$$E_{ij} = (E_{qq} + E_{qu} + E_{\mu\mu} + E_{aq} + E_{a\mu} + E_{aa} + E_{aa} + E_{q\mu a} + E_{rep})_{ij} \quad (3.9)$$

Equation (3.9) is inserted in both Equation (2-30) for UNIFAC and Equation (2-41) for Knox to evaluate global parameters. Parameters A , B , and C are assumed to be positive constants [24]. Parameters D , F , G and H are assumed to be negative constants [24]. Parameter J is assumed to be a positive constant [25, 26]. All values of parameters in the expressions above are the first guesses based on theory ($k_B = 3.166761 \times 10^{-6}$, Boltzmann's constant), but are treated as adjustable values for data regression. After obtaining global parameters for each model from the regression, the result for prediction of vapor-liquid equilibrium is reviewed in Chapter 5.

3.2 Functional Group Definition

New modeling (Arturo, 2005) for the group contribution method of vapor liquid equilibrium depends on defining new groups and testing whether it yields a good correlative result or not. The credibility of a new proposed method can not be acceptable until the fitting of a large experimental dataset shows improvement above previous models. Here, examples of definitions for new groups which Arturo (2005) has developed are reviewed. Some of the groups are the same as currently used in UNIFAC and Knox but some of the groups are different.

- CH_3 , CH_2 , CH , and C groups.
- Hydroxyl group (OH) does not exist; separate O and H atoms.
- Amine groups (NH_2 , NH) do not exist; separate N and H atoms.
- Carboxyl group (HCOO) does not exist; separate H , C , O , and O atoms.
- Water (H_2O); treated as two H atoms and one O atom.

- Classified functional groups in this study; CH₃, CH₂, CH, C, H, N, O, and F.

The choice for group definition of Arturo (2005) is significantly different from other group contribution methods in these following points. O and H atoms adjacent to methyl (CH₃) group can not be considered to be the same as in an ethyl (CH₂) group as a result of different electronic charge. Each O and H atom is considered to interact with neighboring groups and atoms independently. Atoms which are attached to a (CH_n-) group and adjacent atom are defined as a functional group itself in this study. Accordingly, there are no larger groups defined as combinations of atoms except (CH_n-) groups. These proposed new smaller groups can be used to assemble as many different molecules as the set of larger groups used in the current UNIFAC method.

CHAPTER 4

COMPUTATIONAL METHODOLOGY

4.1 Required Data

Reliable prediction of phase equilibria is excessively dependent on reliable data from the literature. In addition to that, use of extensive data over a comprehensive range is able to minimize the amount of error in the adjustable parameters obtained in the fitting procedure: kinds of molecules, wide temperature and pressure ranges. In this study, all kinds of data except functional group properties were collected from extensive published literature or websites. The functional group properties were obtained from Steven G. Arturo (Steven, 2005) through his ab initio molecular orbital calculations.

4.1.1 Molecular Properties

Basic molecular properties to be used in the calculation of total pressure for binary or ternary vapor liquid equilibrium by using UNIFAC or Knox were collected from published literature or websites: property data bank [27], NIST [28], and ChERIC [29]. Vapor pressure correlation parameters which were used in this study are tabulated in Appendix A. Basic constants of molecules, which are critical properties, molecular weight, acentric factor, dipole moment, and liquid properties, are tabulated in Appendix B. Any molecule for which one of the properties is not available was not included in this study to achieve credibility.

Table 4.1 tabulates the molecules according to chemical families and their frequency of use in this study. Figure 4.1 demonstrates the distribution of molecules in chemical families and frequency which are fitted in this study.

Table 4.1 Molecules in use

chemical families	molecule	CAS #	frequency of use
alkanes	propane	74-98-6	3
	butane	106-97-8	2
	hexane	110-54-3	15
	pentane	109-66-0	5
alkenes	propene	115-07-1	1
	1-butene	106-98-9	5
	1-pentene	109-67-1	1
	1-hexene	592-41-6	1
alcohols	methanol	67-56-1	14
	ethanol	64-17-5	18
	1-propanol	71-23-8	8
	2-propanol	67-63-0	9
	1-butanol	71-36-3	3
	2-butanol	78-92-2	5
	2-methyl-2-propanol	75-65-0	4
	2-methyl-1-propanol	78-83-1	2
	1-pentanol	71-41-0	2
	2-methyl-2-butanol	75-85-4	2
3-methyl-1-butanol	123-51-3	3	
ethers	dimethyl ether	115-10-6	14
ketones	propanone	67-64-1	4
	butanone	78-93-3	1
	3-pentanone	96-22-0	1
carboxylic acids	methanoic acid	64-18-6	1
	ethanoic acid	64-19-7	3
esters	methyl ethanoate	79-20-9	6
	methyl propionate	554-12-1	1
	ethyl propionate	105-37-3	1
	ethyl ethanoate	141-78-6	10
	propyl ethanoate	109-60-4	1
	vinyl ethanoate	108-05-4	1
amines	1-butanamine	109-73-9	9
	diethyl amime	109-89-7	4
nitriles	ethanenitrile	75-05-8	4
	propionitrile	107-12-0	4
nitroalkanes	nitromethane	75-52-5	4
	nitroethane	79-24-3	6
inorganics	water	7732-18-5	18
total in use	38 molecules	average frequency	5.15

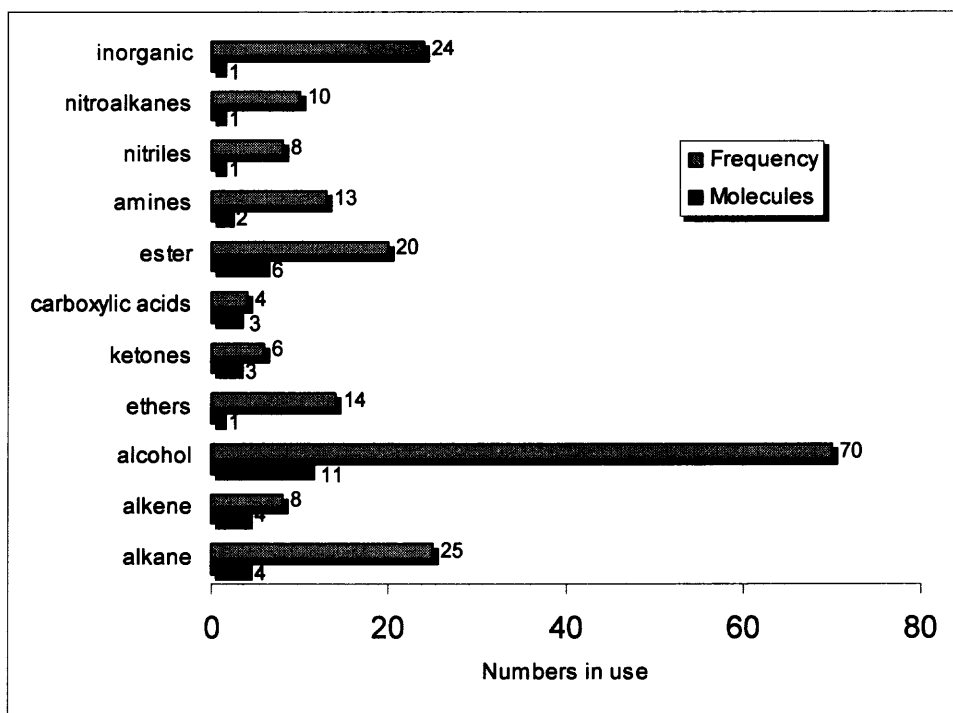


Figure 4.1 Numbers of chemical families in use.

4.1.2 Atomic Group Properties

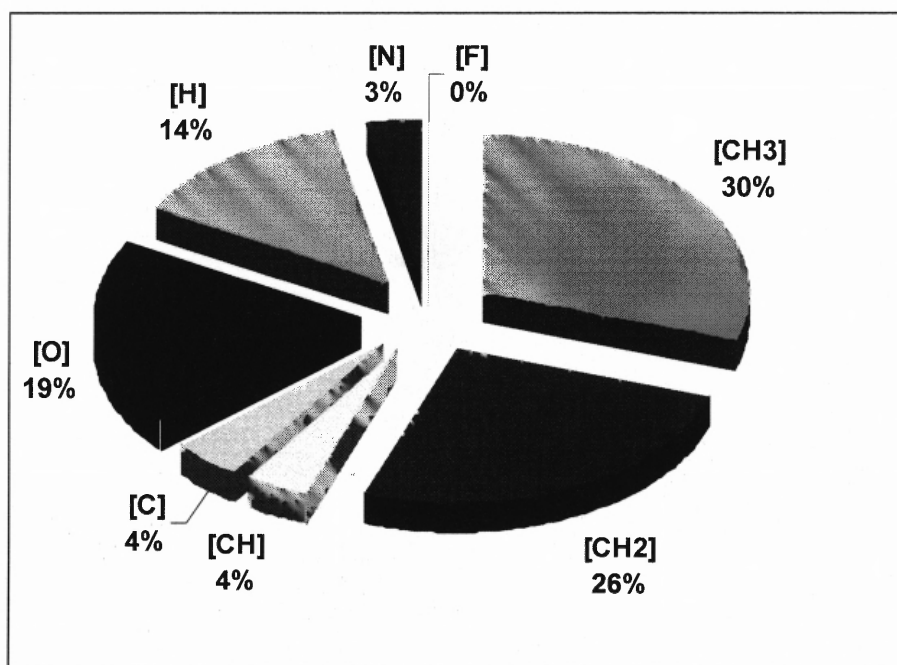
The atomic group properties, which are provided by Steven G. Arturo (2005), are calculated through an *ab initio* computational method which was described in Chapter 3 using Gaussian 98, AIM2000, and AIMPAC software. According to these methods, each molecule has different properties for every group. Calculated properties for each group in each molecule are partial charge (q), dipole moment (μ), polarizability (α), volume (V), exposed surface area (A), and distance to exposed surface (r). Table 4.2 is an example of atomic properties in ethanol by *ab initio* molecular orbital calculations.

Unlike the definitions of other group contribution methods, the OH group does not exist in this study. OH is divided into single atomic groups O and H. Figure 4.2 shows the distribution of AIM properties of molecules and functional groups which were used in this study.

Table 4.2 AIM properties of Ethanol(C_2H_5OH)

group name	q	μ	a	V	A	r
methyl (CH_3)	0.047	0.285	13.6	218.1	145.9	4.138
methylene(CH_2)	0.049	0.757	10.7	151.6	91.73	4.160
oxygen (O)	-1.122	0.240	7.64	127.9	80.26	3.547
hydrogen (H)	0.584	0.180	1.07	22.36	22.51	2.428

- All values are given in atomic units. 1 au= 2.542 Debye, $0.14819 \cdot 10^{-24} \text{ cm}^3$, $0.0892367 \text{ cm}^3/\text{mol}$, $1686.33 \text{ m}^2/\text{mol}$, or $5.29177 \cdot 10^{-11} \text{ m}$.

**Figure 4.2** Distribution of groups which appear in the calculations.

4.1.3 Empirical Data from the Literature

In total 99 experimental data sets are used in this study including 89 binary systems and 10 ternary systems. The total number of data points fitted in this study is 1886 and they represent 76 isothermal systems and 23 isobaric systems. Table 4.3 lists all systems that were used in this study. The temperature range of the isothermal data sets is from 283.15

K to 473.15 K and the pressure range of the isobaric data sets is from 99 kPa to 101.3 kPa. A data set above 425 K was also selected to examine the result by UNIFAC which has a limitation of temperature in prediction. Figures 4.3 and 4.4 show the distribution of systems in use in this study respectively.

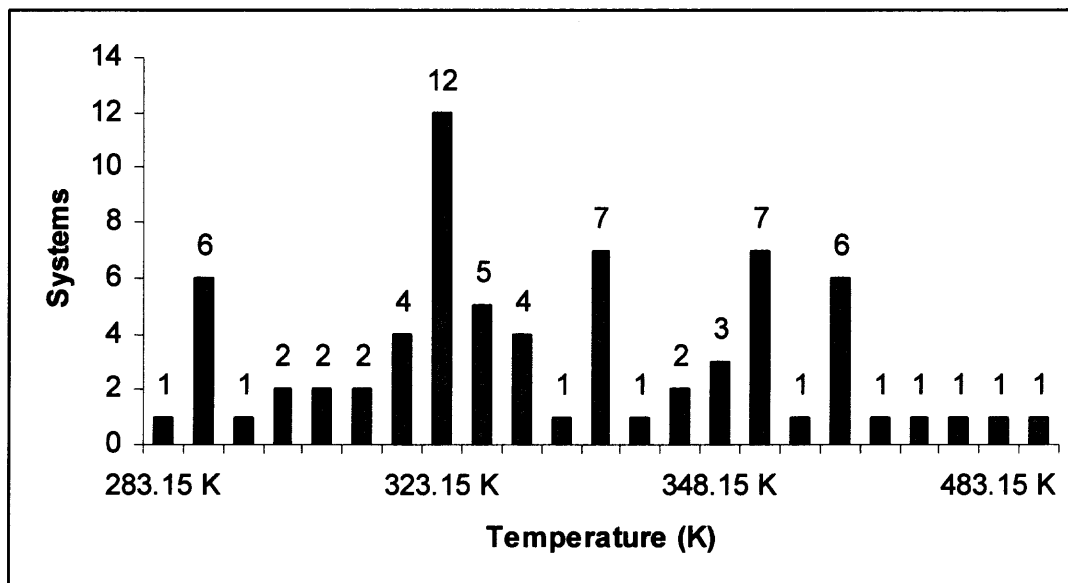


Figure 4.3 Isothermal data sets in use.

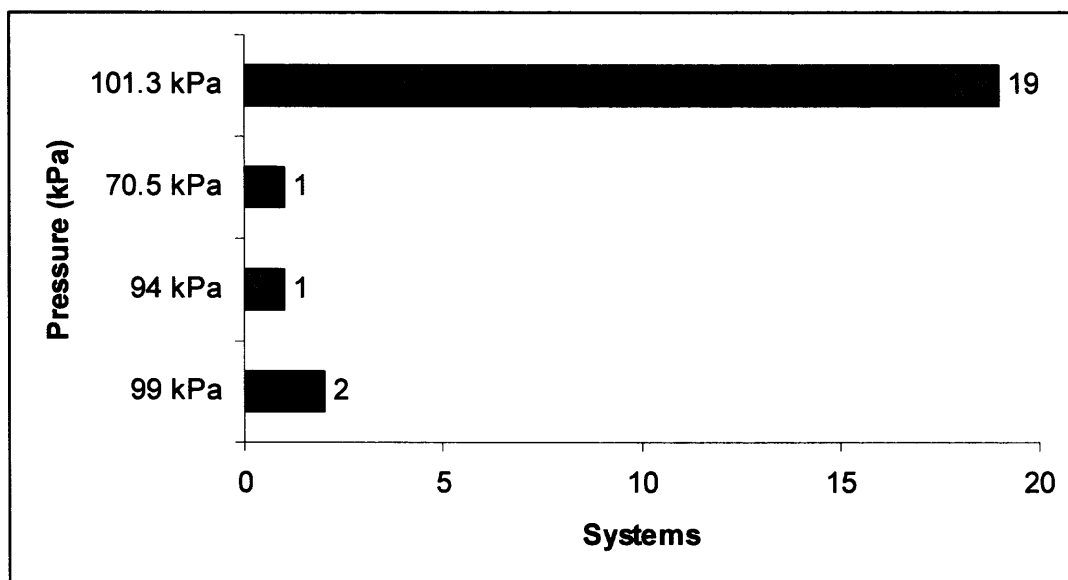


Figure 4.4 Isobaric data sets in use.

Table 4.3 Systems in use

<i>chemical families</i>	<i>mixture</i>
alcohol + alcohol	1-propanol + 1-pentanol 2-propanol + 1-propanol 2-methyl-2-butanol + 3-methyl-1-butanol methanol + 3-methyl-1-butanol 2-methyl-2-propanol + 2-methyl-1-propanol
ester + alcohol	ethyl acetate + methanol methanol + methyl acetate ethyl acetate + 1-butanol ethyl acetate + 2-methyl-2-butanol vinyl ethanoate + 3-methyl-1-butanol
ketones + alcohol	propanone + methanol butanone + 2-methyl-2-butanol 2-propanol + 3-pentanone
alkane + alcohol	hexane + ethanol pentane + ethanol propane + 2-butanol
alkane + amine	1-butanamine + hexane
ether + alcohol	dimethyl ether + ethanol dimethyl ether + methanol dimethyl ether + 2-propanol
ether + alcohol + water	dimethyl ether + ethanol + water
alkane + alcohol + water	propane + 2-butanol + water
alkane + ether	butane + dimethyl ether
alkene + ether	propene + dimethyl ether
ester + alkene	methyl acetate + 1-hexene 1-pentene + methyl acetate
alkene + alcohol	1-butene + 2-methyl-2-propanol
amine + ketones	diethyl amine + propanone
ester + ester	methyl acetate + ethyl acetate
carboxylic + ester	acetic acid + ethyl acetate
amine + ester	diethyl amine + ethyl acetate
alcohol + alcohol + water	methanol + ethanol + water 1-pentanol + 1-propanol + water
alcohol + water	methanol + water ethanol + water 2-methyl-2-propanol + water 2-propanol + water
ester + nitrile	ethyl methanoate + ethanenitrile
ester + nitroalkanes	ethyl acetate + nitromethane propyl ethanoate + nitromethane methyl propanoate + nitromethane
water+carboxyl +carboxyl	water + formic acid + acetic acid water + acetic acid + propanoic acid water + formic acid + propanoic acid
ketone + water	propanone + water
ketone + alcohol + water	propanone + 2-propanol + water

4.2 Program Algorithm

The first part, data input as an initial set up for calculation, includes inputting the number of components, the measured temperature and pressure, the compositions, and all basic properties of molecules.

The second part, calculation of properties, involves the evaluation of the pure vapor pressures, virial coefficients, liquid molar volumes, mole fractions, group properties of energy, molecular structural parameters, pure component group and local group fractions, mixture properties, activity coefficients, and total pressure of equilibrium.

The third part, the dotted box in Figure 4.5, is the step for regression of parameters to obtain the best values of the global parameters through the nonlinear regression method that is described in the next section. In this step, adjusted parameters that do not meet the tolerance of the object function are returned to the calculation of group properties of energy (the second part) and iterated until the tolerance is met.

4.3 Fitting Procedure

Regression analysis is used to predict the dependent variables from the independent variables. The goal in this study is to find best-fit values for the parameters BPAR. BPARs are tabulated and denoted in Table 4.4. Most linear and nonlinear regression assumes that the scatter follows a Gaussian (also called a “normal”) distribution.

In this assumption, the most likely values of the BPARs can be found by minimizing the sum of the squared differences between a pressure of an experimental pressure and calculated pressure:

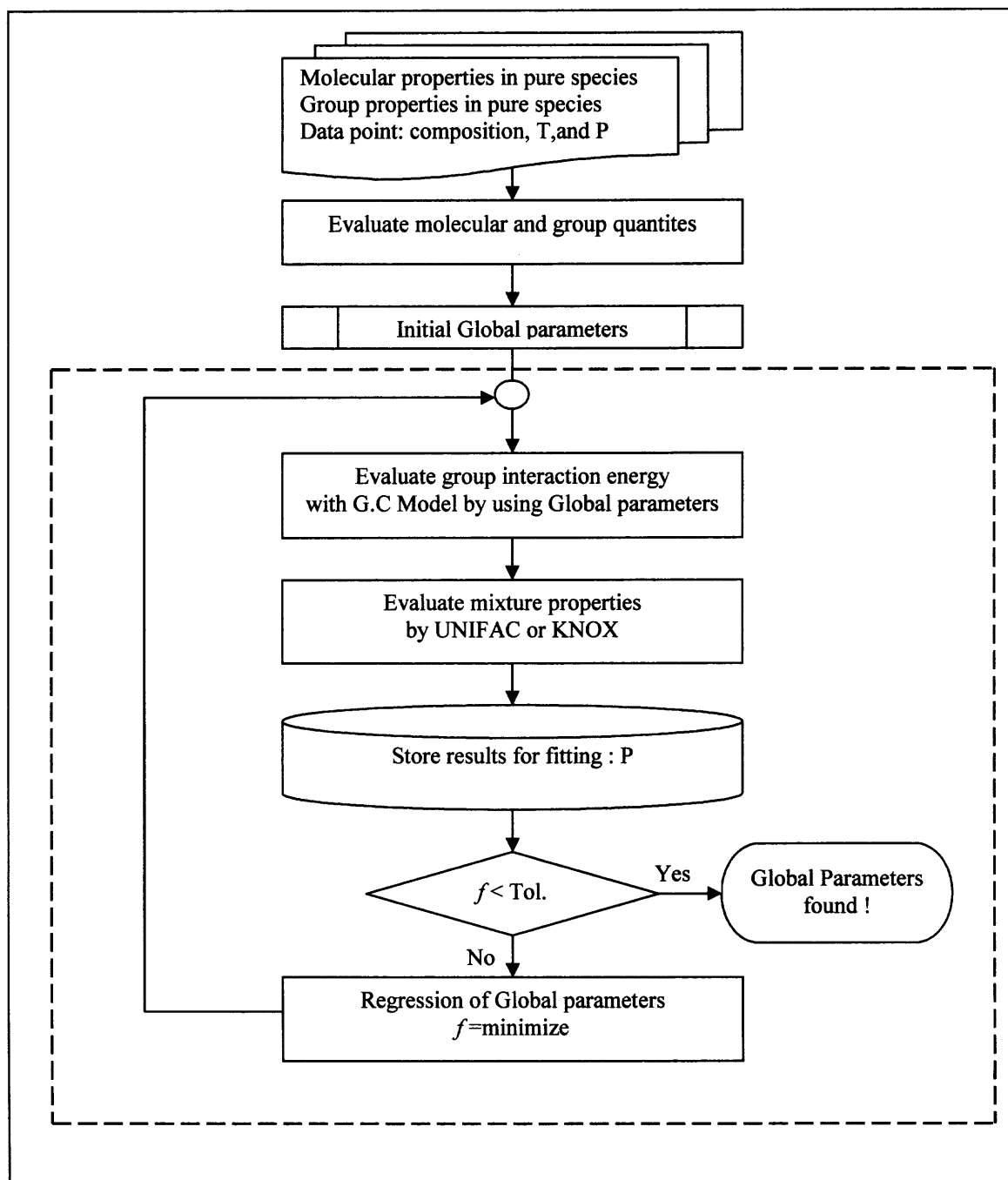


Figure 4.5 Diagram of calculation.

The nonlinear regression minimizes the object function of Equation (4.1).

$$f = \sum z^2 = \sum (P_{\text{experimental}} - P_{\text{calculated}})^2 = \min \quad (4.1)$$

Table 4.4 BPARs

denoted BPARs	descriptions
A	<i>coefficient of E_{qq}</i>
B	<i>coefficient of E_{qu}</i>
C	<i>coefficient of $E_{\mu\mu}$</i>
D	<i>coefficient of $E_{\alpha q}$</i>
F	<i>coefficient of $E_{\alpha u}$</i>
G	<i>coefficient of $E_{\alpha\alpha}$</i>
J	<i>coefficient of E_{rep}</i>
H	<i>coefficient of E_{qua}</i>
Q	<i>group area factor</i>

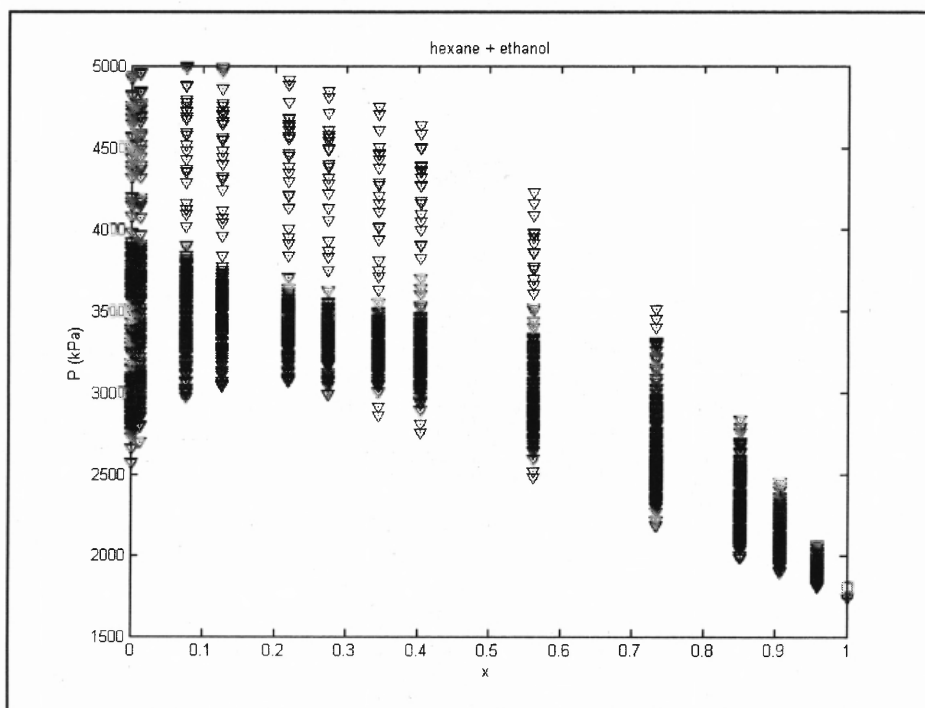
**Figure 4.6** Response of function in fitting parameters in VLE.

Figure 4.6 is an example of data traced with iteration by replacing the BPAR parameters at each point. With data like this example, the sum of the squares of the differences works well in fitting the BPARs.

The optimization used in this study was the Simplex method which Matlab[®] provides. The Simplex methods [31] are based on an initial design of $k+1$ trials, where k

is the number of variables. A $k+1$ geometric Figure in a k -dimensional space is called a simplex.

CHAPTER 5

RESULTS AND DISCUSSION

Global parameters with the new group contribution model (Arturo, 2005) for both UNIFAC and Knox were evaluated using the data sources listed in Appendix D. Global parameters for UNIFAC and Knox are tabulated in Table 5.1.

Table 5.1 Global parameters

Parameters	UNIFAC	Knox*
<i>A</i>	1.51×10^4	1.90×10^{-3}
<i>B</i>	1×10^3	9.71
<i>C</i>	1	2.00×10^{-5}
<i>D</i>	-1	-0.581
<i>F</i>	-3.13×10^3	-1.04×10^6
<i>G</i>	-2.42×10^5	-4.94×10^5
<i>J</i>	4.65×10^3	4.31×10^{-4}
<i>H</i>	-100	-2.98×10^5
<i>Qk</i>	4.50×10^{-3}	0.17

*Parameters evaluated from Carrillo, M. (2005).

Comparison between data from the literature and the prediction of each model has been made and scatter plots demonstrating deviations have been made for each system. Errors are tabulated in Table 5.2. Average gross errors and average deviations for both isothermal and isobaric systems are tabulated in Table 5.3. Figure 5.1 shows the isothermal system of dimethyl ether and 2-propanol at 348 K. Both the UNIFAC and

Knox models are satisfactory with global parameters. Figure 5.2 is a scatter plot for both models and UNIFAC fits well.

Table 5.2 Average errors of results in prediction of equilibrium pressure for VLE systems by UNIFAC and Knox

systems	UNIFAC (%)	Knox (%)	type*
dimethyl ether +2-propanol	0.04	4.58	T
propanenitrile + pentane	-6.62	27.16	T
ethanol + butane	4.80	32.45	T
ethanol + dimethyl ether	-1.9	19.08	T
hexane + 1-propanol	-1.20	9.89	T
ethyl acetate + 1-butanol	-33.83	-1.30	P
1-butanamine + hexane	25.15	-7.035	T
acetate + 1-hexene	10.12	0.35	T
2-propanol + 3-pentanone	-19.66	-5.48	T
n-ethylethanamine + propanone	-19.84	-3.26	T
methanol + water	-28.33	-6.88	T
ethanol+ water	25.03	0.52	T
1-pentene + methyl acetate	41.82	-3.53	T
ethyl acetate + nitromethane	45.70	-3.59	P
propyl ethanoate + nitromethane	54.19	-0.31	P
propanoate + nitromethane	33.74	-2.37	P
1-propanol + 1-pentanol	0.41	0.04	P
acetic acid + ethyl acetate	-4.78	0.91	T
2-propanol + 1-propanol	4.70	2.10	T
methanol + 3-methyl-1-butanol	33.20	44.43	P
1-butene + ethanol	15.21	22.33	T
n-ethylethanmine + ethanenitrile	25.99	16.15	T

* T and P are denoted for isothermal system and isobaric system each.

Table 5.3 Average gross error and deviation from the result in prediction of equilibrium pressure for VLE systems by UNIFAC and Knox

systems		UNIFAC	Knox
Isothermal	average error (%)	4.40	2.02
	average deviation	12.27	10.17
Isobaric	average error (%)	22.23	1.506
	average deviation	18.28	17.56

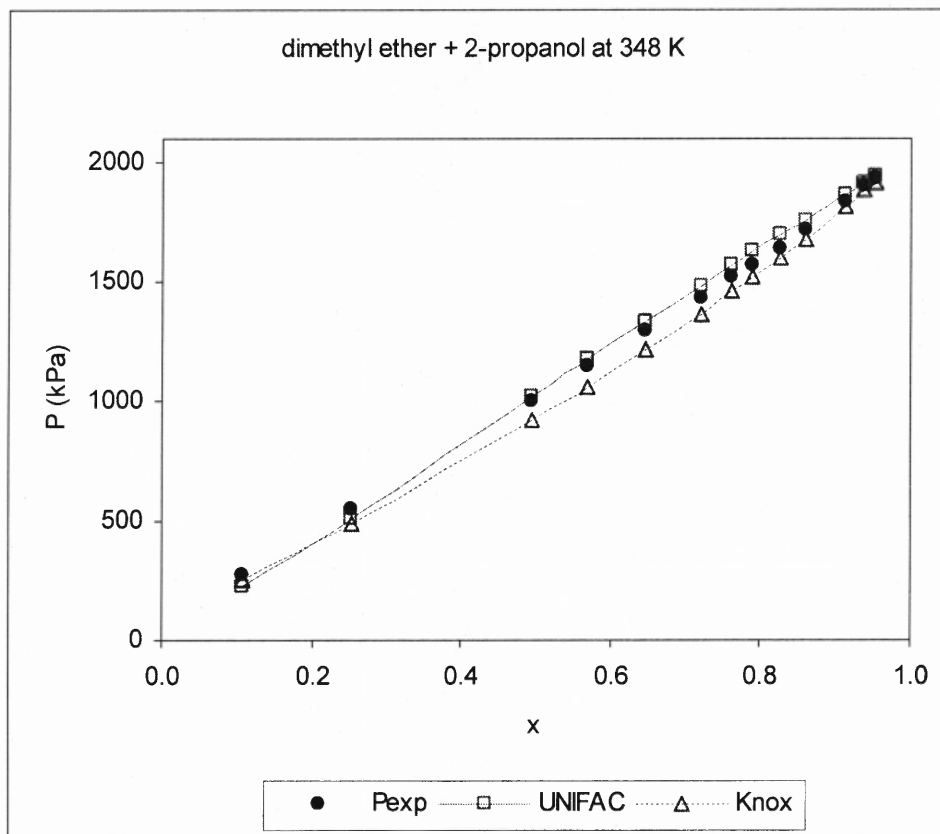


Figure 5.1 Isothermal system of dimethyl ether +2-propanol at 348 K.

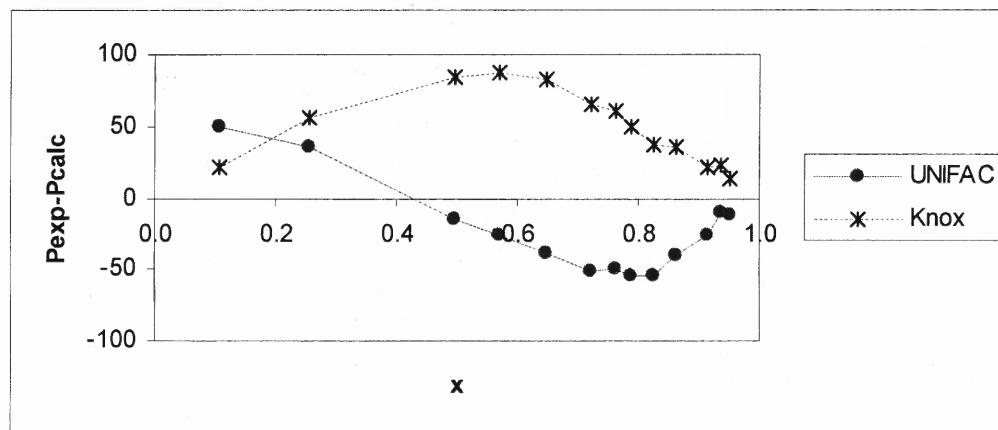


Figure 5.2 Scatter plot of dimethyl ether + 2-propanol at 348 K.

Figure 5.3 shows the isothermal system of propanenitrile and pentane at 313.15 K. UNIFAC follows well with global parameters. Figure 5.4 is a scatter plot for both models and UNIFAC fits well.

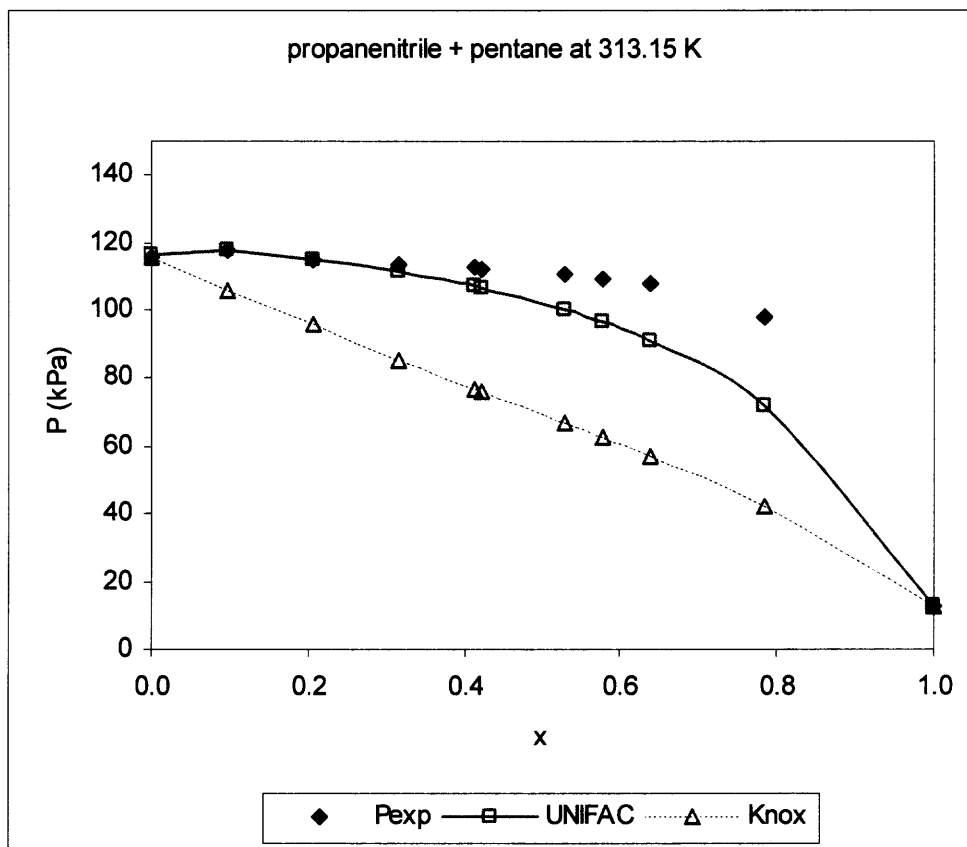


Figure 5.3 Isothermal system of propanenitrile + pentane at 313.15 K.

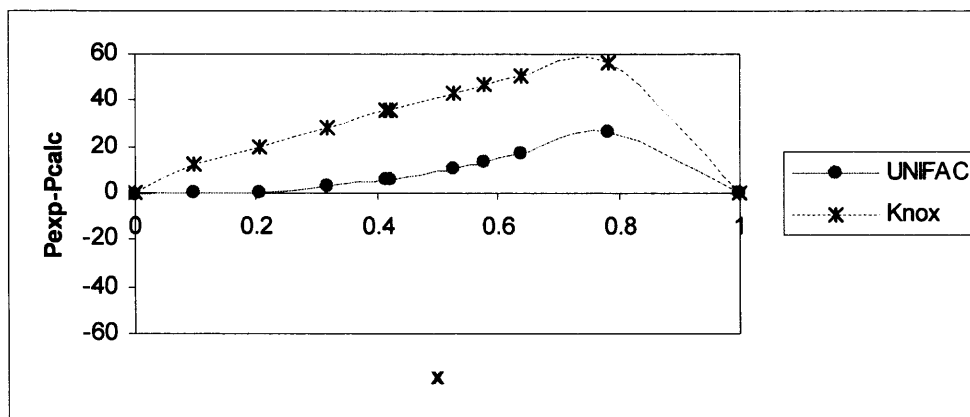


Figure 5.4 Scatter plot of propanenitrile + pentane.

Figure 5.5 shows the isothermal system of ethanol and butane at 293.15 K. UNIFAC fits well with global parameters. Figure 5.6 is a scatter plot for both models and UNIFAC fits well.

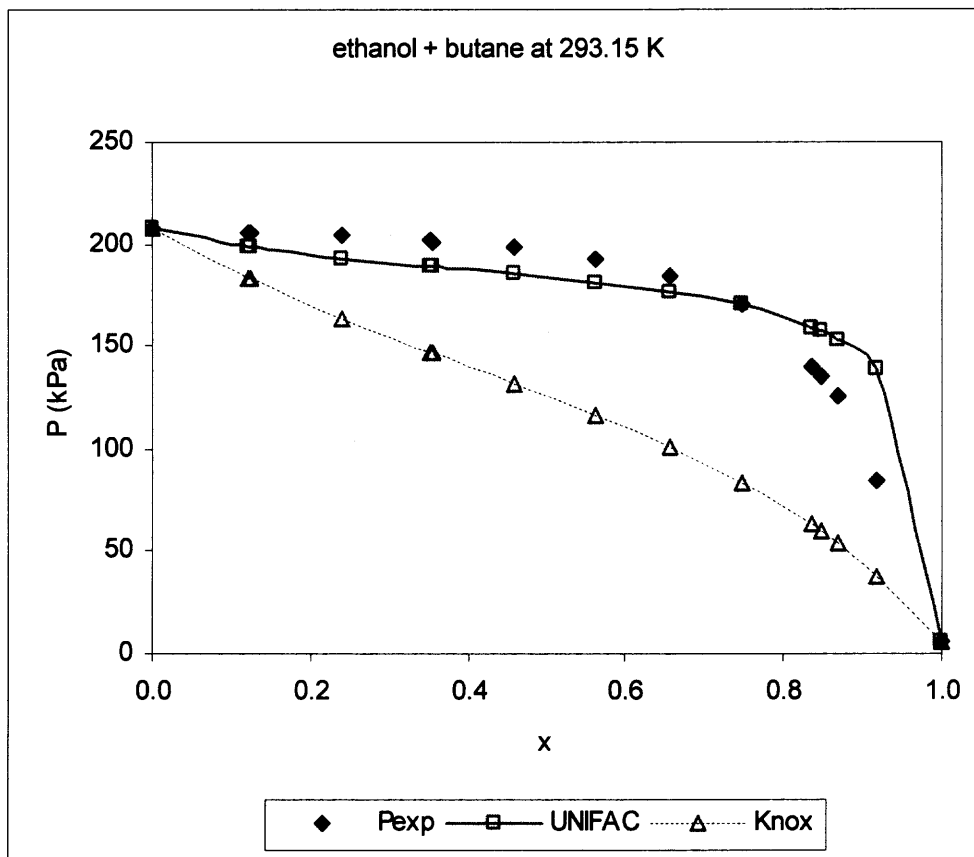


Figure 5.5 Isothermal system of ethanol + butane at 293.15 K.

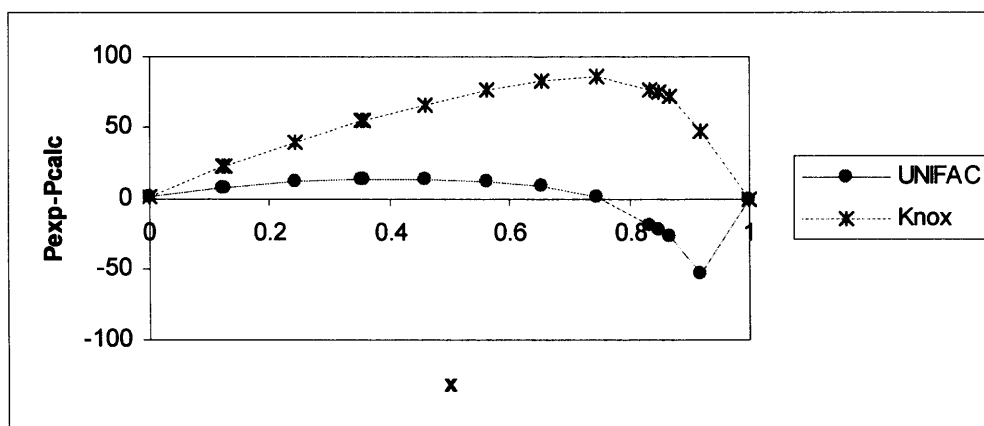


Figure 5.6 Scatter plot of ethanol + butane.

Figure 5.7 shows the isothermal system of ethanol and dimethyl ether at 293.15 K. UNIFAC gives better results than the Knox model in this system with global parameters. Figure 5.8 is a scatter plot for both models and UNIFAC fits well.

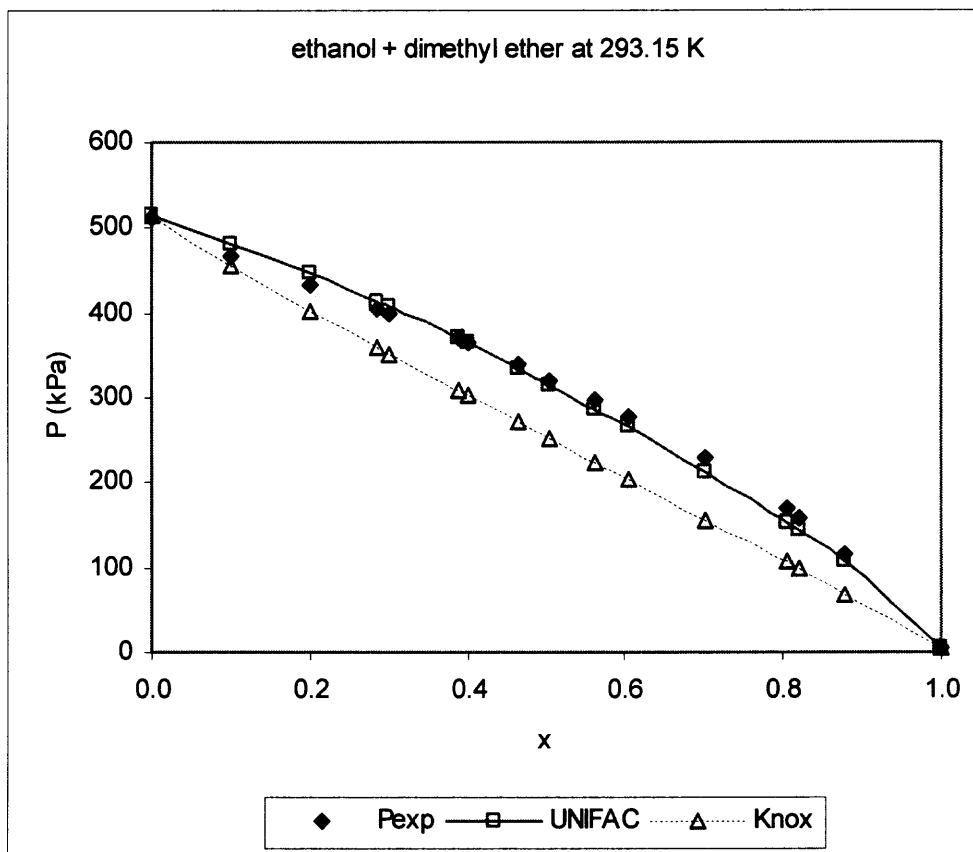


Figure 5.7 Isothermal system of ethanol + dimethyl ether at 293.15 K.

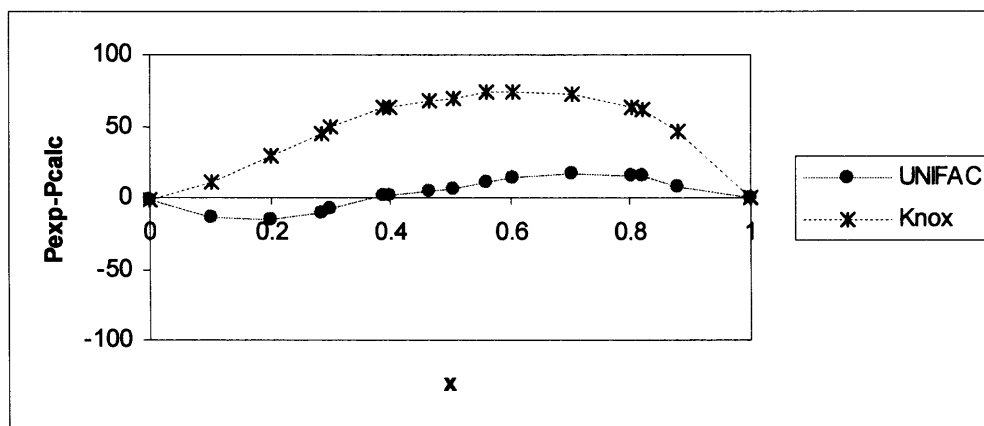


Figure 5.8 Scatter plot of ethanol + dimethyl ether.

Figure 5.9 shows the isothermal system of hexane and 1-propanol at 485.15 K. UNIFAC model is satisfactory with global parameters. Figure 5.10 is a scatter plot for both models and UNIFAC fits well.

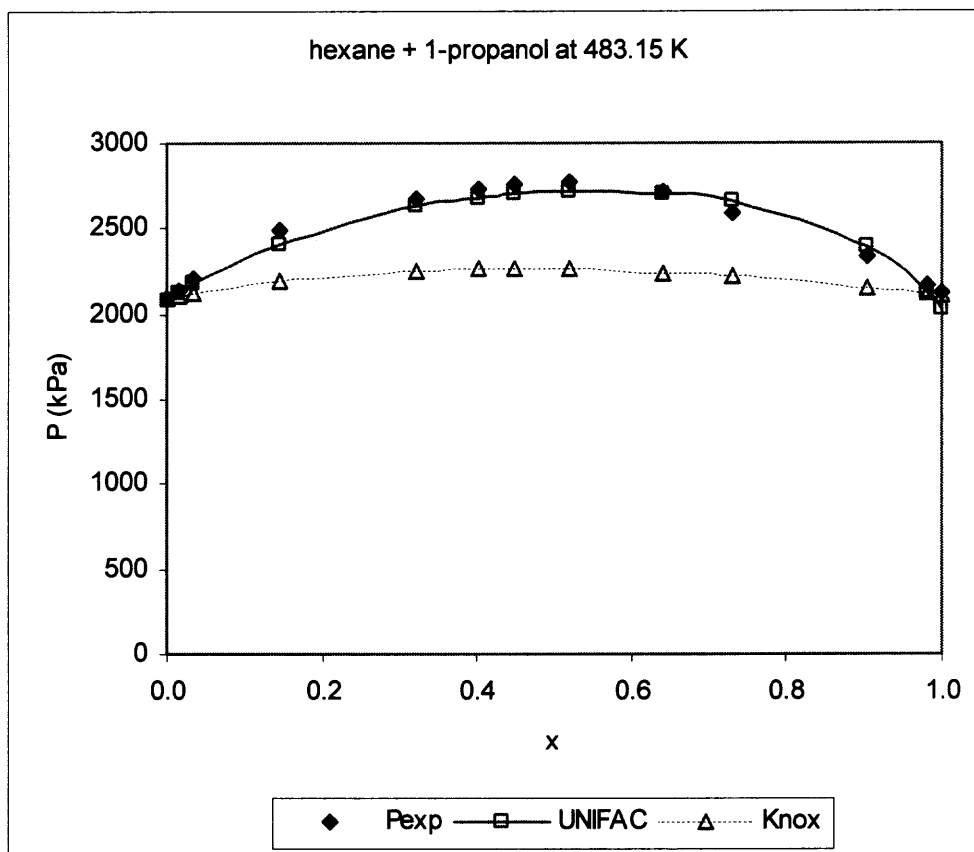


Figure 5.9 Isothermal system of hexane + 1-propanol at 483.15 K.

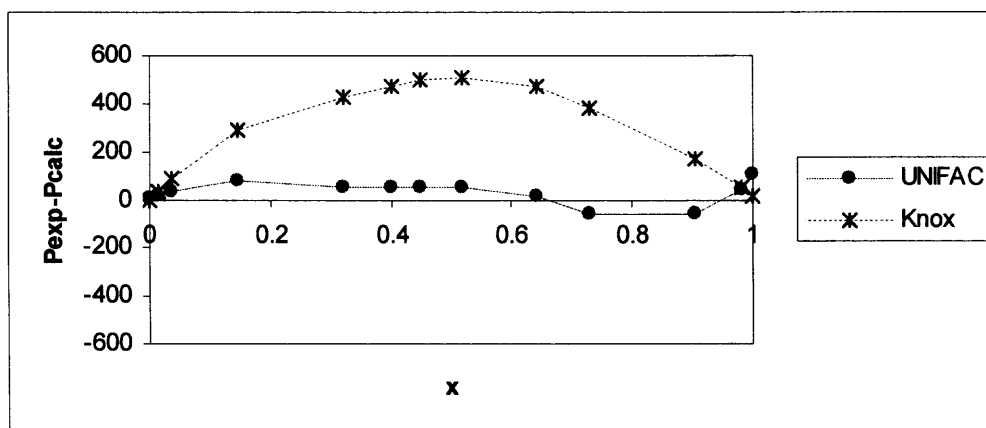


Figure 5.10 Scatter plot of hexane + 1-propanol.

The results shown in Figures 5.1 to 5.10 are satisfactory for the UNIFAC model. All five systems show the satisfactory results better than the Knox model. However, the following figures show the results that are not as satisfactory for UNIFAC in isobaric and

isothermal systems. Figure 5.11 shows the isobaric system of ethyl acetate and 1-butanol at 70.5 kPa. The UNIFAC model is not satisfactory with global parameters. Figure 5.12 is a scatter plot for both models and UNIFAC does not fit well. The Knox model fits well and shows the satisfactory result with global parameters.

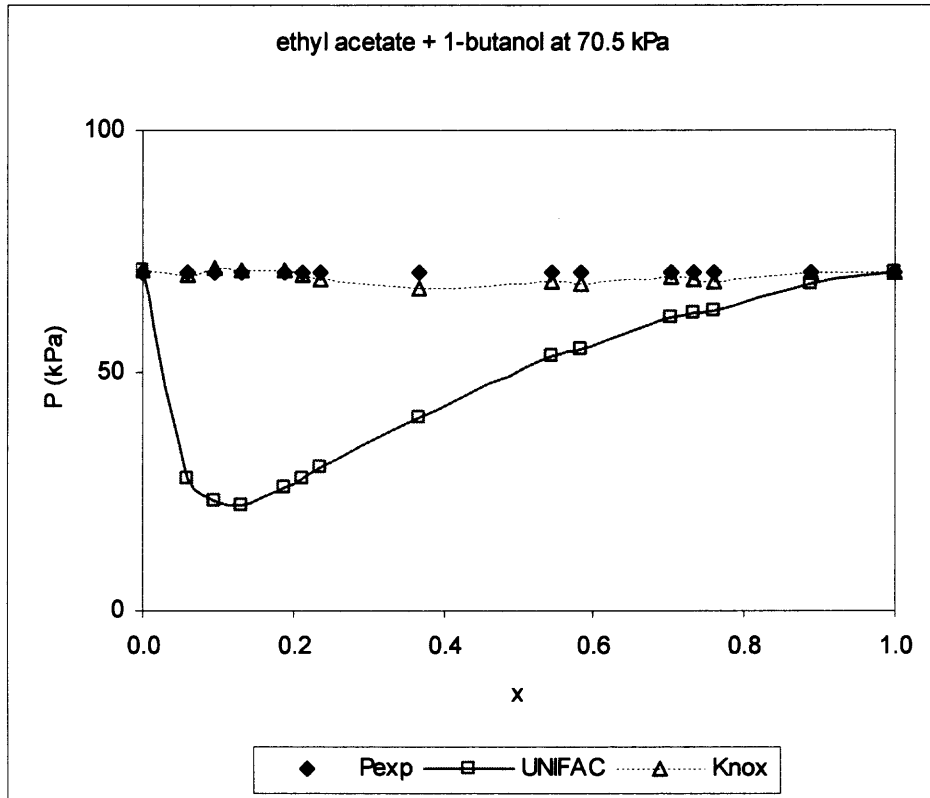


Figure 5.11 Isobaric system of ethyl acetate + 1-butanol at 70.5 kPa.

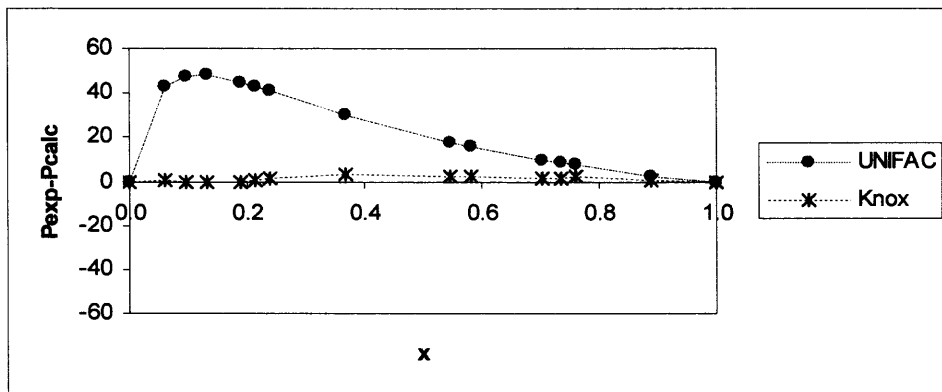


Figure 5.12 Scatter plot of ethyl acetate + 1-butanol.

Figure 5.13 shows the isothermal system of ethyl 1-butanamine and hexane at 293.15 K. The UNIFAC model is less satisfactory than the Knox model with global parameters. Figure 5.14 is a scatter plot for both models and UNIFAC does not fit well. The Knox model fits well and shows a more satisfactory result than the UNIFAC with global parameters.

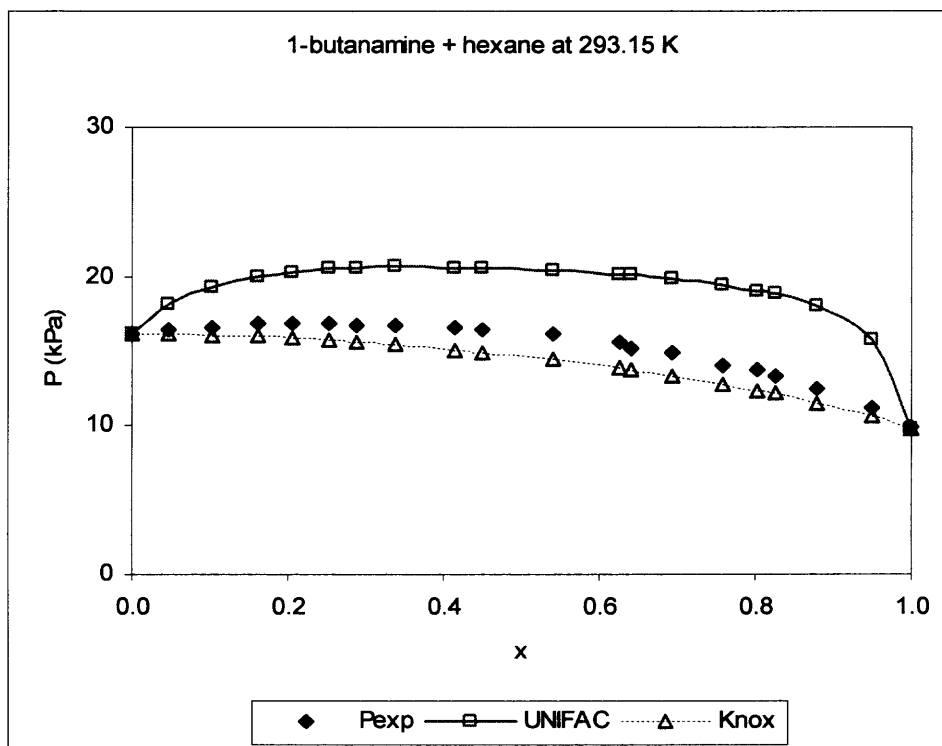


Figure 5.13 Isothermal system of 1-butanamine + hexane at 293.15 K.

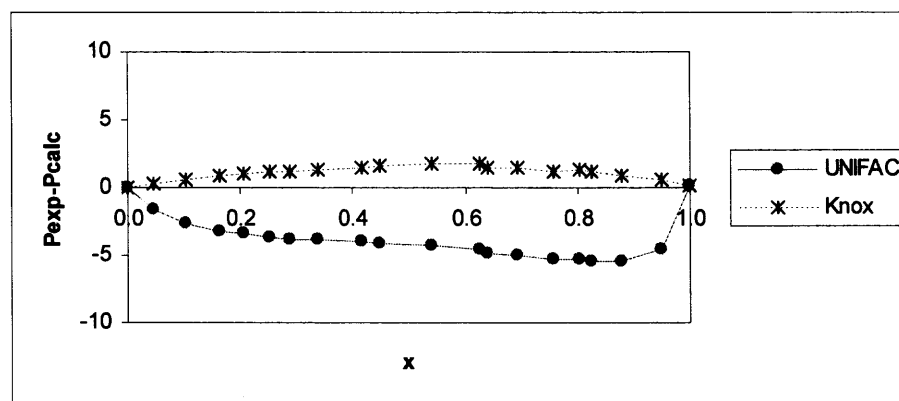


Figure 5.14 Scatter plot of 1-butanamine + hexane.

Figure 5.15 shows the isothermal system of ethyl methyl acetate and 1-hexene at 323.15 K. The UNIFAC model is less satisfactory at lower composition than Knox. Figure 5.16 is a scatter plot for both models for both models and Knox fits well. The Knox model shows a much more satisfactory result than the UNIFAC with global parameters.

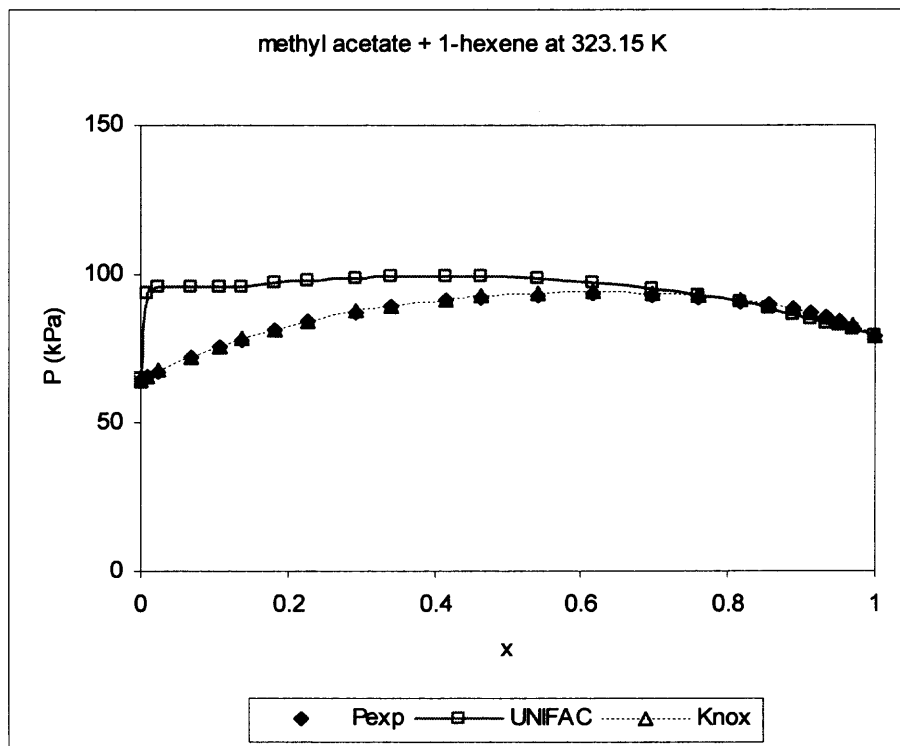


Figure 5.15 Isothermal system of methyl acetate + 1-hexene at 323.15 K.

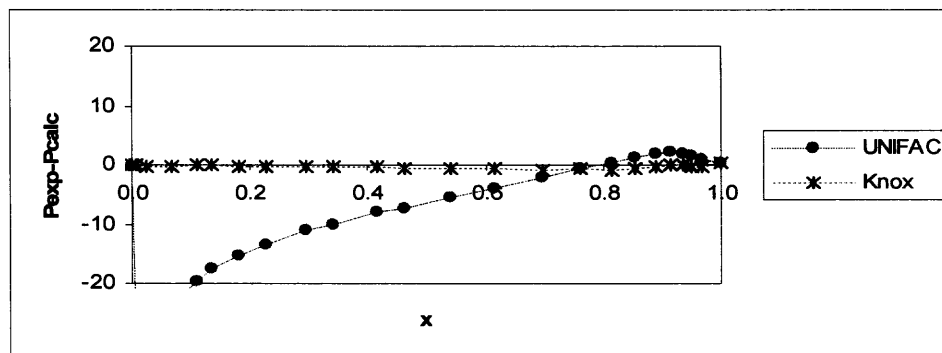


Figure 5.16 Scatter plot of methyl acetate + 1-hexene.

Figure 5.17 shows the isobaric system of 2-propanol and 3-pentanone at 101.3 kPa. The UNIFAC model does not match the experimental data at all compositions. Figure 5.18 is a scatter plot for both models. The Knox model fits well and shows a much more satisfactory result than the UNIFAC with global parameters.

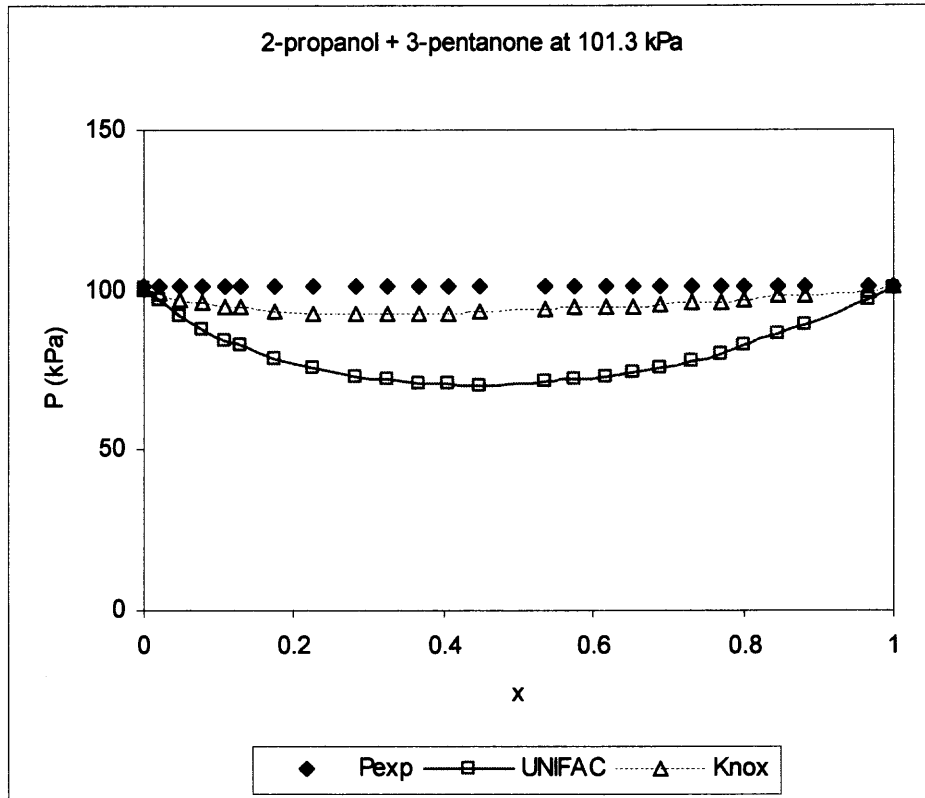


Figure 5.17 Isobaric system of 2-propanol + 3-pentanone at 101.3 kPa.

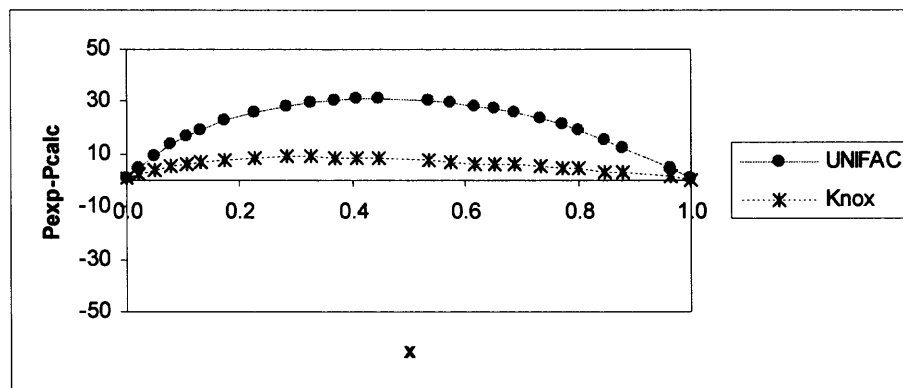


Figure 5.18 Scatter plot of 2-propanol + 3-pentanone.

Figure 5.19 shows the isothermal system of n-ethylethanamine and propanone at 323.15 K. The UNIFAC model is less satisfactory at all compositions than Knox. Figure 5.20 is a scatter plot for both models and Knox fits well. The Knox model shows a much more satisfactory result than the UNIFAC with global parameters.

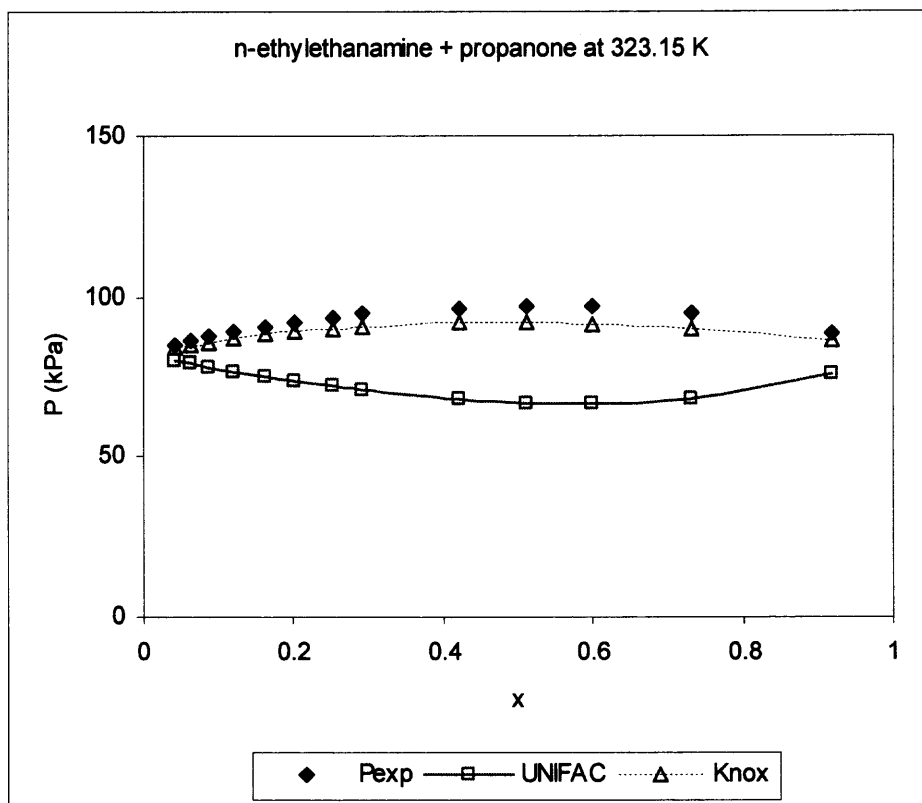


Figure 5.19 Isothermal system of n-ethylethanamine + propanone at 323.15 K.

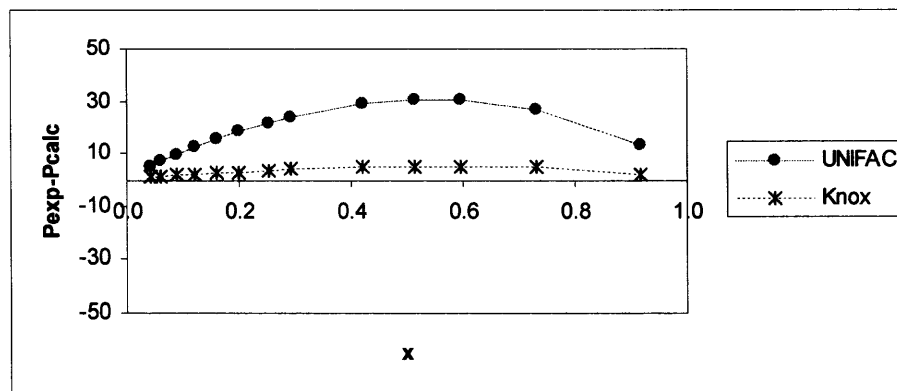


Figure 5.20 Scatter plot of n-ethylethanamine + propanone.

Figure 5.21 shows the isothermal system of methanol and water at 328.15 K. The UNIFAC model is less satisfactory at all compositions than Knox. Figure 5.22 is a scatter plot for both models and Knox fits well. The Knox model shows a more satisfactory result than the UNIFAC with global parameters.

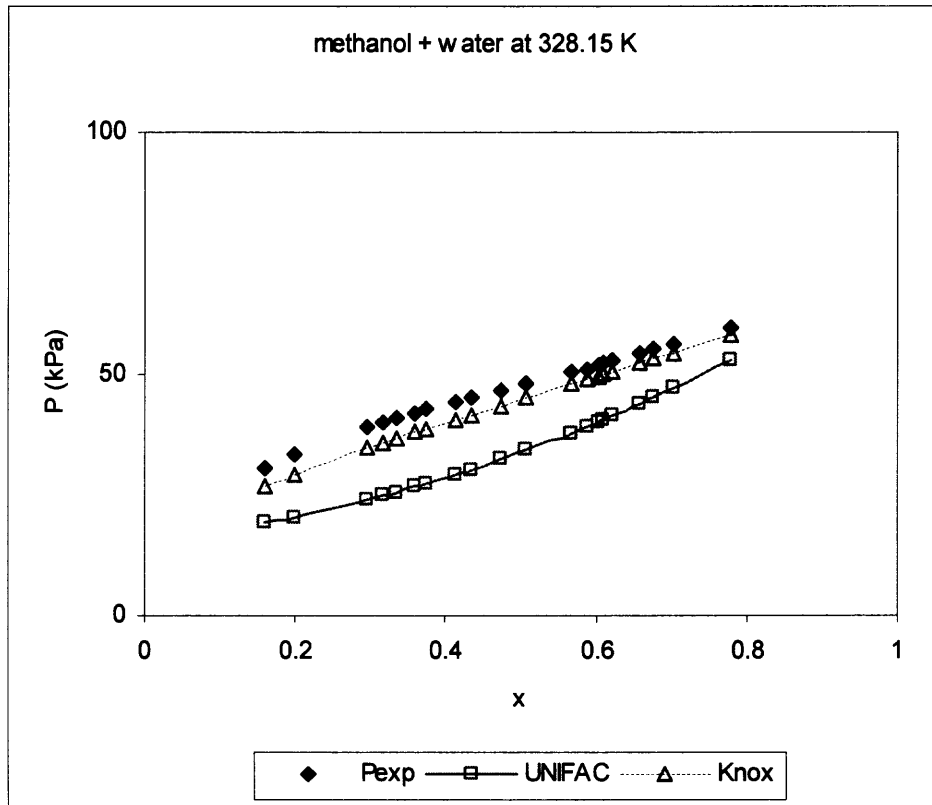


Figure 5.21 Isothermal system of methanol + water at 328.15 K.

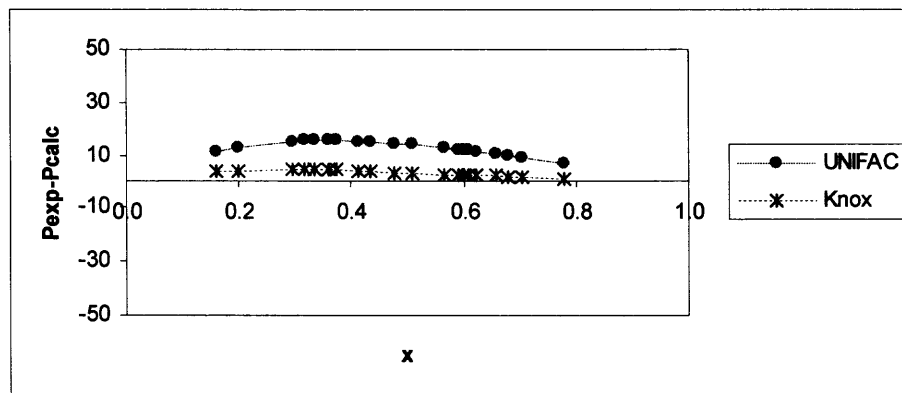


Figure 5.22 Scatter plot of methanol + water.

Figure 5.23 shows the isothermal system of ethanol and water at 323.15 K. The UNIFAC model is less satisfactory at all compositions than Knox. Figure 5.24 is a scatter plot for both models and Knox fits well. The Knox model shows a much more satisfactory result than the UNIFAC with global parameters.

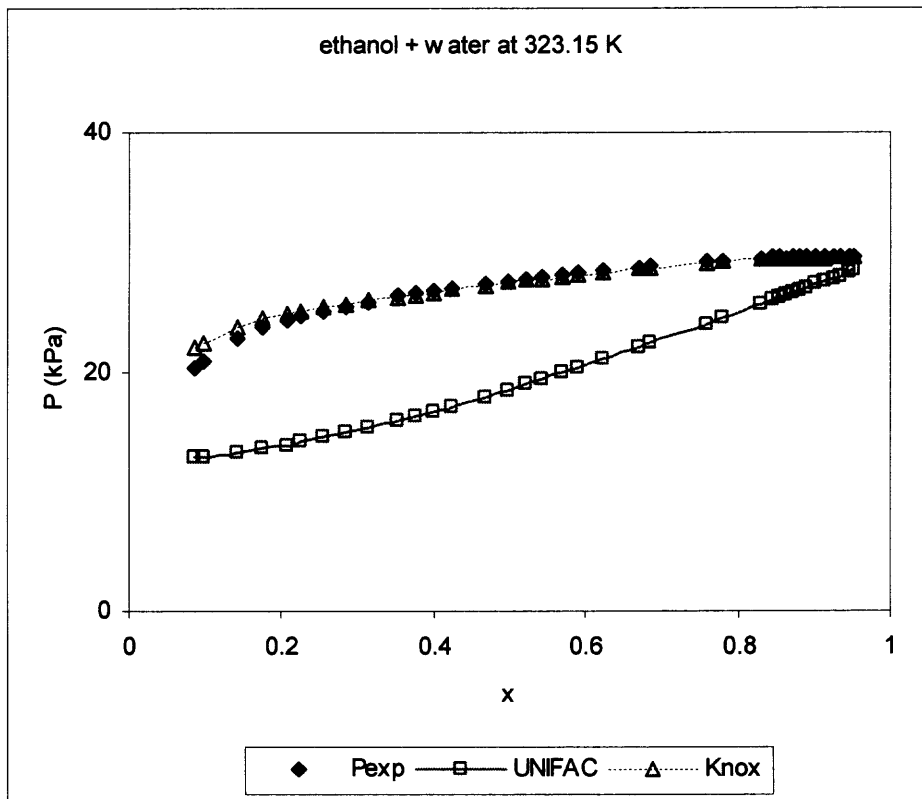


Figure 5.23 Isothermal system of ethanol+ water at 323.15 K.

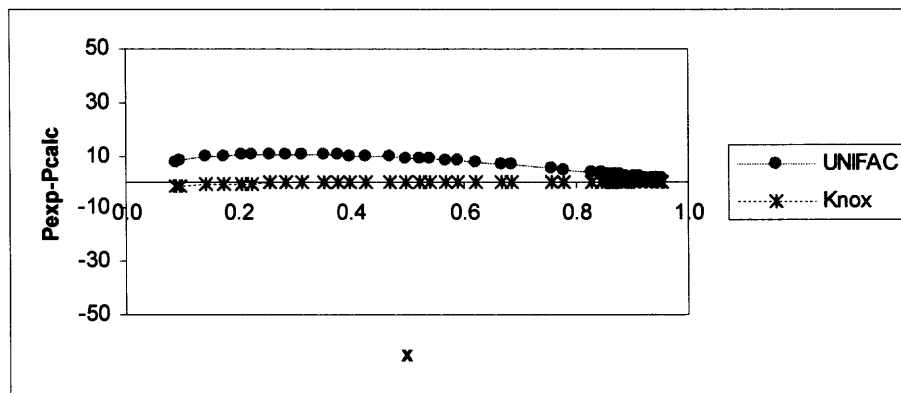


Figure 5.24 Scatter plot of ethanol+ water.

Figure 5.25 shows the isothermal system of 1-pentene and methyl acetate at 323.15 K. The UNIFAC model does not work well with the global parameter correlation. Figure 5.26 is a scatter plot for both models and Knox fits well. The Knox model shows a much more satisfactory result than the UNIFAC with global parameters.

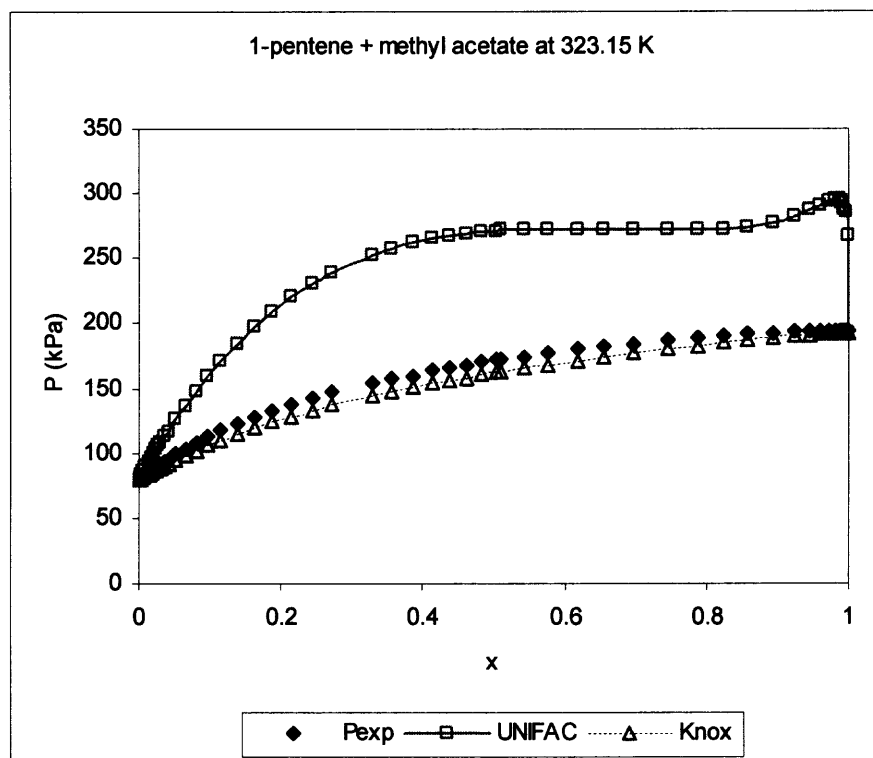


Figure 5.25 Isothermal system of 1-pentene + methyl acetate at 323.15 K.

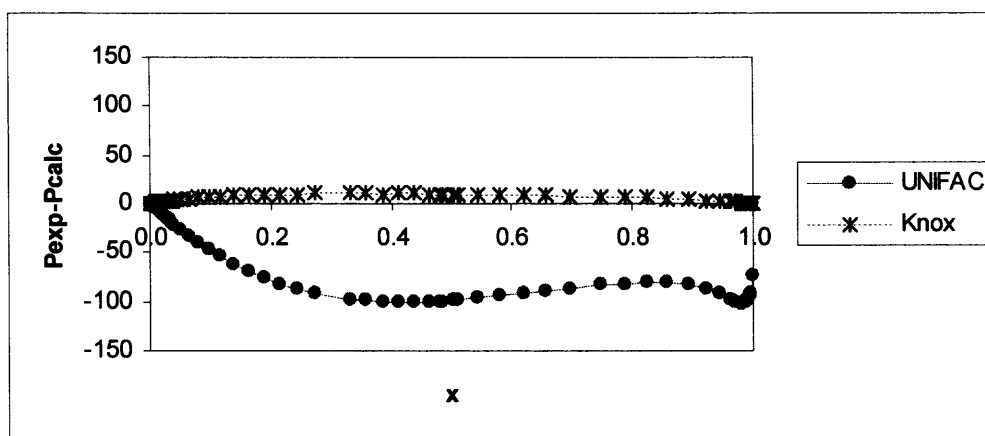


Figure 5.26 Scatter plot of 1-pentene + methyl acetate.

Figure 5.27 shows the isobaric system of ethyl acetate and nitromethane at 101.3 kPa. The UNIFAC model is unsatisfactory at all compositions. Figure 5.28 is a scatter plot for both models and Knox fits well. The Knox model shows a much more satisfactory result than the UNIFAC with global parameters.

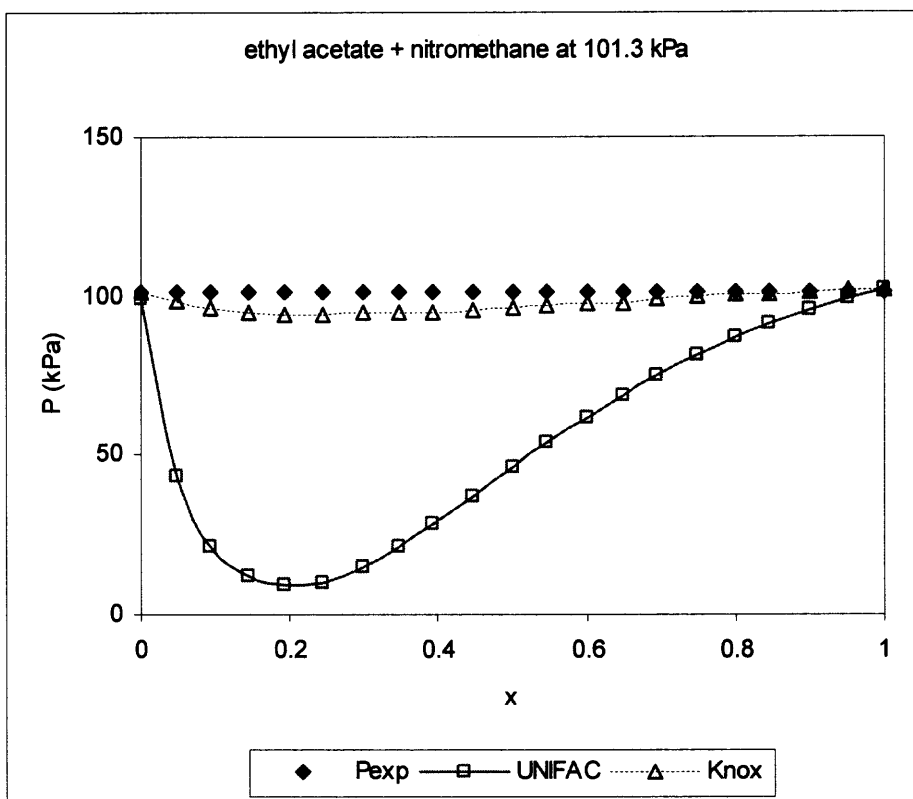


Figure 5.27 Isobaric system of ethyl acetate + nitromethane at 101.3 kPa.

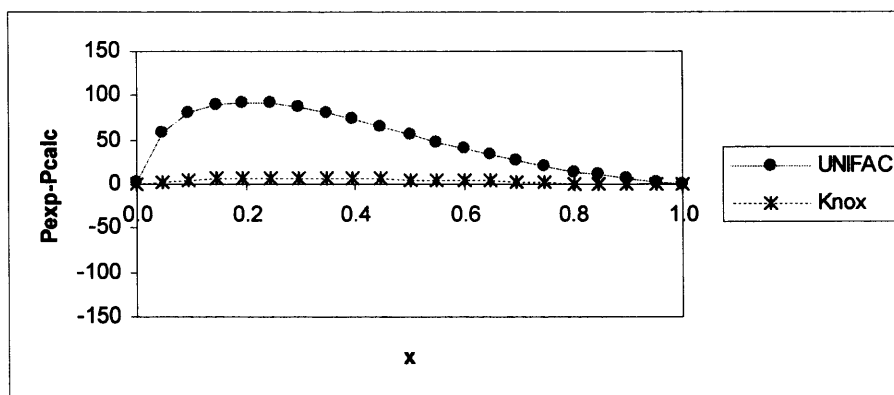


Figure 5.28 Scatter plot of ethyl acetate + nitromethane.

Figure 5.29 shows the isobaric system of propyl ethanoate and nitromethane at 101.3 kPa. The UNIFAC model is unsatisfactory at all compositions. Figure 5.30 is a scatter plot for both models and Knox fits well. The Knox model shows a very satisfactory result with global parameters.

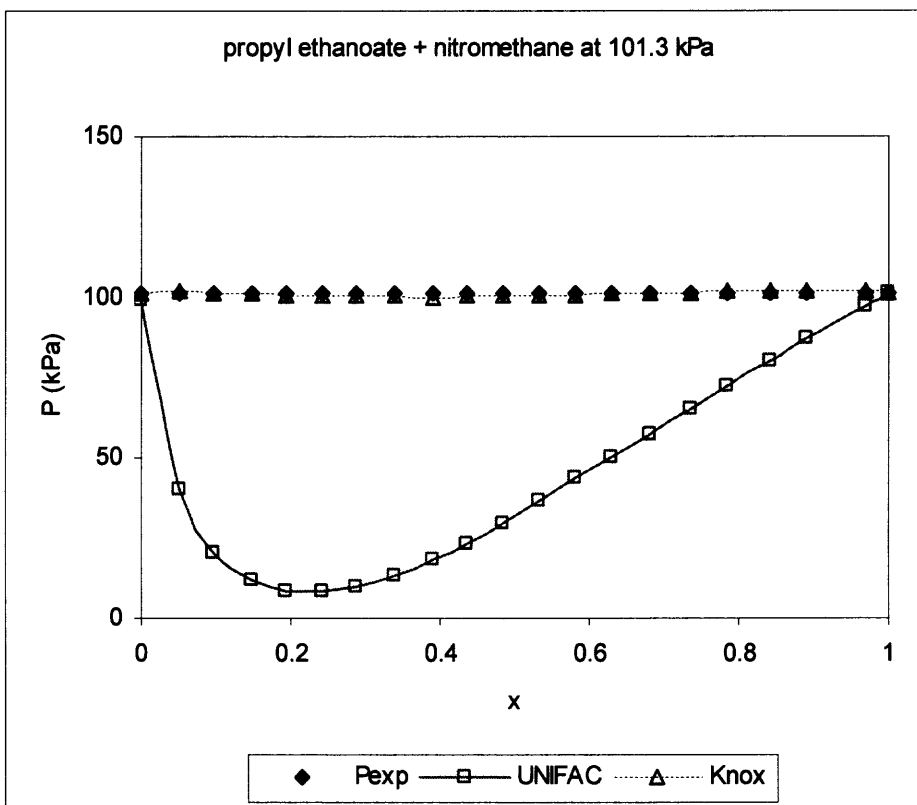


Figure 5.29 Isobaric system of propyl ethanoate + nitromethane at 101.3 kPa.

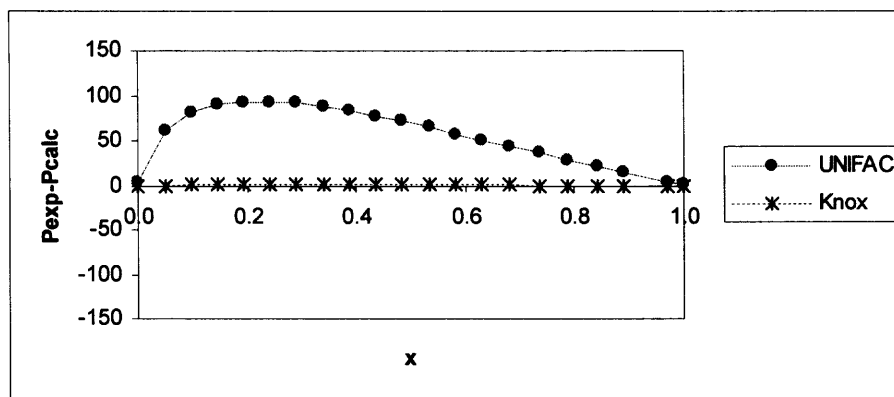


Figure 5.30 Scatter plot of propyl ethanoate + nitromethane.

Figure 5.31 shows the isobaric system of ethyl propanoate and nitromethane at 101.3 kPa. The UNIFAC model is unsatisfactory at all compositions. Figure 5.32 is a scatter plot for both models and Knox fits well. The Knox model shows a much more satisfactory result than the UNIFAC with global parameters.

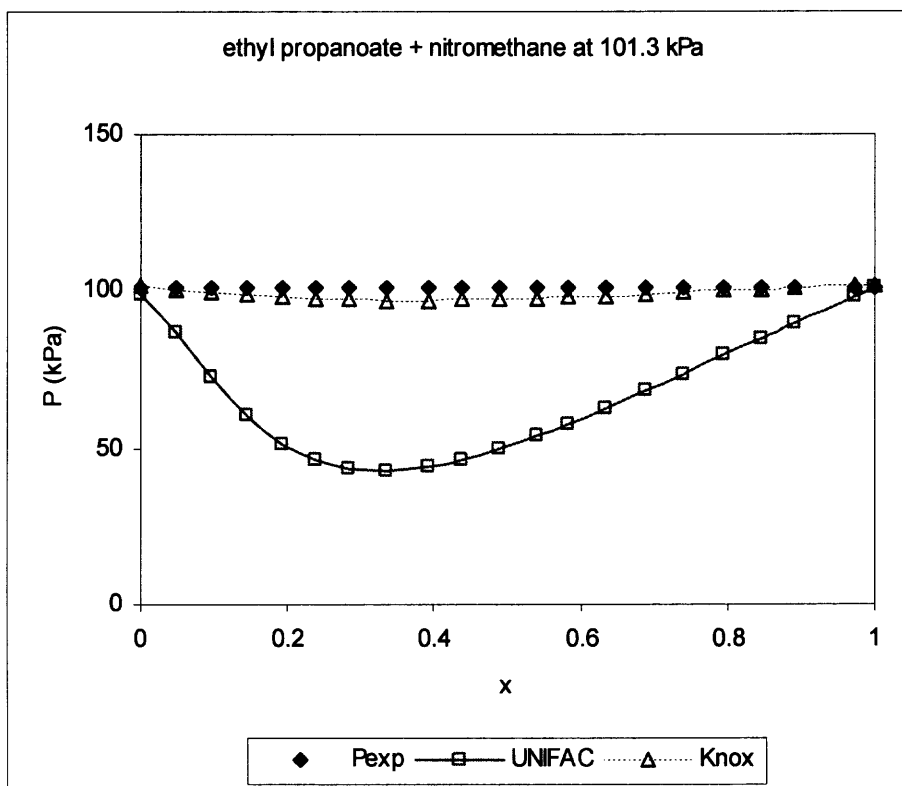


Figure 5.31 Isobaric system of ethyl propanoate + nitromethane at 101.3 kPa.

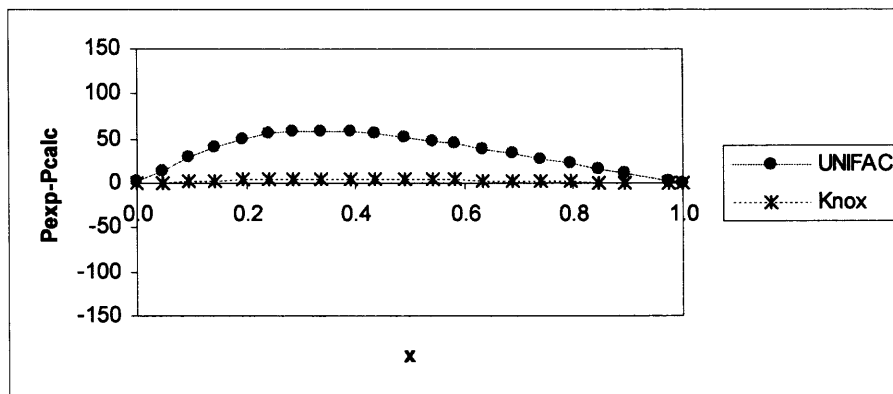


Figure 5.32 Scatter plot of ethyl propanoate + nitromethane.

The following examination will show the satisfactory result for both UNIFAC and Knox. Both models fit very well and show very satisfactory results for isothermal and isobaric systems in 5% error percents. Figure 5.33 shows the isobaric system of 1-propanol and 1-pentanol at 101.3 kPa. Both the UNIFAC and Knox models are very satisfactory in all compositions. Figure 5.34 is a scatter plot for both models and both models show satisfactory results with global parameters.

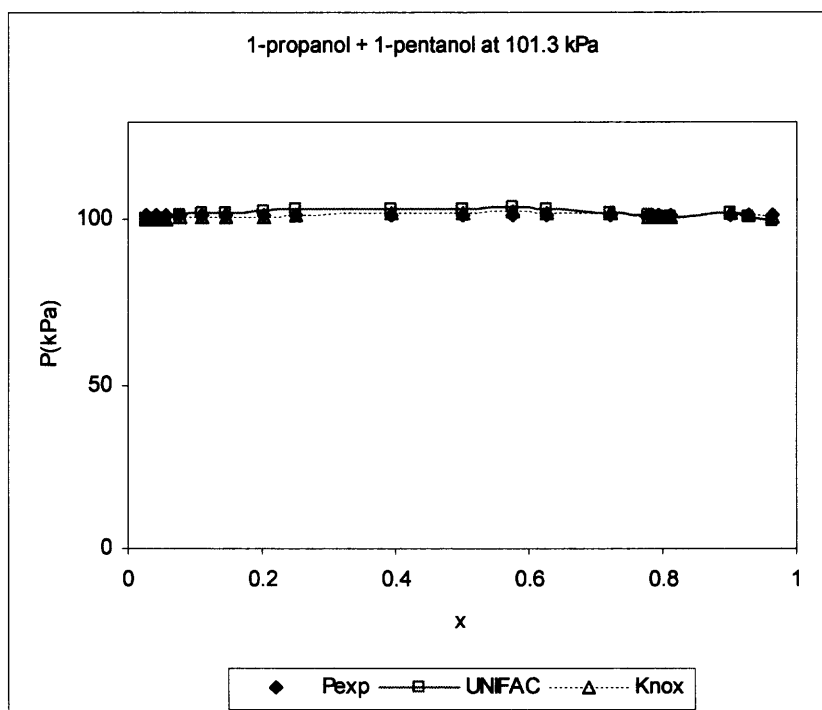


Figure 5.33 Isobaric system of 1-propanol + 1-pentanol at 101.3 kPa.

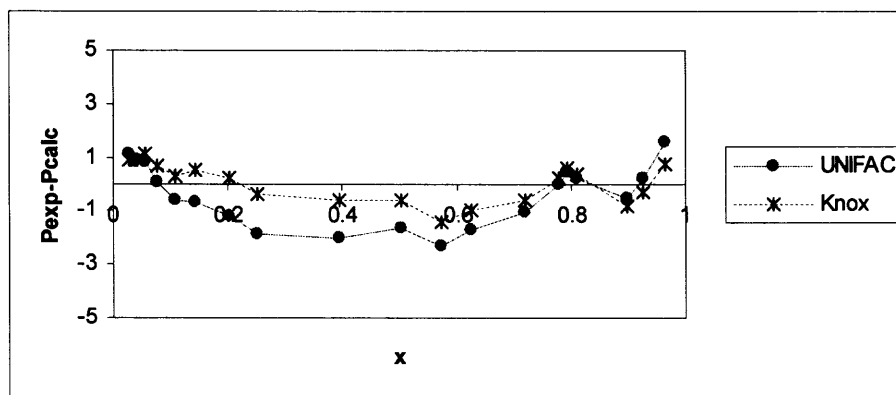


Figure 5.34 Scatter plot of 1-propanol + 1-pentanol.

Figure 5.35 shows the isothermal system of acetic acid and ethyl acetate at 323.2 K. Both the UNIFAC and Knox models are very satisfactory for all compositions. Figure 5.36 is a scatter plot for both models and both models fit well. However, the Knox model shows a better fit than UNIFAC according to Table 5.2. Both models show satisfactory results with global parameters.

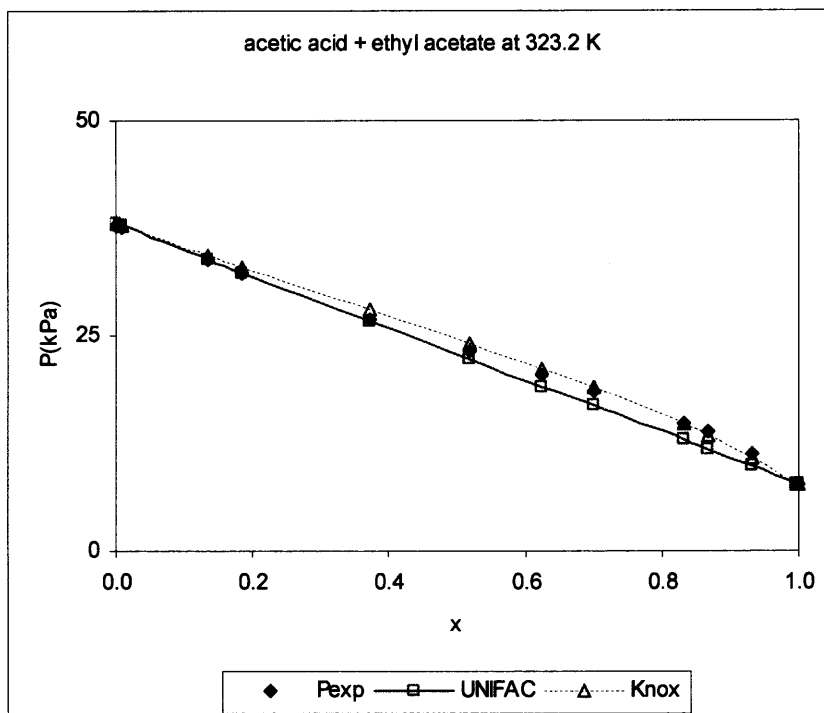


Figure 5.35 Isothermal system of acetic acid + ethyl acetate at 323.2 K.

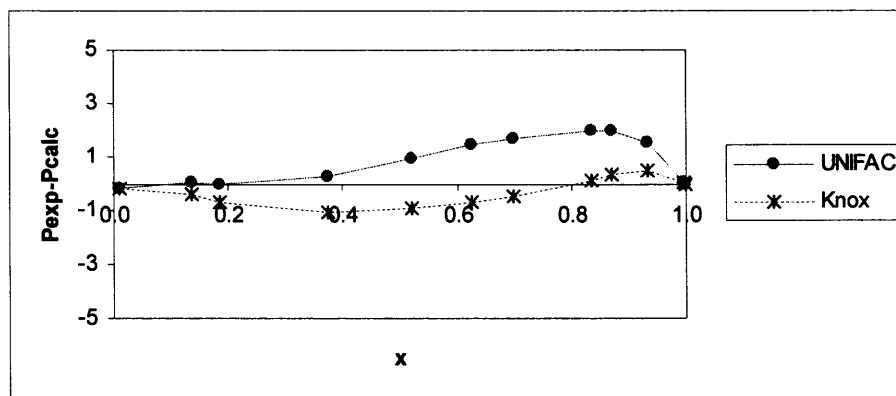


Figure 5.36 Scatter plot of acetic acid + ethyl acetate.

Figure 5.37 shows the isothermal system of 2-propanol and 1-propanol at 298.15 K. Both the UNIFAC and Knox models are very satisfactory at all compositions. Figure 5.38 is a scatter plot for both models and both models fit well. However, the Knox model shows a better fit than UNIFAC according to Table 5.2. Both models show satisfactory results with global parameters.

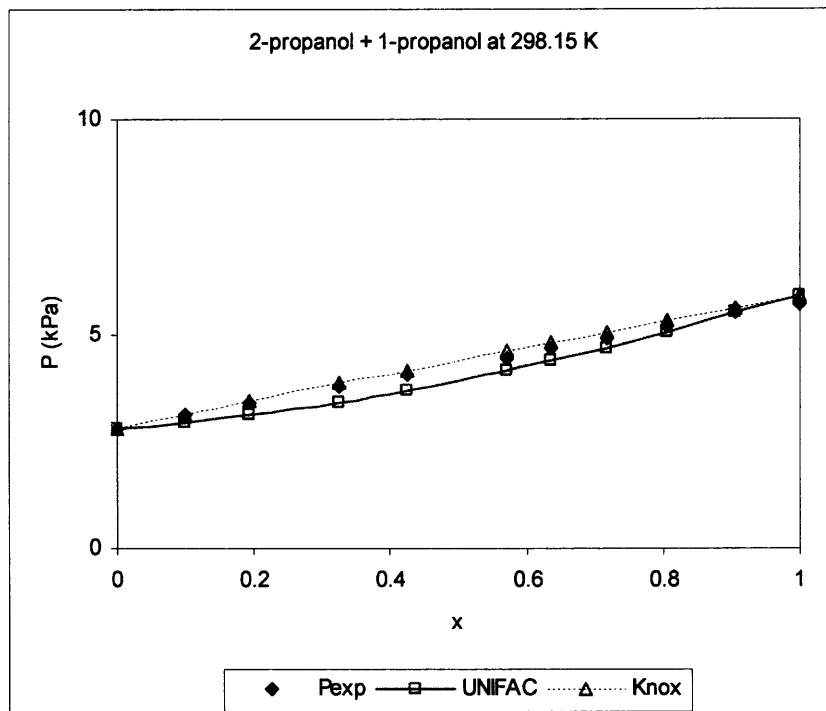


Figure 5.37 Isothermal system of 2-propanol + 1-propanol at 298.15 K.

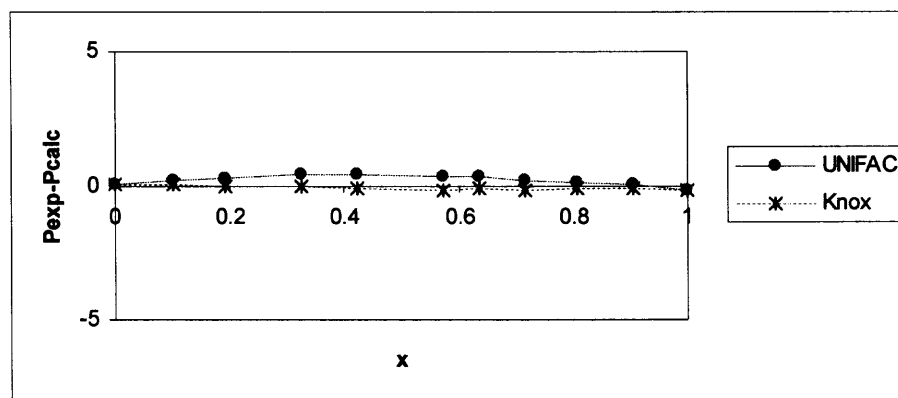


Figure 5.38 Scatter plot of 2-propanol + 1-propanol.

The next figures show the disagreement with the global parameter in both UNIFAC and the Knox model in a wide range of error. Figures 5.39 to 5.42 show the isobaric system of methanol and 3-methyl-1-butanol at 101.3 kPa, isothermal system of 1-butene + ethanol at 326 K, and isothermal system of n-ethylethanamine + ethanenitrile at 323.15 K. Both the UNIFAC and Knox models do not agree with the experimental data.

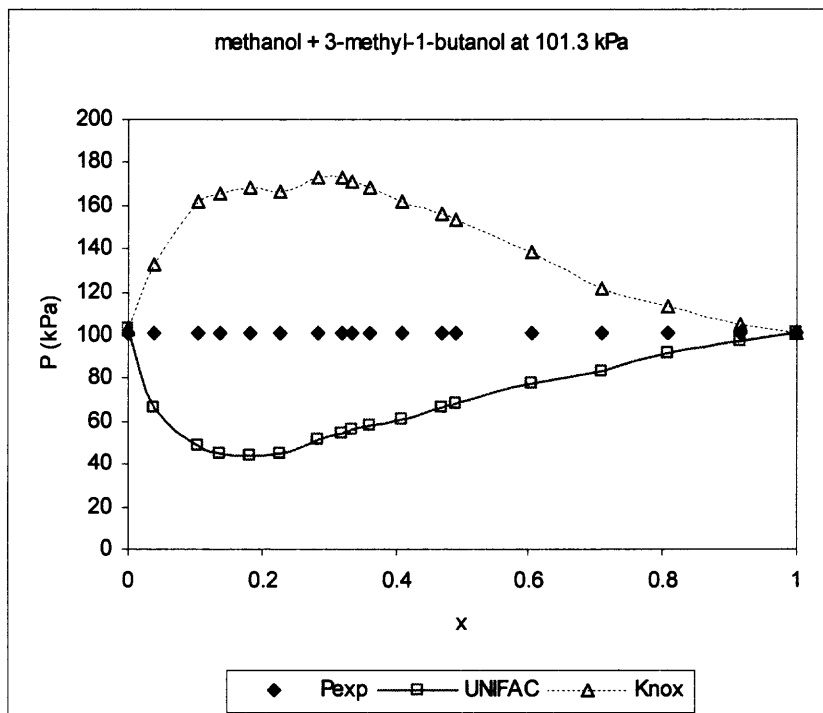


Figure 5.39 Isothermal system of methanol + 3-methyl-1-butanol at 101.3 kPa.

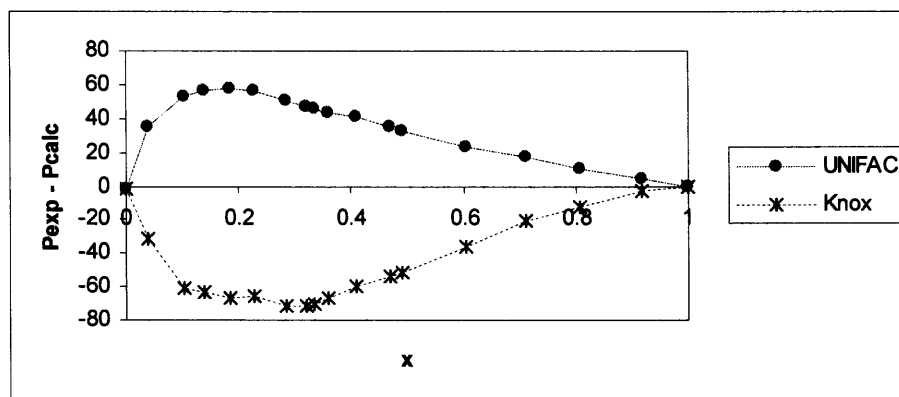


Figure 5.40 Scatter plot of methanol + 3-methyl-1-butanol.

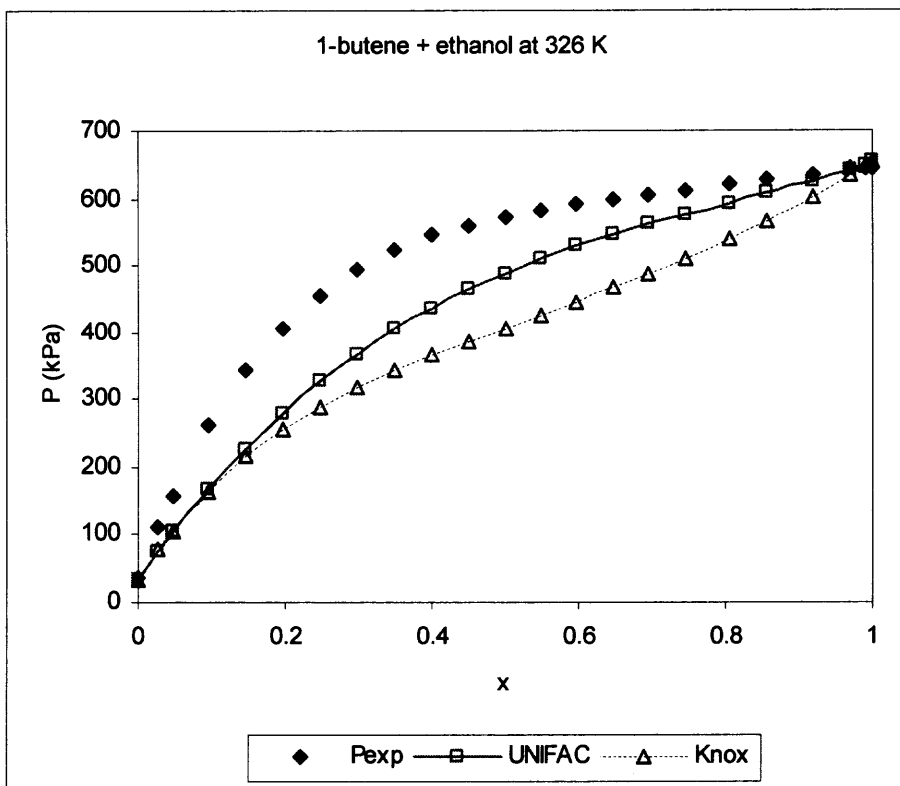


Figure 5.41 Isothermal system of 1-butene + ethanol at 326 K.

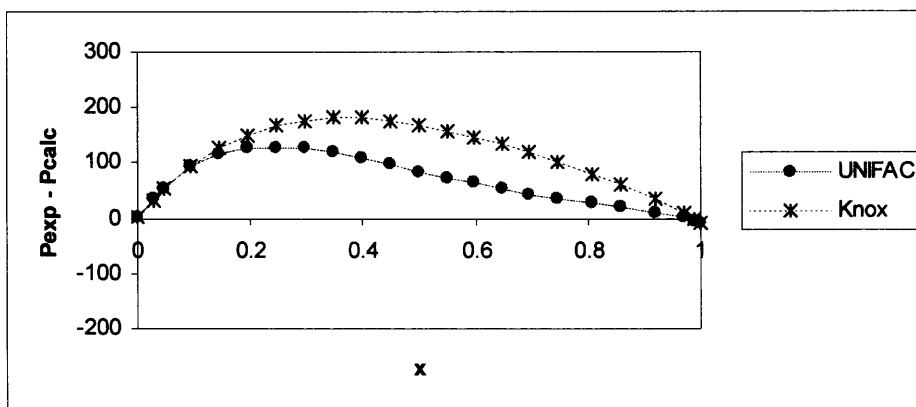


Figure 5.42 Scatter plot of 1-butene + ethanol.

The new group contribution method has been inserted in both the UNIFAC and Knox models to predict the VLE. The results reported in Table 5.2 indicate the average deviation from the experimental data. The average deviations and errors for isothermal systems and isobaric systems are summarized in Table 5.3.

Table 5.3 indicates that the Knox model in both isothermal systems and isobaric systems, achieved better agreement. Knox predicts better than UNIFAC in alcohol + water system and isobaric systems. UNIFAC predicts better than Knox in the system of dimethyl ether + 2-propanol, ethanol + dimethyl ether, and hexane +1-propanol in this study only. UNIFAC obeys the new group contribution model and global parameter in some cases. However, Knox shows a wider range of agreement in isothermal systems and predicts very good consistency in isobaric systems with the new group contribution model.

CHAPTER 6

CONCLUSION AND FUTURE STUDY

A new approach has been used to evaluate the parameters in both the UNIFAC and Knox group contribution methods. Nine global parameters have been evaluated using selected isobaric systems and isothermal systems from the literature. The limits for the parameter values are defined based on theory [32, 33, 34]. The new approach used in the study obtains the group interaction energies by using charges, reduced dipoles, polarizabilities, as well as the repulsive force between a pair of newly defined function groups. The properties have been calculated by Arturo (2005) based on *ab initio* molecular orbital calculations. The pressure has then been calculated employing the UNIFAC or Knox model. The result have been compared to experimental data and discussed.

Both methods obtain similar predictions in 1-propanol + 1-pentanol, acetic acid + ethyl acetate, and 2-propanol + 1-propanol systems. Some systems do not agree with the new group contribution model well either with UNIFAC or Knox. However, Knox shows better results in a wider range of isothermal systems and isobaric systems, with good agreement achieved especially in isobaric systems. The Knox method obtains better results than the UNIFAC method in this study.

Finally, after reviewing and comparing the results from the two group contribution methods, a new group contribution will be needed. Regression with large data sets will be needed to prove the capability of the model for the prediction of vapor liquid equilibria.

Appendix A

Vapor Pressure Correlations Parameters

Table A.1 Vapor pressure correlations parameters

compound	a	b	c	d	CAS #	Eqn.*
propane	-5.395526	-3383.994	48.14260	9.132115E-06	74-98-6	5
butane	3.932660	935.773	238.78900		106-97-8	1
hexane	4.001390	1170.875	224.31700		110-54-3	1
pentane	-10.418400	-5778.024	81.92460	1.178208E-05	109-66-0	5
propene	3.956060	789.624	247.58000		115-07-1	1
1-butene	-7.789791	-4509.829	64.34735	9.816232E-06	106-98-9	5
1-pentene	3.969140	1044.010	233.45000		109-67-1	1
1-hexene	-9.066855	-6020.314	74.33390	8.228353E-06	592-41-6	5
methanol	5.202770	1580.080	239.50000		67-56-1	1
ethanol	-5.089412	-6606.453	53.17030	5.954048E-07	64-17-5	5
1-propanol	-7.702226	-8002.693	71.71697	3.950448E-07	71-23-8	5
2-propanol	-7.694051	-7690.896	71.34113	7.656355E-07	67-63-0	5
1-butanol	4.649300	1395.140	182.73900		71-36-3	1
2-butanol	-12.485090	-9518.041	103.63300	3.342489E-06	78-92-2	5
2-methyl-2-propanol	4.444840	1154.480	177.65000		75-65-0	1
2-methyl-1-propanol	4.345040	1190.380	166.67000		78-83-1	1
1-pentanol	-19.381940	-12196.400	149.34630	9.395708E-06	71-41-0	5
2-methyl-2-butanol	3.644200	863.400	135.30000		75-85-4	1
3-methyl-1-butanol	4.078510	1128.190	146.47000		123-51-3	1
dimethyl ether	-4.793276	-3695.179	45.56573	5.946616E-06	115-10-6	5
propanone	-7.858812	-5784.592	66.96925	7.104956E-06	67-64-1	5
butanone	-7.783651	-6160.169	66.97868	6.139268E-06	78-93-3	5
3-pentanone	4.427080	1481.170	233.01000		96-22-0	1
methanoic	-9.793940	-6677.451	78.90439	1.143160E-05	64-18-6	5
ethanoic acid	4.544560	1555.120	224.65000		64-19-7	1
propanoic	4.754660	1662.582	209.04600		79-09-4	1
methyl ethanoate	4.186210	1156.430	219.69000		79-20-9	1
ethyl methanoate	4.078990	1101.000	215.98000		109-94-4	1
methyl propanoate	3.987450	1129.570	204.24000		554-12-1	1
ethyl ethanoate	4.133610	1195.130	212.47000		141-78-6	1
propyl ethanoate	-11.948620	-7931.973	95.43266	8.274244E-06	109-60-4	5
vinyl ethanoate	-4.867874	-5477.728	48.62488	2.367095E-06	108-05-4	5
1-butanamine	-6.304800	-6041.874	58.45341	2.903891E-06	109-73-9	5
dimethyl amime	-5.114422	-5219.584	49.85691	2.349476E-06	109-73-9	5
ethanenitrile	4.278730	1355.374	-37.85300		75-05-8	1
nitromethane	-10.207780	-7217.173	83.18124	8.369119E-06	75-52-5	5
water	-7.342973	-7276.391	67.02455	4.161914E-06	7732-18-5	5

* Eqn. #1: $\log_{10}(P_{vp})=a-b/(T+c-273.15)$, where P_{vp} in bar.

* Eqn. #5: $\ln(P_{vp}) = a*\ln(T) + b/T + c + d*T^2$, where P_{vp} in kPa.

Appendix B

Basic Properties

Table B.1 Basic properties of molecules

compound	Pc,bar	Tc,K	Vc ,cm ³ /mol	M.W	w	dipole,debye	Vliq,cm ³ /mol	T _{ref.liq} ,K
propane	42.48	369.83	200	44.097	0.152	0	74.87	233.15
butane	80.97	512.64	118	32.042	0.565	1.7	40.73	298.15
hexane	30.25	507.6	368	86.177	0.3	0	131.39	298.15
pentane	33.7	496.7	311	72.15	0.252	0	115.22	298.15
1-butene	40.2	419.5	240.8	56.108	0.194	0.3	95.34	298.15
1-pentene	35.6	464.8	298.4	70.134	0.237	0.4	110.4	298.15
1-hexene	31.43	504	355.1	84.161	0.281	0.4	125.9	298.15
methanol	80.97	512.64	118	32.042	0.565	1.7	40.73	298.15
ethanol	61.48	513.92	167	46.069	0.649	1.7	58.68	298.15
1-propanol	51.72	563.78	219	60.096	0.254	1.7	75.14	298.15
2-propanol	47.62	508.3	220	60.096	0.665	1.7	76.92	298.15
1-butanol	44.23	563.05	275	74.123	0.59	1.8	91.96	298.15
2-butanol	41.79	536.05	269	74.123	0.574	1.7	92.35	298.15
2methyl-2propanol	39.73	506.21	275	74.123	0.613	1.7	94.88	298.15
2methyl-1propanol	43	547.78	273	74.123	0.59	1.7	92.91	298.15
1-pentanol	39.09	588.15	326	88.15	0.579	1.7	108.63	298.15
2-methyl-2butanol	37.9	545	323	88.15	0.478	1.9	109.5	298.15
3-methyl-1butanol	39.1	579.4	325	88.15	0.559	1.8	109.22	298.15
dimethyl ether	54	400.1	170	46.069	0	1.3	69.07	293.15
Propanone	47	508.1	209	58.08	0.307	2.9	73.94	298.15
Butanone	42.1	536.8	267	72.107	0.322	3.3	90.13	298.15
3-pentanone	37.3	561.5	336	86.134	0.342	2.7	106.41	298.15
Methanoic	58.07	588	124.98	46.026	0.316	1.5	37.91	298.15
ethanoic acid	57.9	594.45	171	60.053	0.445	1.3	57.53	298.15
Propanoic	45.3	604	233	74.079	0.539	1.5	74.97	298.15
methyl ethanoate	46.9	506.8	228	74.079	0	1.7	79.89	298.15
ethyl methanoate	47.4	508.5	229	74.079	0.282	2	80.93	298.15
methyl propanoate	40.4	526.8	290	73.138	0.338	1.7	96.93	298.15
ethyl ethanoate	38.3	523.2	268	88.106	0.361	1.9	98.55	298.15
propyl ethanoate	33.6	549.7	345	102.13	0.391	1.8	115.66	298.15
vinyl ethanoate	43.5	525	265	86.09	0.34	1.7	93.1	298.15
1-butanamine	40.4	526.8	290	73.138	0.338	1.3	98.97	298.15
dimethyl amime	37.1	496.6	301	73.138	0.291	1.1	104.24	298.15
ethanenitrile	48.5	545.5	173	41.05	0.327	3.5	52.86	298.15
nitromethane	58.7	588	173	61.04	0	3.1	53.96	298.15
Water	220.64	647.14	55.95	18.015	0.344	1.8	18.07	298.15

Appendix C

Basic Simplex optimization method algorithm

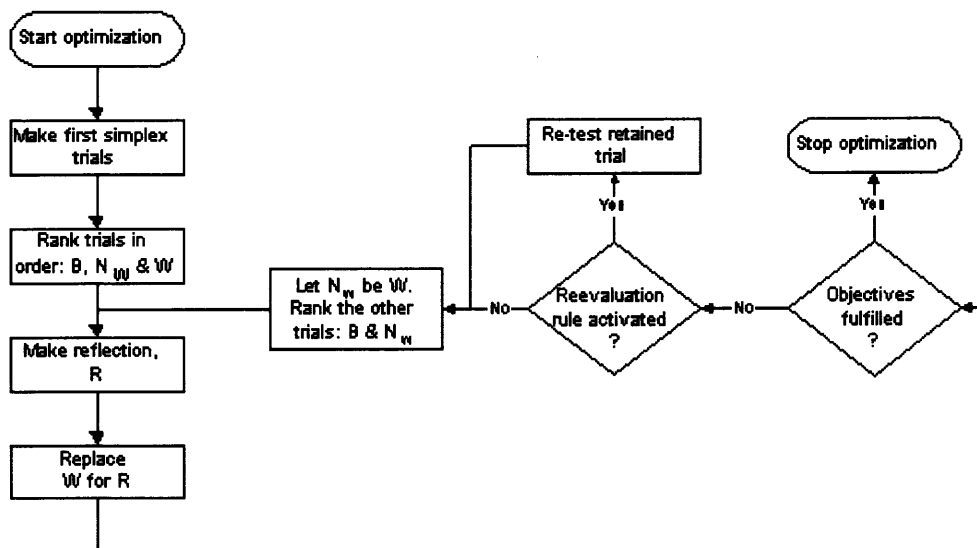


Figure C.1 Diagram of Basic Simplex optimization method algorithm [30].

Following labels are used: W for the least favorable trial or the trial being rejected, B for the most favorable trial and N_w for the second least favorable trial (i.e. next-to-the worst).

Appendix D

Data Sources

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