INVESTIGATION OF CORRELATIONS AND PREDICTION OF EXCESS MOLAR VOLUME USING DIFFERENT EQUATIONS OF STATE

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Certification

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Abstract

Prediction and correlation of accurate value of excess molar volume V^E are of great interest for adequate design of industrial process and for theoritical purpose. In order to obtain accurate V^E values attention has been turned to calculate it from Equation Of State (EOS). It is to be noted that these equations of state were developed primarity for calculating vapour-liquid equilibirum and that the present use is some what outside their usual application. To overcome this problem efforts are directed to modify or improve EOS and EOS mixing and combining rules.

In this study three types of cubic equation of state are used to calculate V^E, they are Soave Redlich Kwong (SRK-EOS), Peng-Robinson (PR-EOS), and Peng-Robinson-Stryjek-Vera (PRSV-EOS), the overall average absolute percent deviations (AAD%) for 14 binary mixture with 158 experimental V^E data point with no adjustable parameter are: for SRK-EOS 32.0919, for PR-EOS 20.6048, and for PRSV-EOS 18.3203.

Five mixing rule are applied on different groups systems with different polarity inorder to predict V^E using CEOS with acceptable accuracy. Conventional mixing rules with one adjustable parameters (k_{ij}) which is introduced in the attraction term of an EOS, the AAD% reduced to: 9.0096, 4.6060, and 3.3630 for SRK-EOS, PR-EOS, and PRSV-EOS respectively. Quadratic mixing rules are used to cancel out the deviation from real covolume parameter of an EOS "b" value due to the assumption of spherical shape of molecules and when used an adjustable parameter h_{ij}, the AAD% are reduced : for SRK-EOS to 4.5594, for PR-EOS to 2.6759, and PRSV-EOS to 1.9972.

Adachi and Sugie mixing rules increases the accuracy of V^E results

obtained from an EOS by having binary adjustable parameters L_{ij} and m_{ij} in attraction term of an EOS. The AAD% are reduced for SRK-EOS, PR-EOS and PRSV-EOS to 3.1374, 2.1170, and 1.6020 respectively .In this work Adachi and Sugie mixing rules modified by using three adjustable parameters L_{ij}, m_{ij}, and h_{ij} in attraction and repulsion terms "a" and "b" this gives more accurate results, without using any interaction parameter, the AAD% are: for SRK-EOS is 1.3318, for PR-EOS is 0.9786, and for PRSV is 0.8357.

Another tried method to extend the applicability of CEOS by using Peng-Robinson Stryjek Vera EOS (which in all cases gives better accuracy than the other two EOS equations), with a new correlation method by using Excess Gibbs free energy (G^E) with Huron-Vidal method.This method links EOS parameter "a" and "b" to Gibbs free energy, the AAD% is 13.6593. In this work the Huron-Vidal method is improved by using an adjustable parameter h_{ij}. This modification are done inorder to make this method more suitable for V^E ,the AAD% is reduced to 1.5487.

The final applied method gives very acceptable results for binary mixtures. This work tried to predict the V^E data for ternary systems from its binaries with their adjustable parameters. The AAD% for ternary systems when applied all tried mixing rules on them various are as follows: (1) using PRSV-EOS with no adjustable parameter AAD% is 18.0718 (2) using conventional mixing rules AAD% is 6.0137 (3) using quadratic mixing rules AAD% is 4.1003 (4) using Adachi and Sugie mixing rules AAD% is 3.1728 (5) using modified Adachi and Sugie in this work AAD% is 1.7701 (6) using Huron-Vidal method AAD% is 11.6824 (7) using modified Huron-Vidal method in this work AAD% is 3.8966.

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Notations

Symbols **Notations**

a = Equation of state attraction term parameter

A_i = Corresponding coefficient

A,B = Equation of state parameters

b = Equation of state covolume term parameter

F = Fugacity (Pa)

G = Gibbs energy (J mol -1)

g =NRTL parameter

Hij = Covolume term adjustable parameter

k_{ij} = Equation of state interaction parameter

L_{ij} = Binary Adachi-Sugie interaction parameters

m_{ij} = Binary Adachi-Sugie interaction parameters

M = Molecular weight kg mol^{-1}

Ni = Number of moles of component i

P = Pressure (Pa)

R = Gas constant (J mol^{-1} K^{-1})

T = Temperature (K)

V = Molar volume (m^3 mol^{-1})

x = mole fraction

Z = Compressibility factor

Zc = critical compressibility factor

w = Acentric factor

γ = Activity

ρ = Density

τ = NTRL parameter

Superscripts

E = excess thermodynamic properties

Id = value of an ideal solution

L = liquid phase

V = vapor phase

$\circ$ = Standard state

Subscripts

C = value for the critical state

Cal. = Calculated

exp. = experimental

R = reduced value

∞ = value at infinite dilution

Abbreviations

AAD = Average Absolute Deviation
AS = Adachi-Sugie
CEOS = Cubic Equation of State
EOS = Equation Of State
NRTL =Non Random Two Liquid
OF = Objective Function
PR = Peng Robinson
PRSV = Peng Robinson Stryjek Vera
RK = Redlick- Kwong
SRK = Soave Redlick- Kwong
VLE = Vapor Liquid Equilibrium

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Chapter One

Introduction

Excess thermodynamic properties of mixtures correspond to the differences between the real and the ideal mixing properties, at the same conditions such as temperature, pressure, composition[1].

The excess thermodynamic property of a binary mixture have gained much importance in recent years in connection with theories of liquid mixtures. The excess properties are due to the molecular interactions. They may be helpful in predicting various physical properties, which are important in equipment design, engineering and science[2,9].

Excess molar volumes have been measured experimentally by using the vibrating-tube densimeter and the flow calorimeter device and since it is difficult to get accurate measurements, researchers tried to find another suitable way. The researchers tried to calculate molar excess volume (V^E) by making a mathematical model, which fits the experimental data. This mathematical model is not supported with any theoretical basis. With development of computers and computer programs, the use of analytical expression interpolate and even predict thermodynamic information has become of increasing importance for process design and for modeling of process operation [17,43].

Because of the long time needed to perform the experimental measurement of data, their accurate prediction arises to be necessary objective. In the last few years a considerable efforts have been developed in order to compile and store the available data in literature d. Despite this work and the wide literature sources, it is not always possible to obtain proper values (P-V-T) and the relation between these properties is known as an

Equation Of State (EOS). The application of common equations of state for prediction the excess molar volume, as well as other properties of mixtures demonstrated that a satisfactory prediction could be obtained also in multicomponent mixtures by means of mixing rules, where only critical properties, acentic factor, and other properties values are necessary [23].

The capability of cubic equations of state in correlating excess molar volume (V^E) of non-electrolyte liquid of binary mixture was reported by several researcher. Djordjevic have shown the satisfactory results for the calculation of V^E of polar and non polar mixtures can be obtained by means of the one-fluid theory of van der Waals with a single interaction parameter[11]. In an attempt to improve the correlation of the data for some non-ideal mixtures, Adachi and Sugie proposed two binary interaction parameters by using modified conventional mixing rules coupled with van der Waals (VDW) with Soave(SRK), Peng-Robinson (PR) and Peng-Robinson Stryjek-Vera(PRSV) [2].

Similarly , Djordjevic and Serbanovic coupled two binary interaction parameters of the Margules and van laar-type mixing rules with Soave, Peng-Robinson and Peng-Robinson Stryjek-Vera EOS [12].

The modern development of combining cubic equation of state (CEOS) with Gibbs free energy models (G^E), known as CEOS/G^E models, presents a quite effective method for correlating VLE data of non-ideal systems [16].

Particularly, the HV-NRTL mixing rule coupled with Peng-Robinson Stryjek-Vera EOS were preliminarily introduced to the analysis of asymmetric non-polar and polar mixtures. Very satisfactory results are obtained by means of PRSV-HV-NRTL models parameters are generated from the experimental V^E data [11].

The aim of this work is:

1. To evaluate various methods available to correlate and predict excess molar volume for binary and ternary systems using an equation of state with suitable mixing rules.
2. To study the effect of the type of equation of state and mixing rules on the accuracy of correlation and prediction of excess molar volumes for binary and ternary systems.
3. To predict the excess molar volume for ternary systems based on the properties of binary systems.

Chapter Two

Literature Review

2.1 Law of Corresponding states

This law expresses the generalization that the property which is dependent on intermolecular forces which are related to the critical properties in the same characteristic way for all compounds. It is the single most important basis for the development of correlations and estimation methods. Van der Waals showed that it is theoretically valid for all substances whose P-V-T properties could be expressed by a two- constant EOS. It is similarly valid if the intermolecular potential function requires only two parameters.

The relation of pressure to volume at constant temperature is different for different substances, but if P-V-T is related to the corresponding critical properties, the function connecting the reduced properties becomes the same for each substance. Critical temperature, pressure, and volume represent three widely used pure component constants[5].

The properties (T ,P ,and V) which are measured at the critical point is called critical temperature, critical pressure and critical volume respectively and the critical point is the point at which both liquid and gas phase are coexisting and appears as only one phase. From the law of corresponding state the compressibility factor at this point is the critical compressibility factor (Z_c) [40].

The reduced property is commonly expressed as a function of critical property:-

$$P_r = \frac{P}{P_c}\ ; \quad V_r = \frac{V}{V_c}\ ; \quad T_r = \frac{T}{T_c} \tag{2-1}$$

An important application of the law of corresponding states is the correlation of P-V-T using the compressibility factor(Z).

$$Z=f(T_r ,P_r) \qquad (2\text{-}2)$$

Which is called law of corresponding states of two parameters. But since critical compressibility factor (Z_c) for many non polar substance is almost constant near 0.27, so it is assumed for these groups as function of the T_r , P_r only [1,5].

For highly polar fluids composed of the large molecules the values of Z_c for most hydrocarbons range from 0.2 to 0.3. thus gives a reason for necessity of using critical compressibility factor (Z_c) as additional parameter. So the law of corresponding states will be of three parameters which is :-

$$Z=f(T_r ,P_r ,Z_c) \qquad (2\text{-}3)$$

However the more common correlation uses the acentric factor (w) as the third parameter, so

$$Z=f(T_r ,P_r ,w) \qquad (2\text{-}4)$$

For polar compounds and because of their polarity (bonding polarity) and shape of the molecules the law of corresponding states of three parameters is not satisfactory, so the law of corresponding states of four parameters is introduced [22].

$$Z=f(T_r ,P_r ,Z_c ,w) \qquad (2\text{-}5)$$

2.2 Acentric Factor

Pitzar introduces acentric factor in 1955 in order to extend the applicability of the theorem of corresponding state to normal fluids.

The acentric factor is defined as:

$$W= -log\ (P_r^{sat})_{T_{r=0.7}} - 1.00 \qquad (2\text{-}6)$$

Where P_r^{sat} is the reduced saturated vapor pressure at reduced temperature (T_r =0.7). This form is chosen to make w=0 for simple fluids like (Ar ,Kr ,and Xe) with simple spherical molecules. Hence acentric factor is a factor that measures deviation of the simple intermolecular potential function from those values of some substances. However , it should be noted that T_r =0.7 is close to the normal boiling point of most substances, thus the particular choice of T_r=0.7 adopted by Pitzar not only provides numerical simplicity because log P_r^{sat} =1.0 for simple fluids but also convenience because vapor-pressure data are most commonly available at pressure near atmospheric [41].

2.3 Intermolecular forces

Thermodynamic properties of any pure substance are determined by intermolecular forces which operate between the molecules of that substance. Similarly , thermodynamic properties of a mixture depend on intermolecular forces, which operate between the molecules of the mixture. The case of a mixture ,however, is necessarily more complicated because consideration must be given not only to interaction between molecules belonging to the same component ,but also to interaction between dissimilar molecules. In order to interpret and correlate thermodynamic properties of solution, it is therefore necessary to have some understanding of the nature of intermolecular forces.

The understanding of intermolecular forces is far from complete and that quantitative results have been obtained for only simple and idealized models of real matter so, we can use our knowledge of intermolecular forces only in an approximation manner to interpret and generalized phase-equilibrium data.

When a molecule is in the approximate of another, forces of attraction and repulsion strongly influence its behavior. If there were no forces of attraction, gases would not condense to form liquids and soilds, and in the absence of repulsive forces, condense matter would not show resistance to compression.

There are many different types of intermolecular forces, these forces are:-

1. Electrostatic forces between charged particles (ions) and between permanent dipoles, quadrupoles and multipoles.
2. Induction forces between a permanent dipoles or quadrupole and induced dipole.
3. Forces of attraction (dispersion forces) and repulsion between non-polar molecules.
4. Specific (chemical) forces leading to association and complex formation, i.e. to the formation of loose chemical bonds of which hydrogen bonds are perhaps the best example [37].

2.4 Excess Volume

Excess volume is the thermodynamic property of a solution which is in excess of those of an ideal solution at the same condition of T, P, and x. For an ideal mixture all excess volume function are zero.

$$V^E = V - V^{id} \tag{2-7}$$

Where V^{id} is the molar volume of an ideal solution [37].

2.5 Property Change of Mixing

Property change of mixing ,defined as:

$$\Delta M = M - \sum_i x_i \; M_i \tag{2-8}$$

Where M is any property.

For volume:

$$\Delta V = V - \sum_i x_i \; V_i \tag{2-9}$$

$$\Delta V = V^E$$

It gives the volume change when pure species are mixed at constant temperature and pressure to form one mole of solution. Data are most commonly available for binary system, for which the above equation can be solved for volume as :

$$V = V_1 x_1 + V_2 x_2 + \Delta V \qquad (2\text{-}10)$$

This equation provides the calculation of the volume of binary mixtures from volume data for pure species 1 and 2, and the excess volume can be expressed as follows:

$$V^E = \Delta V = V_m - \sum_{i=1}^{n} x_i V_i \qquad (2\text{-}11)$$

Where is V_i the molar volume[40,34].

2.6 Ideal Solution

It is a solution which mutual solubility results when the components are mixed. No molecular interaction occurs upon mixing. The chemical structure of the components are the same. And the intermolecular forces of attraction and repulsion are the same between unlike as between like molecules.

These properties of ideal solution leads to two practical results. First, there is no heating effect when the component of an ideal solution are mixed. Second, the volume of the ideal solution equals the sum of the volume of the components that would occupy as pure liquids at the same temperature and pressure. Also it can be defined as a solution in which all activity coefficients are unity (i.e. $\gamma i = 1.0$ for all i). Ideal gas mixture is an ideal solution, and any equation applying to an ideal solution can also be applied to an ideal gas mixture. The converse, however, is not true, there are many ideal solutions that are not ideal gases [37].

Since the formation of ideal solution results is no change in molecular energies or volumes, we can write an equation for the volume of an ideal solution as follows:-

$$V^{id} = \sum_i x_i V_i^0 \qquad (2\text{-}12)$$

Where V_i^0 is the volume of pure species (i) at the mixture temperature and pressure [40].

2.7 Methods of Calculation Molar Excess Volume by Means of Equation of State

Molar Excess Volume can be measured experimentally by using Suitable densimeter and calorimeter because of difficulties and the error which are associated with the experiment authors turned attention to calculate V^E by using EOS.

The calculation of the thermodynamic properties (especially molar excess molar volume) of mixture have been investigated by using different methods, these method are :-

1. The Basic Method

For binary mixture at constant temperature T and pressure P, the excess molar volume V^E is calculated by the following equation:-

$$V^E = V_m - \sum_i x_i V_i \qquad (2\text{-}13)$$

The molar volume of the mixture V_m and the molar volume of the components V_i are calculated by using corresponding models of EOS [6,11].

2. The Least Square Method

The excess molar volume can be calculated by the following equation:-

$$V^E = x_i(1 - x_i) \sum_i ai \ (1 - 2x_i)^{i-1} \qquad (2\text{-}14)$$

The values of coefficient ai are listed in tables for different mixtures [13].

3. Redlich-Kister Method

The experimental V^E results obtained from the density measurement are calculated from the following equation:

$$V^E = x_i\, M_i\, (\rho_m^{-1} - \rho_i^{-1}) + x_j M_j\, (\rho_m^{-1} - \rho_j^{-1}) \qquad (2\text{-}15)$$

Where x , ρ and M designate ,respectively ,the mole fraction, the density and the molecular weight, the results obtained from this equation are fitted to the Redlich- Kister equation.

$$V^E = X(1-x) \sum_i^n A_i\, (1-2x)^i \qquad (2\text{-}16)$$

The corresponding coefficient A_i is given in tables for different mixture [2].

2.8 V^E Calculation Improvement

The main procedure to improve the results from EOS is to improve the mixing rules. They generally give satisfactory results, but suffer from common weakness: they fail to describe asymmetric mixture, namely mixtures constituted by molecules differing very much in size and shape, but especially in intermolecular force. As a consequence the parameters in the combining rules lose their physical significance.

To overcome these problems, many researchers have turned their attention towards the development of new mixing rules. All these attempts can be roughly classified in two categories an empirical mixing rules and statistical mechanics mixing rules [11].

2.9 Equation of State

In the thermodynamic ,an equation of state is a relation between state variables. More specifically, an equation of state is a thermodynamic equation describing the state of matter under a given set of physical condition. It is a constitutive equation which provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, and volume [4].

In the last few years, the interest related to theoretical and semiempirical work based on equation of state for prediction of excess molar volume, partial excess molar and partial molar volumes, saturated molar volumes, vapor-liquid equilibrium or excess molar enthalpies has increased. This fact is due to its high simplicity as theoretical model, relative accuracy, low information requirements, and wide versatility in operation conditions [33].

The most prominent use of an equation of state is to predict the state of gases and liquids. One of the simplest equation of state for this purpose is the ideal gas low, which is roughly accurate for gases at low pressure and high temperature. However, this equation becomes increasingly inaccurate at higher pressures and low temperature, and fails to predict condensation from a gas to a liquid. Therefore, a number of much more accurate equations of state have been developed for gases and liquids. At present, there is no single equation of state that accurately predicts the propertied of all substances under all conditions [4].

Many equations of state have been proposed and each year additional ones appear in the technical literature, but almost of all them are essentially empirical in nature. A few (e.g. the equation of van der Waals) has at least some theoretical basis, but all empirical equations of state for a pure gas have at least only approximate physical significance. It is very difficult (and frequently impossible) to justify mixing rules for expressing the constants of the mixture in terms of the constants of the pure components which comprise the mixture. As a result, such relationship introduces further arbitrary empirical equations of state one set of mixing rules may work for. One or several mixtures but work poorly for others.

The constants which appear in a gas or liquid phase equation of state reflect the non-ideality of the gas and liquid, the fact that there is a need for any constants at all follows from the existence of intermolecular forces. Therefore, to establish the composition dependence of the constant (i.e. mixing rules), it is important that the constants in an equation of state have a clear physical significance. For reliable results, it is desirable to have a theoretically meaningful equation of state in order that mixture properties may be related to pure – component properties with a minimum of arbitrariness[37].

2.10 Classification of Equation of State

The need for accurate prediction of the thermodynamic properties of many fluids and mixtures has led to the development of a rich diversity of equations of state with different degrees of empiricism, predictive capability and mathematical form. Before processing with the discussion of specific equations of state it is useful to make some general classifications into which they may fall.

The main types of EOS may be classified conveniently according to their mathematical form as follows:-

Standard P-V-T forms:

This type of EOS may be written for pure fluids

As

$$P = P(T, V_m) \qquad \text{or} \qquad Z = Z(T, V_m) \qquad (2\text{-}17)$$

While for mixture of 'n' components, there are a further 'n-1' independent composition variables. Sub-classifications may be introduced according to the structure of the function P or Z :

I. Truncated virial equation in which P is given by a polynomial in $1/V_m$ with temperature and composition dependent coefficients.

Π. Cubic equations in which P is given by a cubic function of V_m containing two parameters which are functions of composition and possibly also of temperature.

ΠI.Complex empirical equation which represent P by some combination of polynomial and other terms[30].

2.11 Cubic Equation of State

Engineers must often perform complex phase – equilibria calculations to model systems typically found in the refining and chemical industries. Cubic equations of state (CEOS) are currently the equation of state considered most applicable for such calculations. This article focuses on the enhancement made to the CEOS that are considered industry-wide standards and points out the strengths and limitations of these CEOS and their mixing rules [21].

For an accurate description of the PVT behavior of fluids over wide ranges of temperature and pressure, an EOS required. Such an equation must be sufficiently general to apply to liquids as well as gases and vapors.

The first practical cubic EOS was proposed by J.D. van der Waals in 1873.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad (2\text{-}18)$$

Here 'a' and 'b' are positive constants where 'b' is related to the size of the hard sphere while 'a' can be regarded as measured of the intermolecular attraction force [42].

For correlation and prediction of excess molar volume for binary and ternary mixtures the following well-known cubic equations of state were used :

2.11.1 Soave Redlich Kwong Equation Of State (SRK-EOS)

Soave in (1972)successfully developed a generalized alpha function "α" for cubic equation of state which made the parameter 'α' function of reduced temperature (T_r), and accentic factor (w) [i.e. , $\alpha = f(T_r, w)$].

Soave calculated the values of "α" at a series of temperature for a number of pure hydrocarbons, using the equality of vapor and liquid fugacities along the saturation curve. The fugacity of each component in a mixture is identical in all phases at equilibrium. This is equally true for a single component system having vapor and liquid phases at equilibrium.

In this case,

$$f_i^L = f_i^V \qquad (2\text{-}19)$$

This equation is valid at any point on the saturation curve, where the vapor and liquid coexist in equilibrium.

Soave calculated the values of "α" over a temperature range of $T_r = 0.4$ to 1.0 for a number of light hydrocarbons and found that $\alpha^{0.5}$ was a liner function of $T_r^{0.5}$ with a negative slope for each fluid studied Fig.1-1 shows this relation and it is represented by the following equation

$$\alpha^{0.5} = c - mT_r^{0.5} \qquad (2\text{-}20)$$

Because $\alpha = 1.0$ at $T_r = 1.0$, by definition where

$$a = a_c\alpha \qquad (2\text{-}21)$$

So ,Eq.(2-20) may be written as follows

$$\alpha^{0.5} = 1 + m(1 - T_r^{0.5}) \qquad (2\text{-}22)$$

To obtain the value of 'm' it was calculated for a series of "w" values from 0 to 0.5 with an interval of 0.05, and then correlated as a quadratic function of "w", as follows [41,48].

$$m=0.48 + 1.574w - 0.176w^2 \qquad (2\text{-}23)$$

So, Soave replaced $a/T_r^{0.5}$ of Redlich Kwong equation by $a(T)$ and the, equation of state became as:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \qquad (2\text{-}24)$$

Eq.(2-24) in polynomial form in Z factor is

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \qquad (2\text{-}25)$$

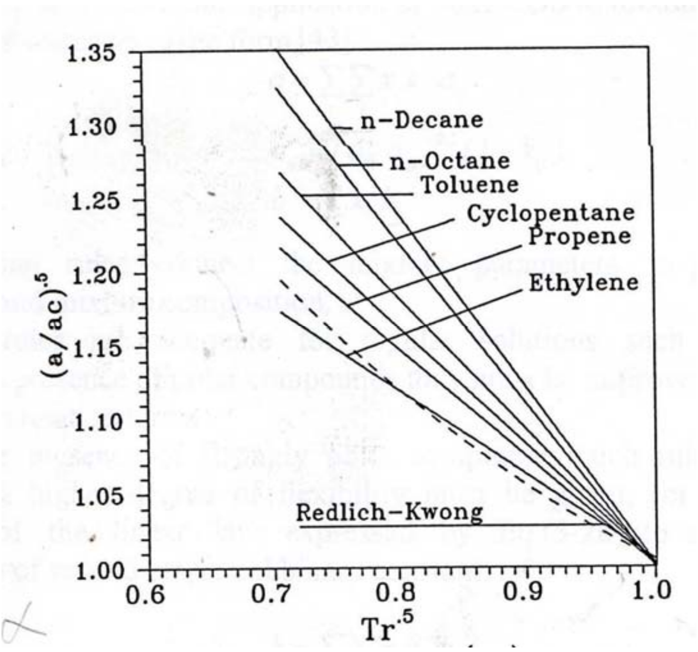

Fig. 1-1 : Derivation of (m) relation [1]

2.11.1.1 SRK-EOS Parameters:

Soave predicated a new method for determining the new equation parameters as follows:[41]

$$\alpha_i = [1 + m_i(1 - T_{ri}^{0.5})]^2 \qquad (2\text{-}26)$$

And since $m_i = 0.48 + 1.574w_i - 0.176w_i$ (2-27)

$$a_c = 0.42748\frac{R^2T_c^2}{P_c} \qquad (2\text{-}28)$$

And since $a = a_c\alpha$ (2-29)

The second parameters was calculated as follows:

$$b = 0.08664\frac{RT_c}{P_c} \qquad (2\text{-}30)$$

$$A = \frac{aP}{R^2T^2} \qquad (2\text{-}31)$$

$$B = \frac{bP}{RT} \qquad (2\text{-}32)$$

2.11.2 Peng-Robinson Equation of State (PR-EOS)

Peng-Robinson (PR) proposed an equation of the form:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \qquad (2\text{-}33)$$

Rearranging Equation (2-33) in cubic form in terms of V gives

$$V^3 - \left(\frac{RT}{P} - b\right)V^2 + \left(\frac{a}{P} - \frac{2bRT}{P} - 3b^2\right)V - b\left(\frac{a}{P} - b - b^2\right) = 0 \quad (2\text{-}34)$$

In PR-EOS "a" is also of "α" and "α" function is:

$$\alpha^{0.5} = 1 + k(1 - T_r^{0.5}) \qquad (2\text{-}35)$$

Where "k" is a constant that has been correlated against the acentric factor. The resulting k equation is

$$k = 0.37464 + 1.54226w - 0.26992w^2 \qquad (2\text{-}36)$$

Both Soave and Peng-Robinson equations are excellent in predicting the vapor pressure. This important capability terms from the remarkably good expressions for "α" Eq. (2-23) for Soave modification, and Eq.(2-36) for Peng-Robinson equation, rather than from the formulation of the EOS. But the form of EOS does effect the predicting of molar volumes in the dense phase region, where PR equation, although not as accurate as desired, shows a mark improvement over the Soave equation [52].

The Peng-Robinson equation was developed in 1976 in order to satisfy the following goals:

1. The parameters should be expressible in terms of the critical properties and acentric factor.
2. The model should provide reasonable accuracy near the critical point, particularly for calculation of the compressibility factor and liquid density.
3. The mixing rules should not employ more than a single binary interaction parameter, which should be independent of temperature pressure and composition.
4. The equation should be applicable to all calculations of all fluid properties in natural gas processes[4].

2.11.2.1 PR-EOS Parameters

PR-EOS parameters are calculated from the following equations [4,52]:

$$a_c = 0.457235\left(\frac{RT_c}{P_c}\right)^2 \qquad (2\text{-}37)$$

$$b=0.07779\left(\frac{RT_c}{P_c}\right) \qquad (2\text{-}38)$$

$$a = a_c\alpha \qquad (2\text{-}39)$$

$$A = \frac{aP}{RT} \qquad (2\text{-}40)$$

$$B = \frac{bP}{RT} \qquad (2\text{-}41)$$

Where α defined by equations (2-35) and (2-36).

2.11.3 SRK and PR Equations of State and Improved Points

SRK and PR are the most successful cubic equations for phase equilibrium calculations. The critical compressibility factor for PR equation $Z_c = 0.307$ this is a marked improvement over the (1/3) that is predicated by Soave modifications.

However, the value is still far from the actual critical compressibility factor of real fluids except for Hydrogen and Helium. On the other hand the failure point of both Soave and Peng-Robinson equation is the assumption of a particular (fixed) value of the critical compressibility factor and, as a result, the predicated densities of the saturated liquids and the predicated critical volumes differ considerably from their experimental values especially for substances whose critical compressibilities are significantly different from the values assumed by these equations [12,52].

2.11.4 Peng-Robinson-Stryjek-Vera Equation

In this work a complete overview the results that can be obtained with a modified Peng-Robinson equation of state, called the PRSV equation is represented . Although in many represents the modifications introduced in the PRSV (Stryjek and Vera.1986) follow ideas of previous workers in the details are significant enough to produce a definite improvement with respect to other versions of cubic equation of state. Vapor-liquid equilibria of many binary systems are well represented with standard one-binary parameter mixing rules. The cases for which the use of two binary parameters is required are indentified. These cases will be treated with more detail in PRSV equation[3,44].

Peng-Robinson Stryjek-Vera(PRSV)EOS[3]:

$$V^3P + V^2(Pb - RT) + V(a - 3Pb^2 - 2RTb) + Pb^3$$
$$+RTb^2 - ab = 0 \qquad (2\text{-}42)$$

PRSV-EOS has the potential to predict more accurately the phase behavior of hydrocarbon systems, particularly for system composed of dissimilar components, and it can also be extended to handle non-ideal system with accuracies that rival traditional activity coefficient models. The only compromise is increased computational time and the additional interaction parameter that is required for the equation[52].

2.11.4.1 PRSV Parameters

$$b_i = 0.077796(RT_{ci}/P_{ci}) \qquad (2\text{-}43)$$

$$a_i = 0.457235(R^2T_{ci}^2/P_{ci})\alpha_i \qquad (2\text{-}44)$$

$$\alpha_i = [1 + k_i(1 - T_{ri}^{0.5})]^2 \qquad (2\text{-}45)$$

$$k_i = k_{oi} + k_{li}(1 + T_{ri}^{0.5})(0.7 - T_{ri}) \qquad (2\text{-}46)$$

$$k_{io} = 0.378893 + 1.4897153w_i - 0.17131848w_i^2 + 0.0196554w_i^3 \qquad (2\text{-}47)$$

k_i was considered to be a function of the acentric factor and k_{li} being an adjustable parameter characteristic of each pure compounds given by Stryjek and Vera [6,43,44,46].

2.12 Application of Cubic Equation of State to Mixtures

Up to now, mixture properties usually predicted by a cubic EOS together with appropriate mixing rules. The most important use of EOS is perhaps as thermodynamic property generators in chemical process simulators. Current simulator architectures are moving away from the traditional sequential modular to equation-oriented and simultaneous modular. Equation of state that yield simple analytical expression and deveratives for thermodynamic properties are desirable. For both theoretical and practical points of view, mixing rules are most useful when they:

1. are simple,
2. avoid excessive use of parameters,
3. require a light computational load for mixtures with many compounds,
4. are reduced to the classical mixing rulers for simple mixtures,

5. perform well for asymmetric non-polar mixtures, and

6. obay the quadratic dependency on composition of the second virial coefficient at low density limits.

Many modifications and improvements of the van der Waals type equations of state appear in the literature. These modifications incorporate new parameters to the equation and/or modify the classical mixing rules[12]. There are two basic concepts in the developing of mixing rules which are :

1. Empirical Mixing Rules

Mixing rules play a fundamental role in extending an equation of state to mixture properties calculations, and the results obtained will depend, to a higher extent, on the selection mode. Consequently, the study of combination of different forms of mixing rules, and the applicability to the mixtures, related to the nature of the components, arises to be essential [19].

The basic concept in developing a mixing rules is to use an equation giving satisfactory results in modeling the fluid state, and then to extend it to high pressure calculations, and the vapor phases. Most models successfully describing the liquid phase are based on local composition concept: they are flexible enough to describe the complex behavior exhibited by system containing polar compounds. Suffice it to say that it can quantitatively describe mixtures where non-randomness is involved.

The first attempts to introduce the local composition concept in EOS were empirical : Heyen[19] and Vidal[51].Although their approaches represented a significant advance in modeling complex mixture phase equilibria , they suffer from several shortcomings . The parameters have no physical significance and do not depend on density [29].

2. Statistical Mixing Rules

Local composition can also be derived from statistical thermodynamic and examined by using computer generator data for model fluids.

In spite of success of some researchers in describing mixtures of real fluids, the rigorous statistical mechanics treatment of complex system for which excess Gibbs free energy (G^E) models have customarily been used is not near ,on the other hand, empiricism should be introduced at some point in the development. This theoretical approach, however, will be very useful in developing more theoretical based function relationships for treatment of real fluids [5,29].

2.13 Introduction of Mixing and Combining Rules to Improve V^E calculation

The introduction of new mixing and combining rules is very important in order to improve EOS mixing rules and as a result improve V^E calculated results. Many researchers and authors introduce different forms of mixing and combining rules as presented in the following sub-section.

2.13.1 Conventional One-Binary-Parameter Form

In order to examine the effect of the number of binary interaction parameters, present in this type of mixing rules, and of their position in various parameters, several forms of van der Waals mixing rules were tested.

The energy parameters a, present in the original two parameter van der Waals one-fluid mixing rules(vdW1), which is a quadratic dependence on composition, can be expressed by the following equation:

$$a = \sum_i \sum_j x_i x_j \, a_{ij} \qquad (2\text{-}48)$$

Where a_{ij}**,** the cross interaction coefficient , has the form

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \quad (2\text{-}49)$$

In this equation , a_i and a_j are the parameters of pure component , whereas k_{ij} denotes the binary interaction parameter or adjustable parameter k_{ij} is a binary constant, small compared to unity, characterizing the interaction between molecules 'i' and 'j' . For most non-polar systems k_{ij} is essential independent of composition . Interaction parameter can be positive or negative, but it is seldom gives quantitative good results. The parameter k_{ij} is especially significant for system containing chemically dissimilar components. However, even for systems of chemically similar components , k_{ij} different from zero as a result of difference in molecular shapes and size [14] .

This adjustable parameter tries to decreases the error that might be associated with EOS and shifts the results to higher degree of accuracy.

The covolume parameter b is given by the linear composition dependence in the form

$$b = \sum_i x_i b_i \quad (2\text{-}50)$$

The conventional one binary parameter combining rule in all case produce not so accurate results for calculation. Such rules may be used for low density components and regular solution, such as approximate similar components in hydrocarbon mixtures . In presence of polar compounds they must be improved by introducing empirical correction terms [16].

2.13.2 Quadratic Two – Binary –Parameter Form

The second modification to mixing rules in order to apply to mixture is required in the presence of dissimilar hydrocarbon mixtures which are greatly differ in their structure and the case of presence polar compounds . Conventional mixing rules are no more adequate . A high degree of flexibility must be given , for instance by an extension of the linear law of covolume parameter $'b'$ to a quadratic rule , and the introduction of a second empirical binary constant :

$$b = \sum\sum x_i x_j\, b_{ij} \qquad (2\text{-}51)$$

The cross interaction parameter b_{ij} is defined by the following equation:-

$$b_{ij} = \frac{b_i + b_j}{2}\,(1 - h_{ij}) \qquad (2\text{-}52)$$

Where h_{ij} is a second binary interaction parameter used to terminate the error associated with similarity assumption of mixture components shape and size.

Such rules, although theoretically well supported and completely adequate for binary systems , yet fail when applied to multicomponent mixture . It is likely more complicated rules , involving ternary and higher order terms have to be considered , but it is an impractical route , awing to the extremely large number of terms and long computation times involved [16,34].

2.13.3 Adachi– Sugie Type Two– Binary–Parameter Form

In order to increase the results accuracy obtained from any EOS used adjustable parameters which are proposed by Y. Adachi and H. Sugie may be applied.With a linear mixing rule for a covolume parameter $'b'$ of a cubic EOS, the calculation of thermodynamic property depends on cohesion parameter $'a'$ only at specific temperature, pressure, and mole fraction (x). Any thermodynamic property calculation is strongly depending on the binary interaction parameters of the modified conventional mixing rules expressed as

$$a = \sum_i \sum_j x_i x_j\, a_{ij} \qquad (2\text{-}48)$$

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \qquad (2\text{-}49)$$

$$k_{ij} = L_{ij} + m_{ij}(x_i - x_j) \qquad (2\text{-}53)$$

Where L_{ij} and m_{ij} are binary interaction parameters x_i , x_j are mole fractions of component 'i' and 'j' respectively [16].

2.13.4 Huron and Vidal Mixing Rules (HV- Mixing Rules)

It is well known that a good reproduction of the V^E behavior of mixture containing polar components can be obtained only with parameter mixing rule with a high degree of flexibility , i.e. containing a sufficient number (at least two) of adjustable binary parameters [50].

Very recently some mixing rules combining free energy model (G^E) and equation of state (EOS) have been successfully applied to very complex system of diversified nature covering wide ranges of temperature and pressure . Among of these models the so – called EOS/G^E that has been used for the correlation and prediction of V^E and other thermodynamic properties . These models have been widely studied and an extensive analysis for their applicability has been reviewed in several excellent articles .

EOS mixing rules , based on local composition concepts for excess Gibbs energy , were introduced by Huron and Vidal which opened away to rich field of the liquid state theories [22] .

The Huron and Vidal mixing rules is successful in combination with a model of Non Random Two Liquids equation (NRTL). This equation was chosen as an activity coefficient model for the calculation of the excess Gibbs energy (G^E) . The NRTL equation can be expressed by the equation [3,37] :

In general:

$$\frac{g^E}{RT} = \sum_{i=1}^{m} x_i \, \frac{\sum_{j=1}^{m} \tau_{ji} \, G_{ji} \, x_j}{\sum_{l=1}^{m} G_{li} x_l} \qquad (2\text{-}54)$$

For binary systems

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \qquad (2\text{-}55)$$

For ternary systems

$$\frac{g^E}{RT} = x_1 \frac{\tau_{21}G_{21}\,x_2+\tau_{31G_{31}}x_3}{x_1+G_{21}\,x_2+G_{31}x_3} + x_2 \frac{\tau_{12}G_{12}x_1+\tau_{32G_{32}}x_3}{x_2+G_{12}x_1+G_{32}x_3} + x_3 \frac{\tau_{13}G_{13}x_1+\tau_{23G_{23}}x_2}{x_3+G_{13}\,x_1+G_{23}x_2} \tag{2-56}$$

Where

$$G_{ij} = \exp\,(-\alpha_{ji}\tau_{ij}) \qquad G_{ji} = \exp\,(-\alpha_{ij}\tau_{ji}) \tag{2-57}$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \qquad \tau_{ji} = \frac{\Delta g_{ji}}{RT} \tag{2-58}$$

$$\Delta g_{ij} = (g_{ij} - g_{jj}) \tag{2-59}$$

$$\Delta g_{ji} = (g_{ji} - g_{ii}) \tag{2-60}$$

$$\frac{g_m^E}{RT} = [-\propto + \textstyle\sum_i x_i \propto_i] \left[\frac{1}{c_1-c_2}\right] ln \left[\frac{1+c_1}{1+c_2}\right] + \left[\frac{PV_m^E}{RT}\right] \tag{2-61}$$

Where

$$c_1 = c_2 = 1 \pm \sqrt{2} \tag{2-62}$$

$$\propto = (\frac{a}{RTb}), \propto_i = (\frac{a_i}{RTb_i}) \tag{2-63}$$

Chapter Three

Investigation and development of the correlation and prediction of excess molar volume for binary and ternary systems

3.1 Why Selecting The Redich Kwong (RK) EOS Family ?

The first historical reason is that , when a systematic work on EOS was began , the only available EOS combining ease of treatment and accuracy was those equations of states , which derived from RK equation. Cubic nature made is very practical to use , and unlike second order virial equations it could be applied to liquid phase also[50] .

The RK-EOS and its derivatives equations they remain until now as the better of all two parameter cubic equations .

To know the applicability and accuracy of any proposed correlation it is very important to know how this correlation fits the experimental data which is done by comparing the obtained results from the proposed correlation with the experimental data.

The accuracy of proposed correlations is determined by the following methods:

1.**Absolute percent of deviation (AD%E)**

$$AD.\%E=\left|\frac{V_{exp}^{E}-V_{cal}^{E}}{V_{exp}^{E}}\right|\times 100\% \qquad (3\text{-}1)$$

2. **Average Absolute Percent Deviation (AAD%)**

$$AAD\% = \frac{\sum_{i}^{n} AD.\%E}{n} \qquad (3\text{-}2)$$

Where n is the number of data points.

3.2 Selecting of an EOS for Excess Molar Volume Calculation and prediction

The interest in the prediction of the thermodynamic properties from equations of state has remarkably increased in the last few year The fact can be explained by the wide range of applicability equation of state in industrial operation conditions. Recently, cubic equation of state become very powerful in correlating and predicting phase equilibrium behavior for either no polar or / and polar systems. This capability comes from the ability of predicting pure component vapor pressure accurately for polar and nonpolar components .

In this work three types of cubic equations of state were used to calculate V^E of binary mixture and these equations are Soave Redlich Kwong (SRK) equation , Peng Robinson (PR) equation , and Peng Robinson stryjek Vera (PRSV) equation while the PRSV equation of state was used to calculate V^E for the ternary mixtures .

Each of the above equations were applied to fourteen binary mixture. The results obtained by calculation as compared with experimental data are shown in table 3-1 .These results were obtained when the mixing rules of the three equations were not changed and no adjustable parameter or interaction parameter were used i,e $k_{ij}=0$.

Table 3-1 shows that PR and PRSV equations of state give approximately the same results or approximately the same deviations from experimental excess molar volume data . On the other hand SRK equation gives relatively larger deviations than those obtained by either PR or PRSV equation of state . As table 3-1 indicates the overall absolute average percent deviation of using SRK , PR and PRSV are 32.0919 , 20.6048 and 18.3203 respectively . These high deviations in the results are certainly due either to the poor mixing rules or the equations of state used.

Although the deviations from experimental data are high but the results proved that equations of state which were used are capable of calculating excess molar volume of a mixture because there are direct relation between V^E obtained by calculation and experimental V^E. In order to improve the accuracy of V^E results , mixing rules have to be modified by introducing one or more adjustable parameter.

Table 3-1: Percentage of average absolute deviations of excess molar volume by using different EOS , with k_{ij}=0

System	Np.	SRK AAD%	PR AAD%	PRSV AAD%
n-Heptane +n-Hexane [27]	23	1.2979	0.8555	0.5986
Methylcyclohexne +n-Hexane [25]	12	22.2803	16.1283	14.1354
Methylcyclohexne + n-Heptane [25]	13	22.4074	18.0327	16.4921
Cyclohexane +n-Hexane [25]	10	20.8733	14.8004	12.8980
Cyclohexane + n-Heptane [25]	10	25.4975	19.2928	17.7669
Methylcyclohexne + Cyclohexane [25]	11	22.8341	18.0201	15.6199
Ethanol+Acetontrile [15]	12	38.9029	33.7668	30.0441
Aceton +Isopropanol [38]	9	39.5962	252413	21.7456
Aceton +Cyclohexane [38]	8	40.9559	23.6669	20.1580
Butylacetate +Benzen [24]	10	51.4665	36.2130	33.4363
Butylacetate + Bromobenzen [24]	10	43.2673	30.9373	28.7295
Buylacetate + Chlorobenzen [24]	10	49.5700	26.6494	24.2225
Buylacetate + Tolune [24]	10	59.2195	22.2179	20.0593
Ethylcetate + Benzen [24]	10	58.1057	28.6894	23.6356
Overall AAD%	158	32.0919	20.6048	18.3203

3.3 Applying Different Mixing Rules on the Selected EOS

Different forms of mixing rules were applied to binary and ternary mixtures. Investigation of the abilility of these forms of mixing and combining rules to predict V^E data and hydrocarbon systems and to find the most suitable one to be used with SRK, PR, and PRSV equations. When applying these forms of mixing and combining rules for V^E .The success of the correlations depends on the accuracy of the EOS used and on the mixing rules at one hand ; and the accuracy of experimental data point at the other hand. These forms of mixing and combining rules are :

1. Conventional Mixing Rules

The oldest method used to improve the excess molar volume results obtained by using an EOS and conventional mixing rules with an adjustable parameter (k_{ij}) which introduced in the attraction term of an EOS. The method used for determining k_{ij} by using minimizing objective function (OF) method given by Eq. (3-3) which has the form .

$$OF = \sum_i \left| V^E_{exp} - V^E_{cal} \right|_i \qquad (3\text{-}3)$$

Where k_{ij} value is the value which gives the lowest V^E deviation from experimental value k_{ij} value is introduced in the attraction term "a" parameter of an EOS as described by Eq. (2-49)

$$a = (a_i a_j)^{0.5} (1 - k_{ij}) \qquad (2\text{-}49)$$

This introduction of an adjustable parameter improves the EOS mixing rules and consequently reduces the error of calculated V^E . Where for SRK–EOS binary systems the overall average absolute percent deviation is reduced from 32.0919 to 9.0774 while for PR-EOS the overall average absolute percent deviation is reduced from 20.6060 to 4.6060 and for PRSV-EOS binary systems the overall average absolute percent deviation is reduced from 18.3203 to 3.3630 ,these results shown in table 3-2.

Table 3-2 :Percentage of average absolute deviations of excess molar volume by using different EOS , with conventional mixing rules

Binary system	Np.	SRK-EOS AAD%	PR-EOS AAD%	PRSV-EOS AAD%
Methylcyclohexne +n-Hexane [25]	12	5.0173	1.9846	1.6855
Methylcyclohexne + n-Heptane [25]	13	6.8089	4.4807	3.9342
Cyclohexane +n-Hexane [25]	10	6.2888	3.2801	1.9891
Cyclohexane + n-Heptane [25]	10	4.8562	6.5613	3.1699
Methylcyclohexne + Cyclohexane [25]	11	8.4432	6.0123	4.0408
Ethanol+Acetontrile [15]	12	11.8979	6.3625	4.9417
Aceton +Isopropanol [38]	9	12.0946	6.6837	4.9950
Aceton +Cyclohexane [38]	8	7.1855	3.2095	2.3130
Butylacetate +Benzen [24]	10	7.6135	7.0990	5.7667
Butylacetate + Bromobenzen [24]	10	15.2250	3.6075	2.5454
Buylacetate + Chlorobenzen [24]	10	9.0925	5.5148	4.0926
Buylacetate + Tolune [24]	10	14.6661	2.3589	1.8167
Ethylcetate + Benzen [24]	10	8.8178	2.7223	2.1650
Overall AAD%	135	9.0096	4.6060	3.3630

2.Quadratic Mixing Rules

This approach method involves the introduction of an adjustable parameter in each parameter of an EOS. The purpose of the mixing rule is to eliminate each parameter of an EOS assumption . The first one for the attraction term parameter , which is responsible for forces between like and unlike molecules where the original EOS derivation theory assumes equal shares of all molecules in the mixture .The second one for the an EOS assumed that all molecules with equal spherical volume. This assumption thus corrected this term by the introduction of a new adjustable parameter h_{ij} in the co volume EOS parameter which eliminates the error associated with this assumption . This adjustable parameter improves the results significantly for mixtures components which have shape far from spherical shape. The quadratic mixing rules have the form :

$$a = \sum_i \sum_j x_i x_j \, a_{ij} \qquad (2\text{-}48)$$

$$a = (a_i a_j)^{0.5} \, (1 - k_{ij}) \qquad (2\text{-}49)$$

$$b = \sum \sum x_i x_j \, b_{ij} \qquad (2\text{-}50)$$

$$b_{ij} = \frac{b_i + b_j}{2} \, (1 - h_{ij}) \qquad (2\text{-}51)$$

Where k_{ij} and h_{ij} are adjustable parameters in the attraction and co volume terms respectively . The overall average absolute percent deviation for SRK –EOS reduced to 4.5594 , for PR-EOS the overall average absolute percent deviation reduced to 2.6759 while for PRSV-EOS the overall average absolute percent deviation for binary systems is reduced to 1.9972 these results shown in table 3-3, also the values of adjustable parameters in conventional and quadratic mixing rules are given in tables 3-4, 3-5 , 3-6.

Table 3-3: Percentage of average absolute deviations of excess molar volume by using different EOS , with quadratic mixing rules

Binary system	Np.	SRK-EOS AAD%	PR-EOS AAD%	PRSV-EOS AAD%
Methylcyclohexne +n-Hexane [25]	12	2.5896	0.9652	0.8450
Methylcyclohexne + n-Heptane [25]	13	3.4037	2.3370	1.8643
Cyclohexane +n-Hexane [25]	10	2.7675	1.9596	1.0691
Cyclohexane + n-Heptane [25]	10	2.2256	3.2356	2.7958
Methylcyclohexne + Cyclohexane [25]	11	4.8428	3.5586	3.0765

Ethanol+Acetontrile [15]	12	6.3305	3.7895	2.5955
Aceton +Isopropanol [38]	9	7.6830	4.2100	2.5563
Aceton +Cyclohexane [38]	8	4.2835	2.7074	1.2328
Butylacetate +Benzen [24]	10	4.9728	4.0817	3.3711
Butylacetate + Bromobenzen [24]	10	3.8267	2.2464	1.8386
Buylacetate + Chlorobenzen [24]	10	4.9728	2.8985	1.7886
Buylacetate + Tolune [24]	10	7.4528	1.3841	1.5549
Ethylcetate + Benzen [24]	10	4.5405	1.7117	1.3349
Overall AAD%	135	4.5594	2.6759	1.9972

Table 3-4: Conventional and Quadratic mixing rules adjustable parameters value when applying SRK-EOS

System	Np.	Conventional mixing rules k_{ij}	Quadratic mixing rules k_{ij}	Quadratic mixing rules h_{ij}
Methylcyclohexne +n-Hexane [25]	12	0.0060	0.0098	- 0.0842
Methylcyclohexne + n-Heptane [25]	13	0.0400	0.0000	0.0666
Cyclohexane +n-Hexane [25]	10	0.0090	-0.0070	-0.0650
Cyclohexane + n- Heptane [25]	10	0.0100	0.0050	-0.0580
Methylcyclohexne + Cyclohexane [25]	11	-0.0040	-0.0580	0.0910
Ethanol+Acetontrile [15]	12	-0.0147	0.0001	0.0450
Aceton +Isopropanol [38]	9	0.0095	0.0000	0.0500
Aceton +Cyclohexane [38]	8	0.0499	0.0000	0.0240
Butylacetate +Benzen [24]	10	0.0014	0.0074	0.0678
Butylacetate + Bromobenzen[24]	10	0.0064	0.0004	0.0315
Buylacetate + Chlorobenzen[24]	10	0.0024	0.0022	-0.0610
Buylacetate + Tolune [24]	10	0.0088	0.0003	-0.0580
Ethylacetate + Benzen [24]	10	-0.0458	0.0000	-0.0384

Table 3-5: Conventional and Quadratic mixing rules adjustable parameters value when applying PR-EOS

System	Np.	Conventional mixing rules k_{ij}	Quadratic mixing rules k_{ij}	Quadratic mixing rules h_{ij}
Methylcyclohexne +n-Hexane [25]	12	0.0084	-0.0058	0.0190
Methylcyclohexne + n-Heptane [25]	13	0.0032	0.0080	0.0432
Cyclohexane +n-Hexane [25]	10	-0.0020	-0.0624	0.0530
Cyclohexane + n- Heptane [25]	10	0.0340	0.0027	0.0850
Methylcyclohexne + Cyclohexane [25]	11	0.0860	0.0000	-0.0650
Ethanol+Acetontrile [15]	12	0.0020	-0.0050	0.0590
Aceton +Isopropanol [38]	9	-0.0010	0.0090	-0.0300
Aceton +Cyclohexane [38]	8	0.0230	0.0300	-0.0560
Butylacetate +Benzen [24]	10	-0.0790	0.0000	-0.0180
Butylacetate + Bromobenzen[24]	10	0.0120	-0.0050	0.0380
Buylacetate + Chlorobenzen[24]	10	0.0803	0.000	0.0160
Buylacetate + Tolune [24]	10	-0.0053	-0.0060	0.0390
Ethylacetate + Benzen [24]	10	0.0858	-0.0319	0.0129

Table 3-6: Conventional and Quadratic mixing rules adjustable parameters value when applying PRSV-EOS to binary systems

System	Np.	Conventional mixing rules k_{ij}	Quadratic mixing rules k_{ij}	Quadratic mixing rules h_{ij}
Methylcyclohexne +n-Hexane [25]	12	0.0047	0.0000	0.0854
Methylcyclohexne + n-Heptane [25]	13	0.0050	-0.0392	0.0920
Cyclohexane +n-Hexane [25]	10	-0.0560	0.0024	0.0938
Cyclohexane + n- Heptane [25]	10	0.0059	0.0080	-0.0473
Methylcyclohexne + Cyclohexane [25]	11	0.0044	-0.0009	0.0537
Ethanol+Acetontrile [15]	12	-0.0039	0.0020	0.0150
Aceton +Isopropanol [38]	9	0.0480	-0.0350	0.0900
Aceton +Cyclohexane [38]	8	0.0440	0.0080	0.0230
Butylacetate +Benzen [24]	10	0.0065	0.0040	0.0860
Butylacetate + Bromobenzen[24]	10	0.0210	-0.0081	0.0226
Buylacetate + Chlorobenzen[24]	10	- 0.0480	0.0007	- 0.0930

Buylacetate + Tolune [24]	10	0.0831	0.0096	0.0161
Ethylacetate + Benzen [24]	10	0.0595	-0.0010	0.0160

3. Adachi-Sugie Mixing Rules

In this approach method Adachi-Sugie (AS) increased the accuracy of V^E results obtained from any EOS by using binary adjustable parameters in attraction term of an EOS which combines a CEOS for V^E data and correlation method . AS-mixing rules has the form

$$a = (a_i a_j)^{0.5}\,(1 - k_{ij}) \qquad (2\text{-}49)$$

$$b = \sum\sum x_i x_j\, b_{ij} \qquad (2\text{-}51)$$

$$k_{ij} = L_{ij} + m_{ij}(x_i - x_j) \qquad (2\text{-}53)$$

Adachi and Sugie directed their efforts on eliminating the errors resulted from the attraction term parameter . They discovered that an EOS is more sensitive to any changes in the value of "a" parameter than the change in the "b" parameter. They related the adjustable parameter to composition and two new adjustable parameters that are introduced which are L_{ij} and m_{ij} respectively. The value of L_{ij} and m_{ij} for all systems used are shown in table 3-7 through 3-9. The overall average percent deviations for SRK-EOS are reduced to 3.1374, for PR-EOS are reduced to 2.1170 and the overall average percent deviations for PRSV-EOS to binary systems are reduced to 1.6020. These results are shown in table 3-10.

Table 3-7: Adachi –Sugie mixing rules constants by SRK-EOS to binary Systems

Systems	Np.	L_{ij}	m_{ij}
Methylcyclohexne +n- Hexane[25]	12	-0.0004	0.0065
Methylcyclohexne + n-Heptane[25]	13	-0.0243	0.0505
Cyclohexane +n-Hexane [25]	10	0.0083	0.0547
Cyclohexane + n- Heptane [25]	10	0.0010	0.0530
Methylcyclohexne + Cyclohexane [25]	11	-0.0196	0.0643
Ethanol+Acetontrile [15]	12	0.047	-0.0095
Aceton +Isopropanol [38]	9	0.0040	-0.0155
Aceton +Cyclohexane [38]	8	0.0083	-0.0726
Butylacetate +Benzen [24]	10	-0.0330	0.0058
Butylacetate + Bromobenzen [24]	10	0.0152	0.0094
Buylacetate + Chlorobenzen [24]	10	-0.0018	0.0007
Buylacetate + Tolune [24]	10	0.0009	0.0011
Ethylacetate + Benzen [24]	10	0.0092	0.0232

Table 3-8: Adachi –Sugie mixing rules constants by PR-EOS to binary Systems

Systems	Np.	L_{ij}	m_{ij}
Methylcyclohexne +n- Hexane[25]	12	0.0282	0.0068
Methylcyclohexne + n-Heptane[25]	13	0.0732	-0.0058
Cyclohexane +n-Hexane [25]	10	0.0073	0.0148
Cyclohexane + n- Heptane [25]	10	0.0846	-0.0050
Methylcyclohexne + Cyclohexane [25]	11	0.0268	-0.0809
Ethanol+Acetontrile [15]	12	-0.0387	0.0078
Aceton +Isopropanol [38]	9	0.0112	0.0088
Aceton +Cyclohexane [38]	8	-0.0091	0.0045
Butylacetate +Benzen [24]	10	0.0017	0.0501
Butylacetate + Bromobenzen [24]	10	0.0112	-0.0068
Buylacetate + Chlorobenzen [24]	10	0.0529	0.0740
Buylacetate + Tolune [24]	10	-0.0514	0.0090
Ethylacetate + Benzen [24]	10	0.0070	-0.0620

Table 3-9: Adachi –Sugie mixing rules constants by PRSV-EOS to binary Systems

Systems	Np.	L_{ij}	m_{ij}
Methylcyclohexne +n- Hexane[25]	12	0.0088	-0.0100
Methylcyclohexne + n-Heptane[25]	13	-0.0849	0.0432
Cyclohexane +n-Hexane [25]	10	-0.0848	0.0320
Cyclohexane + n- Heptane [25]	10	-0.0705	0.0038
Methylcyclohexne + Cyclohexane [25]	11	0.0018	-0.0064
Ethanol+Acetontrile [15]	12	0.0160	0.0670
Aceton +Isopropanol [38]	9	-0.0950	0.0020
Aceton +Cyclohexane [38]	8	-0.0280	0.0300
Butylacetate +Benzen [24]	10	0.0785	- 0.0047
Butylacetate + Bromobenzen [24]	10	-0.0089	0.0321
Buylacetate + Chlorobenzen [24]	10	0.0050	0.0100
Buylacetate + Tolune [24]	10	0.0193	-0.0499
Ethylacetate + Benzen [24]	10	-0.0690	0.0503

4.Modification of Adachi –Sugie Mixing Rules

In this work Adachi –Sugie mixing rules are modified by using three adjustable parameter L_{ij}, m_{ij}in attraction and repulsion terms "a" and "b" which has the form :

$$a = (a_i a_j)^{0.5} (1 - k_{ij}) \quad (2\text{-}49)$$

$$b = \sum\sum x_i x_j \, b_{ij} \quad (2\text{-}51)$$

$$k_{ij} = L_{ij} + m_{ij}(x_i - x_j) \quad (2\text{-}53)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - h_{ij}) \quad (2\text{-}52)$$

This method gives more accurate results of V^E. The overall average percent deviations for SRK-EOS are reduced to 1.3318, for PR-EOS are reduced to 0.9586 and for PRSV-EOS to binary systems are reduced to 0.8235. These results are shown in table 3-8. The values of L_{ij}, m_{ij} and h_{ij} for all systems used are shown in the table 3-11 through 3-13.

Table 3-10: Comparison between Adachi-Sugie method of calculating excess molar volume and Modified this method in this work using SRK-EOS

Binary system	Np.	Adachi-Sugie method AAD%	This work AAD%
Methylcyclohexne +n-Hexane [25]	12	2.0258	0.5451
Methylcyclohexne + n-Heptane [25]	13	2.8897	0.8894
Cyclohexane +n-Hexane[25]	10	2.3854	0.4870
Cyclohexane + n-Heptane [25]	10	1.9035	0.7055
Methylcyclohexne + Cyclohexane [25]	11	3.8645	2.2238
Ethanol+Acetontrile [15]	12	4.0696	0.9886
Aceton +Isopropanol [38]	9	3.6997	1.4065
Aceton +Cyclohexane [38]	8	3.0124	0.9548
Butylacetate +Benzen [24]	10	4.8404	1.4614
Butylacetate + Bromobenzen [24]	10	3.0762	1.4535
Buylacetate + Chlorobenzen [24]	10	1.3768	3.5781
Buylacetate + Tolune [24]	10	4.1238	1.8287
Ethylacetate + Benzen [24]	10	3.5874	0.9936
Overall AAD%	135	3.1374	1.3318

Table 3-11:Modified Adachi –Sugie mixing rules constants by applying SRK-EOS to Binary systems

System	Np.	L_{ij}	M_{ij}	h_{ij}
Methylcyclohexne +n-Hexane [25]	12	0.0050	-0.0158	0.0340
Methylcyclohexne + n-Heptane [25]	13	0.0030	0.0870	0.0120
Cyclohexane +n-Hexane [25]	10	0.0118	0.0006	0.0.0470
Cyclohexane + n-Heptane [25]	10	-0.0080	0.0028	-0.0740
Methylcyclohexne + Cyclohexane [25]	11	0.0600	-0.0156	-0.0390
Ethanol+Acetontrile [15]	12	-0.0369	0.0095	-0.0413
Aceton +Isopropanol [38]	9	0.0118	-0.0817	0.0200
Aceton +Cyclohexane [38]	8	0.0050	0.0622	-0.0350
Butylacetate +Benzen [24]	10	0.0008	0.0038	-0.0920

Butylacetate + Bromobenzen[24]	10	0.0008	0.0017	-0.0150
Buylacetate + Chlorobenzen[24]	10	0.0013	0.0280	-0.0930
Buylacetate + Tolune[24]	10	0.0840	-0.0060	0.0270
Ethylacetate + Benzen[24]	10	0.0086	-0.0460	0.0219

Table 3-12:Modified Adachi –Sugie mixing rules constants by applying PR-EOS to Binary systems

System	Np.	L_{ij}	M_{ij}	h_{ij}
Methylcyclohexne +n-Hexane[25]	12	0.0116	0.0052	-0.0947
Methylcyclohexne + n-Heptane[25]	13	-0.0400	0.0532	-0.0808
Cyclohexane +n-Hexane[25]	10	-0.0095	0.0326	0.0487
Cyclohexane + n-Heptane[25]	10	0.0501	0.0246	-0.0568
Methylcyclohexne + Cyclohexane[25]	11	0.0049	-0.0188	0.0533
Ethanol+Acetontrile[15]	12	-0.0100	0.0505	-0.0062
Aceton +Isopropanol[38]	9	0.0065	0.0317	-0.0931
Aceton +Cyclohexane[38]	8	-0.0980	0.0315	0.0900
Butylacetate +Benzen[24]	10	-0.092	0.0355	-0.072
Butylacetate + Bromobenzen[24]	10	-0.0140	0.0079	0.0240
Buylacetate + Chlorobenzen[24]	10	-0.018	0.0075	-0.0349
Buylacetate + Tolune[24]	10	-0.0317	0.0626	0.031
Ethylacetate + Benzen[24]	10	-0.0063	0.0017	-0.0523

Table 3-13:Modified Adachi –Sugie mixing rules constants by applying PRSV-EOS to binary systems

System	Np.	L_{ij}	M_{ij}	h_{ij}
Methylcyclohexne +n-Hexane[25]	12	0.0390	0.0050	-0.0670
Methylcyclohexne + n-Heptane[25]	13	0.0038	-0.0770	0.0928
Cyclohexane +n-Hexane[25]	10	-0.0013	0.0692	0.0288
Cyclohexane + n-Heptane[25]	10	0.0041	0.0355	-0.0159
Methylcyclohexne + Cyclohexane[25]	11	0.0132	-0.0050	0.0400

Ethanol+Acetontrile [15]	12	0.0039	0.0010	0.0168
Aceton +Isopropanol [38]	9	0.0088	-0.0411	0.0311
Aceton +Cyclohexane [38]	8	0.0551	0.0069	0.0302
Butylacetate +Benzen [24]	10	0.0020	0.0034	0.0550
Butylacetate + Bromobenzen [24]	10	0.0328	0.068	0.0549
Buylacetate + Chlorobenzen [24]	10	0.0415	-0.0148	-0.0355
Buylacetate + Tolune [24]	10	0.075	0.0292	-0.0653
Ethylacetate + Benzen [24]	10	0.0090	-0.0347	0.1720

3.4 Prediction of excess molar volume from Activity coefficient model

We used the Huron-Vidal Method to increase the accuracy of V^E results from PRSV-EOS .To simplify , Huron and Vidal chose the special case $p_{\rightarrow}\infty$ which is given in the following terms.

$$\frac{g_m^E}{RT} = [-\propto + \textstyle\sum_i x_i \propto_i] \left[\frac{1}{c_1-c_2}\right] ln \left[\frac{1+c_1}{1+c_2}\right] + \left[\frac{PV_m^E}{RT}\right] \qquad (2\text{-}61)$$

Where

$$c_1 = c_2 = 1 \pm \sqrt{2} \qquad (2\text{-}62)$$

$$\propto = (\frac{a}{RTb}), \propto_i = (\frac{a_i}{RTb_i}) \qquad (2\text{-}63)$$

It was further assumed that b= $\sum_i$ $x_i b_i$ so that $V_{m\rightarrow}^E 0$ and , it was argued , $PV_{m\rightarrow}^E 0$ as $P_{\rightarrow}\infty$. Then , inserting a model expression for g_m^E and setting $PV_m^E = o$, Eq. (3-2) may be solved to obtain the mixture parameter α , and hence a , as a function of composition. The Huron and Vidal method is successful in combination with NRTL equation when the parameter refitted to V^E data , with modified mixing rule b in this work as follows

$$b = \sum \sum x_i x_j \, b_{ij} \qquad (2\text{-}51)$$

$$b_{ij} = \frac{b_i+b_j}{2} \, (1 - h_{ij}) \qquad (2\text{-}52)$$

The overall average percent deviations for binary systems are reduced from 18.3203 to 13.6593 when $b=\sum_i x_i b_i$ and when using Eq. (2-52) the overall average percent errors are reduced to 1.5487 as shown in table 3-14 together with the value of h_{ij} of binary systems

Table 3-14 : Percentage of average absolute deviations of excess molar volume by using Huron Vidal Method by PRSV-EOS to Binary Systems with the constants

Binary system	Np.	h_{ij}=0 AAD%	h_{ij}	This work AAD%
Methylcyclohexne +n-Hexane [25]	12	6.8744	-0.0561	0.6974
Methylcyclohexne + n-Heptane [25]	13	9.8120	-0.0849	1.9770
Cyclohexane +n-Hexane [25]	10	5.5196	0.1044	0.9113
Cyclohexane + n-Heptane [25]	10	8.9580	0.0716	0.9726
Methylcyclohexne + Cyclohexane [25]	11	8.7351	-0.0996	2.3636
Ethanol+Acetontrile [15]	12	18.1226	-0.0022	2.4969
Aceton +Isopropanol [38]	9	12.9460	-0.0149	2.7298
Aceton +Cyclohexane [38]	8	17.7197	0.0070	0.9495
Butylacetate +Benzen [24]	10	19.6862	-0.0958	2.3742
Butylacetate + Bromobenzen [24]	10	23.2031	-0.0728	1.5949
Buylacetate + Chlorobenzen [24]	10	13.6704	0.0246	0.8857
Buylacetate + Tolune [24]	10	16.9654	0.0247	0.7164
Ethylacetate + Benzen [24]	10	15.6589	-0.1104	1.4650
Overall AAD%	135	13.6593		1.5487

3.5 Prediction of V^E for ternary systems from experimental data of binary systems that constitute the ternary systems

All methods used for calculating of V^E of binary systems were used to predict the V^E of the ternary systems . It is to be noted that all the constants calculated for binary systems were employed for ternary systems . These methods are :

1- When $k_{ij}=0$ the overall average percent deviations are 18.0718% .

2- For Conventional mixing rules, the overall average percent deviations are reduced to 6.0137.

3- For Quadratic mixing rules, the overall average percent deviations are reduced to 4.1003.

4- For Adachi-Sugie mixing rules, the overall average percent deviations are reduced to 3.1728.

5- For Modified Adachi-Sugie mixing rules, the overall average percent deviations are reduced to 1.7701.

6- For the Activity coefficient model, the overall average percent deviations are reduced to 11.6842 and when Eq.(2-52) is used in this work the overall average percent deviations are reduced to 3.8966.

The results of ternary systems are shown in table (2-15) through (2-28), the value of adjustable parameter of all above mixing rules for ternary system are shown in table (2-29) through (2-35).

Table 3-15: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3) without using adjustable parameter k_{ij}=0

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2025	0.7117	0.0831	0.0522	0.0445	17.3033
0.1901	0.6502	0.1598	0.0778	0.0653	19.1424
0.1536	0.5304	0.3161	0.0841	0.0708	18.7853
0.1337	0.4737	0.3926	0.0790	0.0639	23.6306
0.1148	0.4055	0.4796	0.0676	0.0567	19.2239
0.1005	0.3475	0.5520	0.0567	0.0499	13.6272
0.0810	0.2829	0.6361	0.0428	0.0362	18.2320
0.0645	0.2247	0.7108	0.0333	0.0288	15.6250
0.0479	0.1590	0.7931	0.0252	0.0230	9.5652
0.0285	0.0961	0.8753	0.0140	0.0118	18.6440
AAD%					18.0718

Table 3-16: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3) when applying conventional mixing rules

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2025	0.7117	0.0831	0.0522	0.0478	9.2050
0.1901	0.6502	0.1598	0.0778	0.0752	3.4574
0.1536	0.5304	0.3161	0.0841	0.0793	6.0529
0.1337	0.4737	0.3926	0.0790	0.0731	8.0711
0.1148	0.4055	0.4796	0.0676	0.0649	4.1602
0.1005	0.3475	0.5520	0.0567	0.0534	6.1797
0.0810	0.2829	0.6361	0.0428	0.0418	2.3923
0.0645	0.2247	0.7108	0.0333	0.0308	8.1168
0.0479	0.1590	0.7931	0.0252	0.0241	4.5643
0.0285	0.0961	0.8753	0.0140	0.0135	3.7037
AAD%					5.5184

Table 3-17: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3) when applying quadratic mixing rules

x_1	x_2	x_3	V^E exp.	V^E cal.	Ab.%E
0.2025	0.7117	0.0831	0.0522	0.0504	3.5856
0.1901	0.6502	0.1598	0.0778	0.0760	2.3684
0.1536	0.5304	0.3161	0.0841	0.0816	3.0637
0.1337	0.4737	0.3926	0.0790	0.0737	7.1913
0.1148	0.4055	0.4796	0.0676	0.0658	2.7355
0.1005	0.3475	0.5520	0.0567	0.0540	5.0000
0.0810	0.2829	0.6361	0.0428	0.0413	3.6319
0.0645	0.2247	0.7108	0.0333	0.0324	2.7777
0.0479	0.1590	0.7931	0.0252	0.0244	3.2786

0.0285	0.0961	0.8753	0.0140	0.0134	4.7387
AAD%					3.8255

Table 3-18: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3) when applying Adachi-Sugie mixing rules

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2025	0.7117	0.0831	0.0522	0.0512	1.9531
0.1901	0.6502	0.1598	0.0778	0.0767	1.4341
0.1536	0.5304	0.3161	0.0841	0.0803	4.7322
0.1337	0.4737	0.3926	0.0790	0.0768	2.8645
0.1148	0.4055	0.4796	0.0676	0.0668	1.1976
0.1005	0.3475	0.5520	0.0567	0.0546	3.8461
0.0810	0.2829	0.6361	0.0428	0.0419	2.1479
0.0645	0.2247	0.7108	0.0333	0.0321	3.7323
0.0479	0.1590	0.7931	0.0252	0.0238	5.8823
0.0285	0.0961	0.8753	0.0140	0.0136	2.9411
AAD%					2.7640

Table 3-19 : The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3) when applying modified Adachi-Sugie mixing rules in this work

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2025	0.7117	0.0831	0.0522	0.0518	0.7722
0.1901	0.6502	0.1598	0.0778	0.0772	0.7720
0.1536	0.5304	0.3161	0.0841	0.0825	1.9393
0.1337	0.4737	0.3926	0.0790	0.0779	1.4120
0.1148	0.4055	0.4796	0.0676	0.0671	0.4751
0.1005	0.3475	0.5520	0.0567	0.0555	2.1621
0.0810	0.2829	0.6361	0.0428	0.0423	1.1182
0.0645	0.2247	0.7108	0.0333	0.0328	1.5243
0.0479	0.1590	0.7931	0.0252	0.0241	4.5643
0.0285	0.0961	0.8753	0.0140	0.0138	1.4492
AAD%					1.6188

Table 3- 20: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3) when applying Huron Vidal method

x_1	x_2	x_3	V^E exp.	V^E cal.	AD.%
0.2025	0.7117	0.0831	0.0522	0.0476	9.6638
0.1901	0.6502	0.1598	0.0778	0.0705	10.3546
0.1536	0.5304	0.3161	0.0841	0.7730	8.7968
0.1337	0.4737	0.3926	0.0790	0.0862	8.3526
0.1148	0.4055	0.4796	0.0676	0.0580	16.5517

0.1005	0.3475	0.5520	0.0567	0.0528	7.3863
0.0810	0.2829	0.6361	0.0428	0.0469	8.7420
0.0645	0.2247	0.7108	0.0333	0.0386	13.7305
0.0479	0.1590	0.7931	0.0252	0.0281	10.3202
0.0285	0.0961	0.8753	0.0140	0.0153	8.4967
AAD%					10.5239

Table 3- 21: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3) when applying modified Huron Vidal method in this work

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2025	0.7117	0.0831	0.0522	0.0531	1.6949
0.1901	0.6502	0.1598	0.0778	0.0761	2.2339
0.1536	0.5304	0.3161	0.0841	0.0893	5.8230
0.1337	0.4737	0.3926	0.0790	0.0782	1.0230
0.1148	0.4055	0.4796	0.0676	0.0664	1.8072
0.1005	0.3475	0.5520	0.0567	0.0538	5.3903
0.0810	0.2829	0.6361	0.0428	0.0436	1.8348
0.0645	0.2247	0.7108	0.0333	0.0348	4.3103
0.0479	0.1590	0.7931	0.0252	0.0263	4.1825
0.0285	0.0961	0.8753	0.0140	0.0140	2.0979
AAD%					3.0397

Table 3- 22: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3) without using any adjustable parameter $k_{ij}=0$

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2051	0.7165	0.0784	0.1058	0.1236	14.4012
0.1862	0.6539	0.1599	0.1633	0.1873	12.8136
0.1511	0.5295	0.3195	0.2414	0.2218	8.8367
0.1336	0.4102	0.3963	0.2439	0.2055	18.6861
0.1157	0.4701	0.4740	0.2378	0.1906	24.7639
0.0988	0.3471	0.5541	0.2221	0.2826	21.4083
0.0798	0.2845	0.6357	0.1991	0.2574	22.6495
0.0562	0.2250	0.7188	0.1710	0.1480	15.5405
0.0464	0.1595	0.7941	0.0749	0.0610	22.7868
0.0112	0.0326	0.9562	0.0121	0.0163	25.7668
AAD%					18.7652

Table 3- 23: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3) when applying conventional mixing rules

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2051	0.7165	0.0784	0.1058	0.1104	4.7531
0.1862	0.6539	0.1599	0.1633	0.1764	7.4263
0.1511	0.5295	0.3195	0.2414	0.2311	4.4569
0.1336	0.4102	0.3963	0.2439	0.2171	12.3445
0.1157	0.4701	0.4740	0.2378	0.2168	9.6863
0.0988	0.3471	0.5541	0.2221	0.2408	7.7657
0.0798	0.2845	0.6357	0.1991	0.2016	1.2400
0.0562	0.2250	0.7188	0.1710	0.1622	5.4254
0.0464	0.1595	0.7941	0.0749	0.0708	5.7909
0.0112	0.0326	0.9562	0.0121	0.0132	6.2015
AAD%					6.5090

Table 3- 24: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3) when applying quadratic mixing rules

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2051	0.7165	0.0784	0.1058	0.1024	3.3203
0.1862	0.6539	0.1599	0.1633	0.1688	3.2582
0.1511	0.5295	0.3195	0.2414	0.2332	3.5162
0.1336	0.4102	0.3963	0.2439	0.2216	10.0631
0.1157	0.4701	0.4740	0.2378	0.2241	6.1133
0.0988	0.3471	0.5541	0.2221	0.2311	3.8944
0.0798	0.2845	0.6357	0.1991	0.2004	0.6487
0.0562	0.2250	0.7188	0.1710	0.1634	4.6511
0.0464	0.1595	0.7941	0.0749	0.0718	4.3175
0.0112	0.0326	0.9562	0.0121	0.0126	3.9682
AAD%					4.3751

Table 3- 25: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3) when applying Adachi-Sugie mixing rules

x_1	x_2	x_3	V^E exp.	V^E cal.	Ab.%E
0.2051	0.7165	0.0784	0.1058	0.1030	2.7184
0.1862	0.6539	0.1599	0.1633	0.1672	2.3325
0.1511	0.5295	0.3195	0.2414	0.2466	2.1086
0.1336	0.4102	0.3963	0.2439	0.2234	9.1763
0.1157	0.4701	0.4740	0.2378	0.2284	4.1155
0.0988	0.3471	0.5541	0.2221	0.2296	3.2665
0.0798	0.2845	0.6357	0.1991	0.1999	0.4002
0.0562	0.2250	0.7188	0.1710	0.1651	3.5735
0.0464	0.1595	0.7941	0.0749	0.0727	3.1261

0.0112	0.0326	0.9562	0.0121	0.0125	3.2000
AAD%					3.5817

Table 3- 26: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3) when applying modified Adachi-Sugie mixing rules in this work

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2051	0.7165	0.0784	0.1058	0.1042	1.5355
0.1862	0.6539	0.1599	0.1633	0.1654	1.2696
0.1511	0.5295	0.3195	0.2414	0.2448	1.3888
0.1336	0.4102	0.3963	0.2439	0.2349	3.8386
0.1157	0.4701	0.4740	0.2378	0.0230	2.5000
0.0988	0.3471	0.5541	0.2221	0.2251	1.3327
0.0798	0.2845	0.6357	0.1991	0.1996	0.2505
0.0562	0.2250	0.7188	0.1710	0.1670	2.3952
0.0464	0.1595	0.7941	0.0749	0.0738	1.4905
0.0112	0.0326	0.9562	0.0121	0.0123	1.6260
AAD%					1.9215

Table 3- 27: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3) when applying Huron Vidal mixing rules

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2051	0.7165	0.0784	0.1058	0.1241	14.7461
0.1862	0.6539	0.1599	0.1633	0.1509	8.2173
0.1511	0.5295	0.3195	0.2414	0.2816	14.2755
0.1336	0.4102	0.3963	0.2439	0.2347	3.9198
0.1157	0.4701	0.4740	0.2378	0.2210	7.6018
0.0988	0.3471	0.5541	0.2221	0.2888	23.0609
0.0798	0.2845	0.6357	0.1991	0.2172	8.3333
0.0562	0.2250	0.7188	0.1710	0.1280	33.1937
0.0464	0.1595	0.7941	0.0749	0.0764	1.8633
0.0112	0.0326	0.9562	0.0121	0.0130	15.3846
AAD%					12.8409

Table 3- 28: The results of ternary systems Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3) when applying modified Huron Vidal mixing rules in this work

x_1	x_2	x_3	V^E exp.	V^E cal.	AD%
0.2051	0.7165	0.0784	0.1058	0.1183	10.5663
0.1862	0.6539	0.1599	0.1633	0.1689	3.3155
0.1511	0.5295	0.3195	0.2414	0.2316	4.2314
0.1336	0.4102	0.3963	0.2439	0.2382	2.3929
0.1157	0.4701	0.4740	0.2378	0.2328	2.1477

0.0988	0.3471	0.5541	0.2221	0.2410	7.8423
0.0798	0.2845	0.6357	0.1991	0.2050	2.8780
0.0562	0.2250	0.7188	0.1710	0.1931	11.4448
0.0464	0.1595	0.7941	0.0749	0.0752	0.3989
0.0112	0.0326	0.9562	0.0121	0.0124	2.4188
AAD%					4.7536

Table 3-29: Conventional mixing rules adjustable parameters value when applying PRSV-EOS to Ternary systems

System	Np.	k_{12}	k_{13}	k_{23}
Methycyclohexane(1)+ Cyclohexane(2) + n- Hexane(3) [25]	10	0.0044	0.0047	-0.0560
Methycyclohexane(1)+ Cyclohexane (2)+ n- Heptane(3) [25]	10	0.0044	0.0050	0.0059

Table 3-30: Quadratic mixing rules adjustable parameters value when applying PRSV-EOS to Ternary systems

System	Np.	k_{12}	k_{13}	k_{23}	h_{12}	h_{13}	h_{23}
Methycyclohexane(1) + Cyclohexane(2) + n-Hexane(3) [25]	10	-0.0009	0.000	0.0024	0.0537	0.0854	0.0938
Methycyclohexane(1) + Cyclohexane (2)+ n-Heptane(3) [25]	10	-0.0009	-0.0392	0.008	0.0537	0.092	-0.0473

Table 3-31: Adachi –Sugie mixing rules constants by PRSV-EOS to ternary systems

System	Np.	L_{12}	L_{13}	L_{23}	m_{12}	m_{13}	m_{23}
Methycyclohexane(1) + Cyclohexane(2) + n- Hexane(3) [25]	10	0.0018	0.0088	-0.0848	-0.0064	-0.0100	0.0320
Methycyclohexane(1) + Cyclohexane (2)+ n- Heptane(3) [25]	10	0.0018	-0.0849	-0.0705	-0.0064	0.0432	0.0038

Table 3-33: Huron – Vidal Method constant by applying PRSV-EOS to Ternary Systems

System	Np.	h_{12}	h_{13}	h_{23}
Methycyclohexane(1)+ Cyclohexane(2) + n-Hexane(3) [25]	10	-0.0996	-0.0561	0.1044
Methycyclohexane(1)+ Cyclohexane (2)+ n-Heptane(3) [25]	10	-0.0996	-0.0849	0.0716

Table 3-34: Percentage of average absolute deviations of excess molar volume by using PRSV- EOS for ternary systems

Ternary systems	Np.	kij =0 AAD%	Conventional mixing rules AAD%	Quadratic mixing rules AAD%	Adachi-Sugie mixing rules AAD%	Modified Adachi-Sugie AAD%
Methycyclohexane(1)+ Cyclohexane(2) + n-Hexane(3) [25]	10	17.3785	5.5184	3.8255	2.7640	1.6188
Methycyclohexane(1)+ Cyclohexane (2)+ n-Heptane(3) [25]	10	18.7652	6.5090	4.3751	3.5817	1.9215
Overall AAD%	20	18.0718	6.0137	4.1003	3.1728	1.7701

Table 3-35: Percentage of average absolute deviations of excess molar volume by using PRSV-EOS for ternary systems with Huron-Vidal method

Ternary systems	Np.	h_{ij}=0 AAD%	This work AAD%
Methycyclohexane(1)+ Cyclohexane(2) + n-Hexane(3) [25]	10	10.5239	3.0397
Methycyclohexane(1)+ Cyclohexane (2)+ n-Heptane(3) [25]	10	12.8409	4.7536
Overall AAD%	20	11.6824	3.8966

Chapter Four

Discussion

Excess molar volume (V^E) exhibition of positive or negative deviation. Positive excess molar volumes are due to the competition between strong interactions and equally strong unlike H-bond interactions. Negative excess molar volumes generally occur when unlike interactions pervail over self-association. They may also be due to packing effects between two molecules with large difference in size. In order to get accurate values of excess molar volume which are suitable for design purpose attention has been turned to calculate it from equations of state since the experimental measurements of excess molar volume are time consuming . Thus efforts are directed to modify or improve EOS and EOS mixing rules to be suitable for excess molar volume calculations.

The ability of an EOS for generating V^E data and the role played by mixing rules in EOS calculation of V^E for various types of binary and ternary mixtures have been tested. Several type of mixing rules which are: conventional, quadratic, Adachi-Sugie with its modification and Huron-Vidal with its modification were used with the three equations of state: SRK-EOS, PR-EOS, and PRSV-EOS .

To develop a correlation to predict basic method for V^E calculation is selected according to equation (2-13) since this method is generalized.The other methods (The Least Square, Redlich-Kister) are not generalized methods and needed certain different coefficients for each binary and ternary systems.

Basic method equation for V^E calculation has the following form:

$$V^E = V_m - \sum_i x_i V_i \qquad (2\text{-}13)$$

Where by applying this equation for V^E calculation and using EOS the errors due to EOS are canceled and only the effects of an EOS mixing rules are appeared. So this method is selected for calculating V^E using an EOS and the attention was focused by modifying EOS mixing and combining rules to obtain more accurate results.

The overall average absolute percent deviations (AAD%) when using the three equations of state (SRK, PR, and PRSV) without any adjustable parameter (k_{ij}) are: 32.0919, 20.6048, and 18.3203 respectively. However this method that is using no adjustable can be applied for normal hydrocarbon systems with relatively higher accuracy.

In order to increase any EOS accuracy k_{ij} is introduced. The parameter k_{ij} is a symmetric ($k_{ij} = k_{ij}$) binary interaction parameter obtained from experimental data using Matlab optimization program prepered in this work. In general, k_{ij} is constant for specified system at certain temperature and pressure. For non-ideal systems, however k_{ij} depends on temperature, and small changes in its value can cause large changes in the properties predicted by the EOS. Each system mixture has a k_{ij} values that represents that system. The effect of this adjustable parameter is to shift the V^E data results to higher degree of accuracy.

Conventional Method

Improvement to V^E calculations has been increased by increasing the number of adjustable parameters in the mixing rules. Therefore, the fitting effects might cause those improvement, i.e by increasing the flexibility of the mixing rules. However, the issue of how many parameters are necessary for the practical application is not well defined. For example if mixing rules have one, two, or three adjustable parameters in the cohesion parameter of an EOS "a" the results shows that for the same system:

1- The difference between the V^E results of the two, three and higher number of adjustable parameters are quiet small. Indicating that more than two and sometimes three adjustable are not necessary ; and
2- The V^E results of the one parameter and those of the two parameters are fairly different . However, the V^E results of the two parameters and those of three parameters are close to each other

These phenomena indicate that the parameters required in the mixing rules for binary systems are two. Which are quite enough for V^E calculation. While for covolume parameter of an EOS "b" an adjustable parameter has very small effect if it is compared to results of non-ideal systems.

When applying conventional mixing rules using EOS is by using an adjustable parameter which is a value calculated by minimizing objective function . Each system mixture has a k_{ij} value that represents that system. The effect of this method is by shifting the obtained V^E results to higher degree of accuracy where the overall average absolute percent deviations for SRK, PR, and PRSV equation of state are reduced from 32.0919 to 9.0096, from 20.6048 to 4.6060, and from 18.3203 to 3.3630 respectively . This method is used to reduce the mixing rules errors and many authors used it but in this work it is adopted for comparison with other improved methods. Conventional mixing rules eliminate the error associated in the assumption of equal forces of attraction between the like and unlike molecules in each individual component in the mixture. The adjustable parameter "k_{ij}" is one of the oldest and till know is used depending on the required accuracy of the calculation and design purpose .

Quadratic Method

Quadratic mixing rules try to cancel out the deviation from the real covolume parameter of an EOS "b" value due to the assumption of molecules spherical shape . The introduction of h_{ij} adjustable parameter tries to cancel out the effect of shape and size of molecules and their deviations from the assumption of having a spherical shape type . The use of this type of mixing rules modified the results over the conventional mixing rules . The overall average absolute percent deviations for SRK-EOS is reduced to 4.5594, for PR-EOS is reduced to 2.6759, and for PRSV-EOS is reduced to 1.9972.

Adachi-Sugie Method

It is found that an adjustable parameter is a function of temperature, pressure, and composition where at constant temperature and pressure adjustable parameter is a function of mixture composition only . Adachi and Sugie proposed that an adjustable parameter is a linear function of composition . The adjustable parameter equation have the following form :

$$k_{ij} = L_{ij} + m_{ij}\left(x_i - x_j\right) \qquad (2\text{-}53)$$

Where two adjustable parameters are used (L_{ij} and m_{ij}). Adachi and Sugie applied this relation to an EOS to calculate excess molar volume . When this relation was applied for V^E calculation the overall average absolute deviations decreased from 32.0919 to 3.1347, from 20.6048 to 2.1170, and from 18.320 to 1.6020 for SRK, PR, PRSV equations of state respectively.

Modification of Adachi-Sugie Method

Adachi-Sugie mixing rules in this work was modified to obtain more accuracy results for parameter "b" and using an adjustable parameter in the combining rule "h_{ij}" . These improvement were done in order to make mixing rules suitable for V^E calculation .Very reasonable reduction in average absolute deviation of V^E calculated was obtained . An adjustable parameter in the attraction term (k_{ij}) reduces the effect of intermolecular attraction forces while the second adjustable parameter h_{ij} in the repulsion term of an EOS "b" eliminates the molecular shape deviation from having a spherical shape ; i.e it terminates the error which may results from the assumed spherical shape of molecules .

There is a relation between the two adjustable parameter (k_{ij} and h_{ij}) where the value of one parameter (a or b) and the value of each adjustable parameter can not be found separately from each other . If this is done the accuracy of calculating V^E is greatly improved. Since the second adjustable parameter (h_{ij}) minimizes the error associated with V^E calculation ; this means that there is an influence of parameter "b" (its value) on V^E calculation which indicates that molecules shape of systems which are present in this work deviate from having a spherical shape as proposed by van der Waals and, the introduction of h_{ij} adjustable parameter show the amount of this deviation from having a spherical shape . By applying this modification to the systems that used in this work , a large amount of error reduction in V^E calculation were obtained. The overall average absolute percent deviations are reduced from 32.0919 to 1.3318 for SRK-EOS, for PR-EOS are reduced from 20.6048 to 0.9786, and for PRSV-EOS are reduced from 18.3203 to 0.8357. The results of using SRK, PR, and PRSV equations with these three different type of mixing rules for binary systems are shown in tables 4-1, 4-2, and 4-3 respectively.

Table 4-1: Application of conventional, quadratic, Adachi-Sugie and its modified mixing rules on SRK-EOS for binary systems

Binary system	NP.	Conventional AAD%	Quadratic AAD%	Adachi-Sugie AAD%	Modification in this work AAD%
Methylcyclohexne +n-Hexane[25]	12	5.0173	2.5896	2.0258	0.5451
Methylcyclohexne + n-Heptane[25]	13	6.8089	3.4037	2.8897	0.8894
Cyclohexane +n-Hexane [25]	10	6.2888	2.7675	2.3854	0.4870
Cyclohexane + n-Heptane [25]	10	4.8562	2.2256	1.9035	0.7055
Methylcyclohexne + Cyclohexane [25]	11	8.4432	4.8428	3.8645	2.2238
Ethanol+Acetontrile [15]	12	11.8979	6.3305	4.0696	0.9886
Aceton +Isopropanol[38]	9	12.0946	7.6830	3.6997	1.4065
Aceton +Cyclohexane[38]	8	7.1855	4.2835	3.0124	0.9548
Butylacetate +Benzen[24]	10	7.6135	4.9728	4.8404	1.4614
Butylacetate + Bromobenzen [24]	10	15.2250	3.8267	3.0762	1.4535
Buylacetate + Chlorobenzen [24]	10	9.0925	4.9728	1.3768	3.5781
Buylacetate + Tolune[24]	10	14.6661	7.4528	4.1238	1.8287
Ethylacetate + Benzen[24]	10	8.8178	4.5405	3.5874	0.9936
Overall AAD%	135	9.0096	4.5594	3.1374	1.3318

Table 4-2: Application of conventional, quadratic, Adachi-Sugie and its modified mixing rules on PR-EOS for binary systems

Binary system	NP.	Conventional AAD%	Quadratic AAD%	Adachi-Sugie AAD%	Modification in this work AAD%
Methylcyclohexne +n-Hexane[25]	12	1.9846	0.9652	0.9212	0.4359
Methylcyclohexne + n-Heptane[25]	13	4.4807	2.3370	2.2611	0.8529
Cyclohexane +n-Hexane [25]	10	3.2801	1.9596	1.6987	0.4536
Cyclohexane + n-Heptane [25]	10	6.5613	3.2356	2.1045	0.7650
Methylcyclohexne + Cyclohexane [25]	11	6.0123	3.5586	3.2262	1.9196
Ethanol+Acetontrile [15]	12	6.3625	3.7895	2.6384	0.9161
Aceton +Isopropanol[38]	9	6.6837	4.2100	2.8026	1.3257
Aceton +Cyclohexane[38]	8	3.2095	2.7074	1.7388	0.9356
Butylacetate +Benzen[24]	10	7.0990	4.0817	3.3629	1.3862
Butylacetate + Bromobenzen [24]	10	3.6075	2.2464	1.9612	1.3231
Buylacetate + Chlorobenzen [24]	10	5.5148	2.8985	1.8983	0.7816
Buylacetate + Tolune[24]	10	2.3589	1.3841	1.4406	0.8965
Ethylacetate + Benzen[24]	10	2.7223	1.7117	1.4409	0.8211
Overall AAD%	135	4.6060	2.6759	2.1170	0.9786

Table 4-3: Application of conventional, quadratic, Adachi-Sugie and its modified mixing rules on PRSV-EOS for binary systems

Binary system	NP.	Conventional AAD%	Quadratic AAD%	Adachi-Sugie AAD%	Modification in this work AAD%
Methylcyclohexne +n-Hexane[25]	12	1.6855	0.8450	0.8797	0.4687
Methylcyclohexne + n-Heptane[25]	13	3.9342	1.8643	1.5609	0.7963
Cyclohexane +n-Hexane [25]	10	1.9891	1.0691	0.9693	0.4043

Cyclohexane + n-Heptane [25]	10	3.1699	2.7958	1.9036	0.6933
Methylcyclohexne + Cyclohexane [25]	11	4.0408	3.0765	2.2981	1.3763
Ethanol+Acetontrile [15]	12	4.9417	2.5955	2.0142	0.8970
Aceton +Isopropanol[38]	9	4.9950	2.5563	1.6213	0.9308
Aceton +Cyclohexane[38]	8	2.3130	1.2328	0.9637	0.8374
Butylacetate +Benzen [24]	10	5.7667	3.3711	3.4109	1.1946
Butylacetate + Bromobenzen [24]	10	2.5454	1.8386	1.8518	1.0830
Buylacetate + Chlorobenzen [24]	10	4.0926	1.7886	1.1157	0.7284
Buylacetate + Tolune[24]	10	1.8167	1.5549	0.8636	0.6595
Ethylacetate + Benzen[24]	10	2.1650	1.3349	1.2588	0.8243
Overall AAD%	135	3.3630	1.9972	1.6020	0.8357

It is generally belived that CEOS can be applied successfully to calculate V^E of normal hydrocarbon mixture n-Heptane +n-Hexane without using any adjustable parameter. The overall average absolute percent deviations are 1.2979, 0.8555, and 0.5986 for SRK-EOS, PR-EOS, and PRSV-EOS respectively as shown in Fig. 4-1.

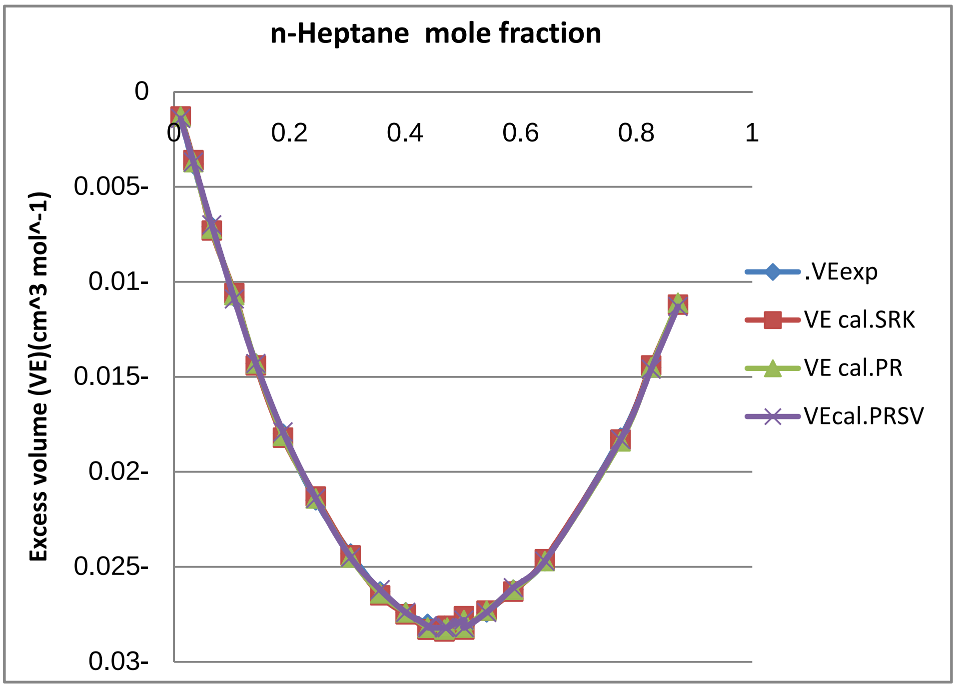

Fig. 4-1: Excess volume of n-Heptane n-Hexane system

By the application of conventional, quadratic, and Adachi-Sugie with its modification for SRK, PR, PRSV equations of state, all results are improved and PRSV-EOS shows slightly better results than PR and SRK so we used PRSV to calculate V^E for ternary systems and Huron-Vidal method.

Huron-Vidal Method

Equation of state mixing rules derived at infinite pressure results in different mixing rules . The Huron-Vidal approach using excess Gibbs free energy required the equation of state b parameter be a traditional linear mixing rules . Cubic equation of state becomes very powerful in correlating and predicting phase equilibrium behavior for either non polar or polar systems . Excess Gibbs free energy model in an EOS mixing rules are used available activity coefficient model parameters from low pressure data , without change, for predicting phase equilibria at high pressure and temperature .

The connection of EOS with Gibbs free energy, allows EOS to become predictive tools .This methods links the EOS parameters "a" and "b" to Gibbs free energy . Large amount of reduction in the average absolute percent deviations are obtained without using adjustable parameter is 13.6593 for binary systems.

Modification of Huron-Vidal Method

In this work improvements of Huron –Vidal mixing and combining rules were modified by changing the mixing rules for parameter "b" and using an adjustable parameter in the combining rule (h_{ij}). These modifications for Huron and Vidal mixing rules were done in order to make mixing rules more suitable for V^E calculation. The overall average absolute percent deviations for binary systems is reduced to 1.5487, the results are shown in table 4-4.

Table 4-4: Application of Huron-Vidal method on PRSV-EOS for binary systems

Binary system	Np.	h_{ij}=0 AAD%	This work AAD%
Methylcyclohexne +n-Hexane[25]	12	6.8744	0.6974
Methylcyclohexne + n-Heptane[25]	13	9.8120	1.9770
Cyclohexane +n-Hexane [25]	10	5.5196	0.9113
Cyclohexane + n-Heptane [25]	10	8.9580	0.9726
Methylcyclohexne + Cyclohexane [25]	11	8.7351	2.3636
Ethanol+Acetontrile [15]	12	18.1226	2.4969
Aceton +Isopropanol [38]	9	12.9460	2.7298
Aceton +Cyclohexane [38]	8	17.7197	0.9495
Butylacetate +Benzen [24]	10	19.6862	2.3742
Butylacetate + Bromobenzen [24]	10	23.2031	1.5949
Buylacetate + Chlorobenzen [24]	10	13.6704	0.8857

Buylacetate + Tolune [24]	10	16.9654	0.7164
Ethylacetate + Benzen [24]	10	15.6589	1.4650
Overall AAD%	135	13.6593	1.5487

Ternary Systems

Although prediction of the physical properties of mixtures from those of their pure components is generally unreliable because of mixing effect, numerous schemes have been put forward for predictions based on the properties of the binary systems. The overall average absolute deviation is reduced from 18.0718 to 6.0137, 4.1003, 3.1728, 1.7701, 11.6824, and 3.8966 for conventional, quadratic, Adachi-Sugie, modification of Adachi-Sugie in this work, Huron-Vidal method and modification of Huron-Vidal method in this work respectively. The results of using PRSV equations with these different type of mixing rules for ternary systems are shown in tables 4-5 and 4-6 respectively.

Table 4-5: Application of Conventional, Quadratic, Adachi-Sugie and its modified mixing rules on PRSV-EOS for ternary systems

Ternary systems	Np.	Conventional mixing rules AAD%	Quadratic mixing rules AAD%	Adachi-Sugie mixing rules AAD%	Modificatin Adachi-Sugie(in this work) AAD%
Methycyclohexane(1)+ Cyclohexane(2) + n-Hexane(3) [25]	10	5.5184	3.8255	2.7640	1.6188
Methycyclohexane(1)+ Cyclohexane (2)+ n-Heptane(3) [25]	10	6.5090	4.3751	3.5817	1.9215
Overall AAD%	20	6.0137	4.1003	3.1728	1.7701

Table 4-6: Application of Huron-Vidal method for prediction of excess volume of ternary systems using PRSV-EOS

Ternary systems	Np.	h_{ij}=0 AAD%	This work AAD%
Methycyclohexane(1)+ Cyclohexane(2) + n-Hexane(3) [25]	10	10.5239	3.0397
Methycyclohexane(1)+ Cyclohexane (2)+ n-Heptane(3) [25]	10	12.8409	4.7536
Overall AAD%	20	11.6824	3.8966

It is a fact that any successful correlation for prediction of V^E or other thermodynamic property must satisfies two points . The first points is that it must be general and the second point is the accuracy of the results obtained by the methods . The new correlation method developed in this work satisfies these two points . All selected equations of state behave the same behavior with they modification . PRSV-EOS is selected to show the results of these modifications in tables and also in the following figures.

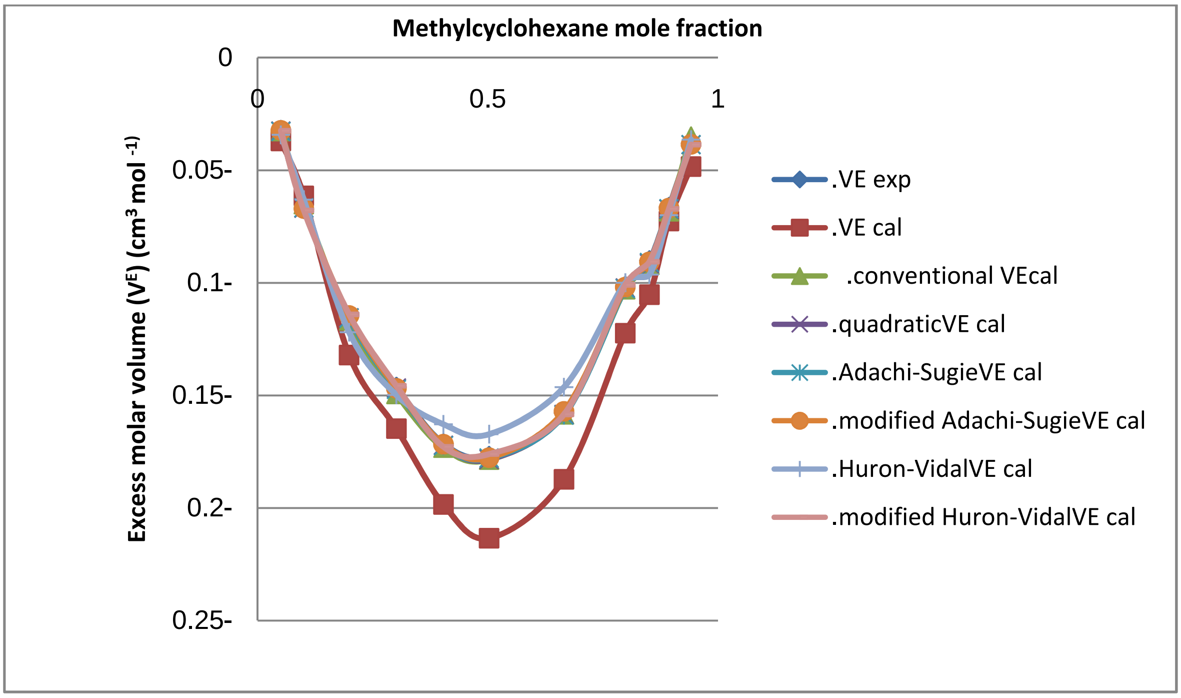

Fig. 4-2 :Excess volume of Methylcyclohexane n –Hexane system

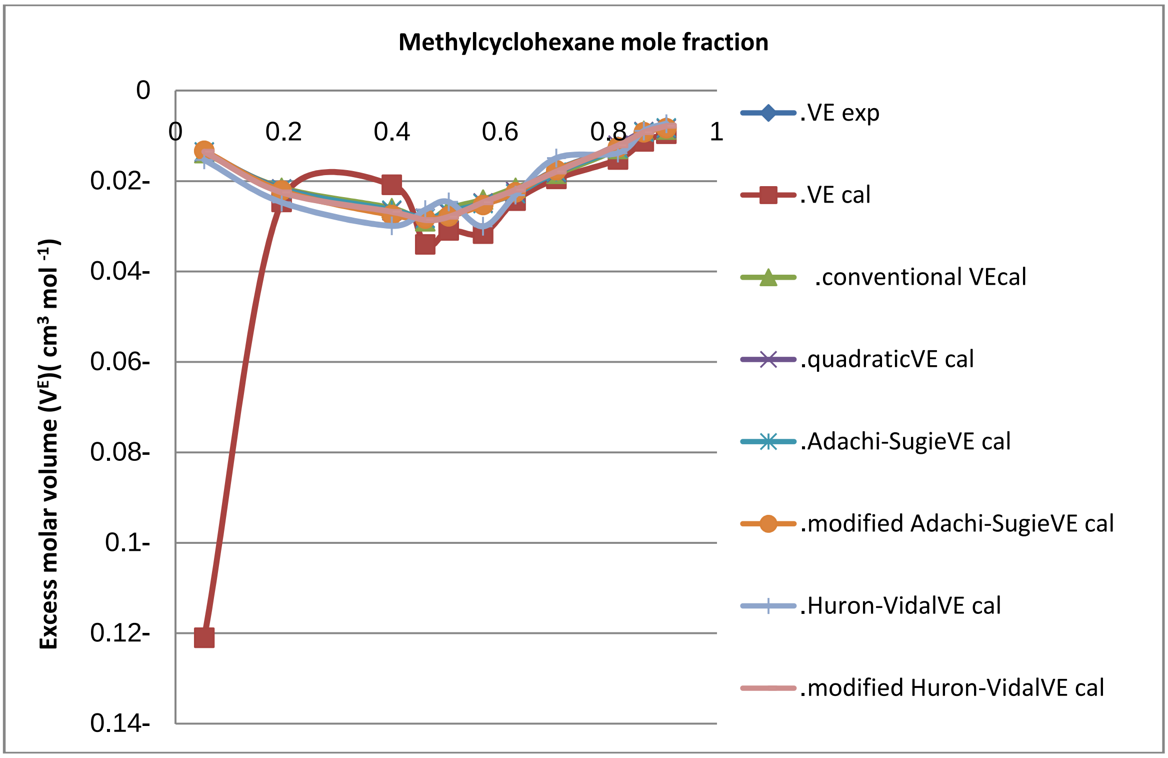

Fig. 4-3 : Excess volume of Methylcyclohexane n –Heptane system

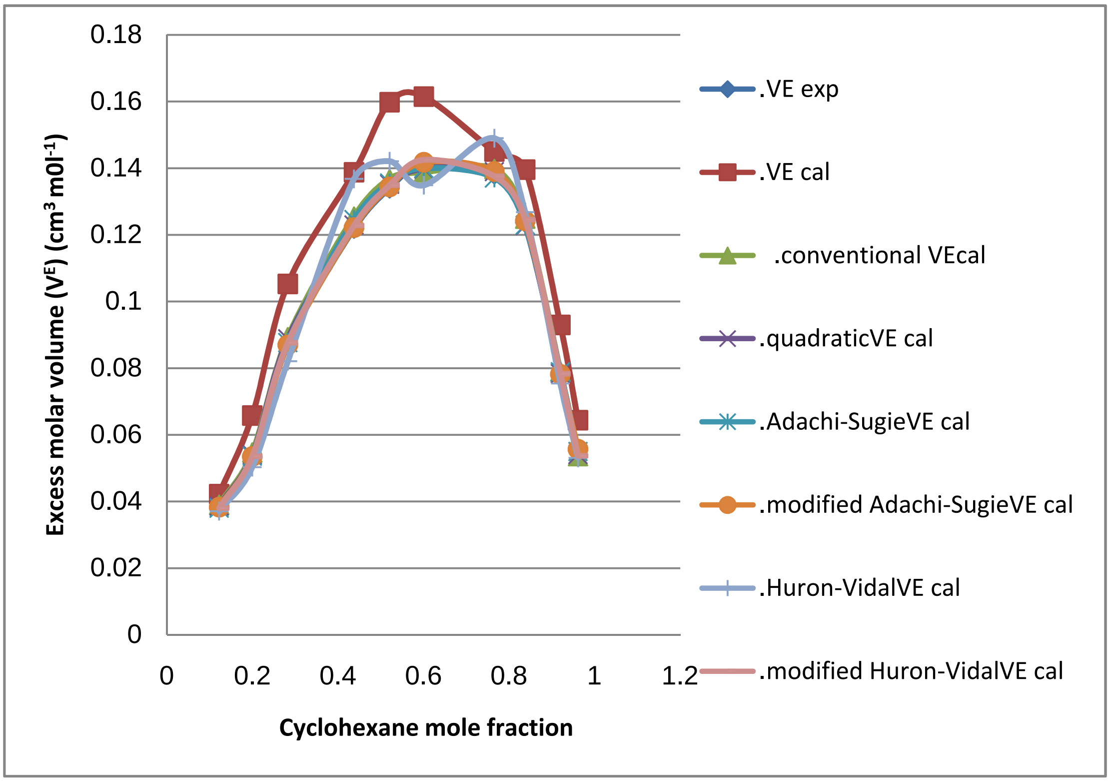

Fig. 4-4 : Excess volume of Cyclohexane n –Hexane system

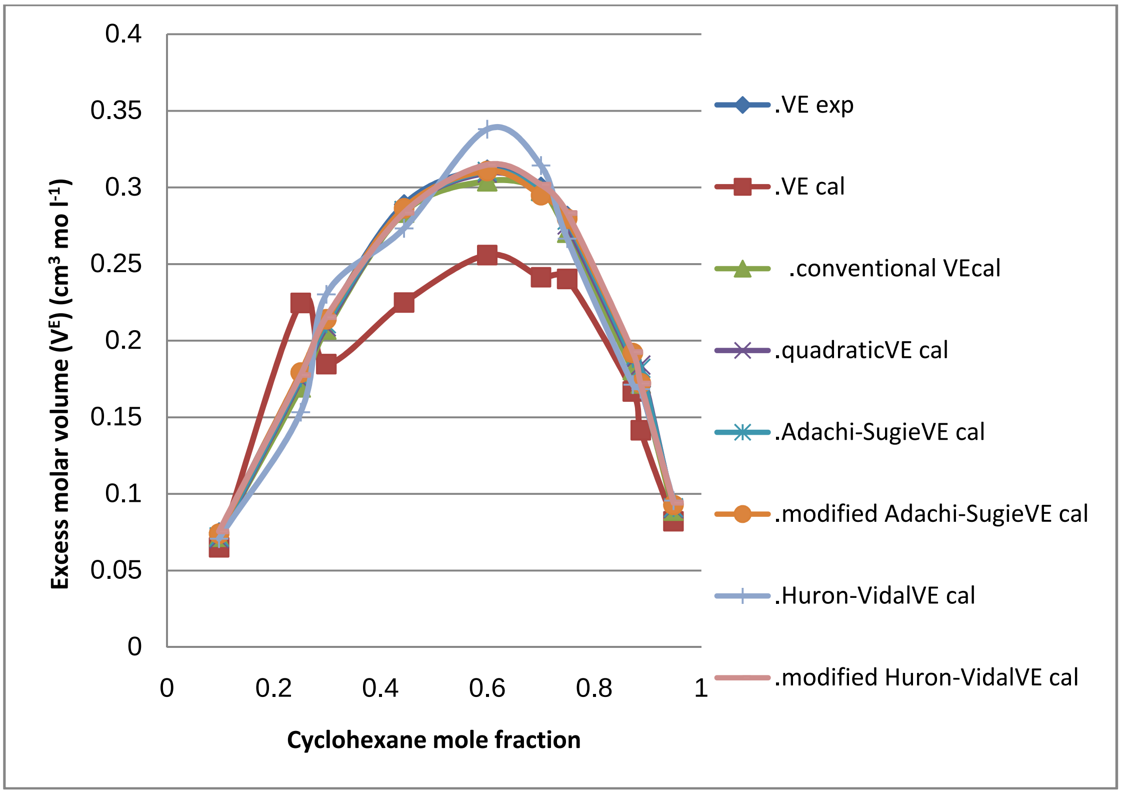

Fig. 4-5 : Excess volume of Cyclohexane n-Heptane system

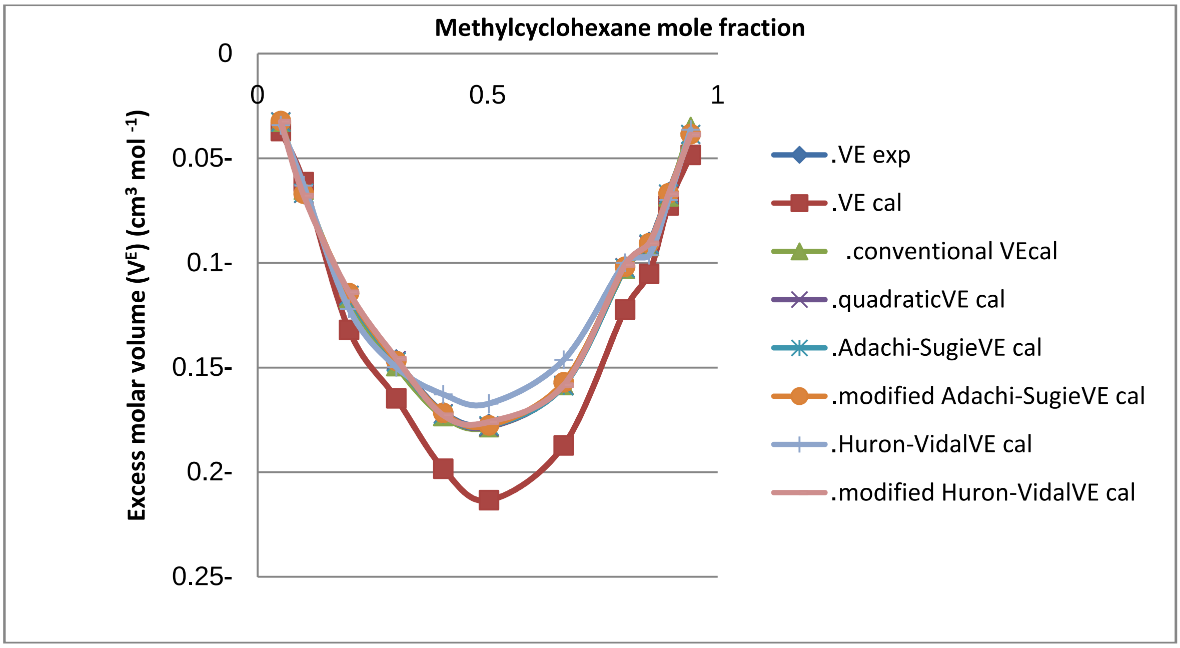

Fig. 4-6 : Excess volume of Methylcyclohexane Cyclohexane system

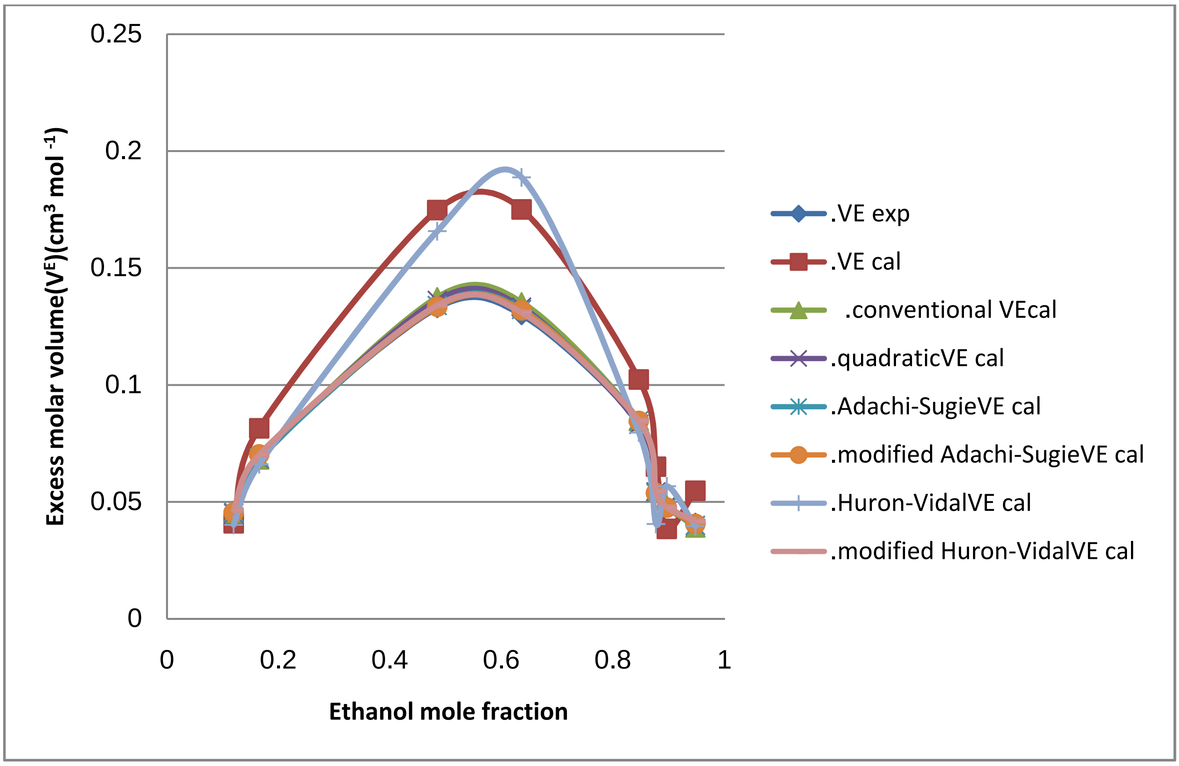

Fig 4-7 :Excess volume of Ethanol Acetontrile system

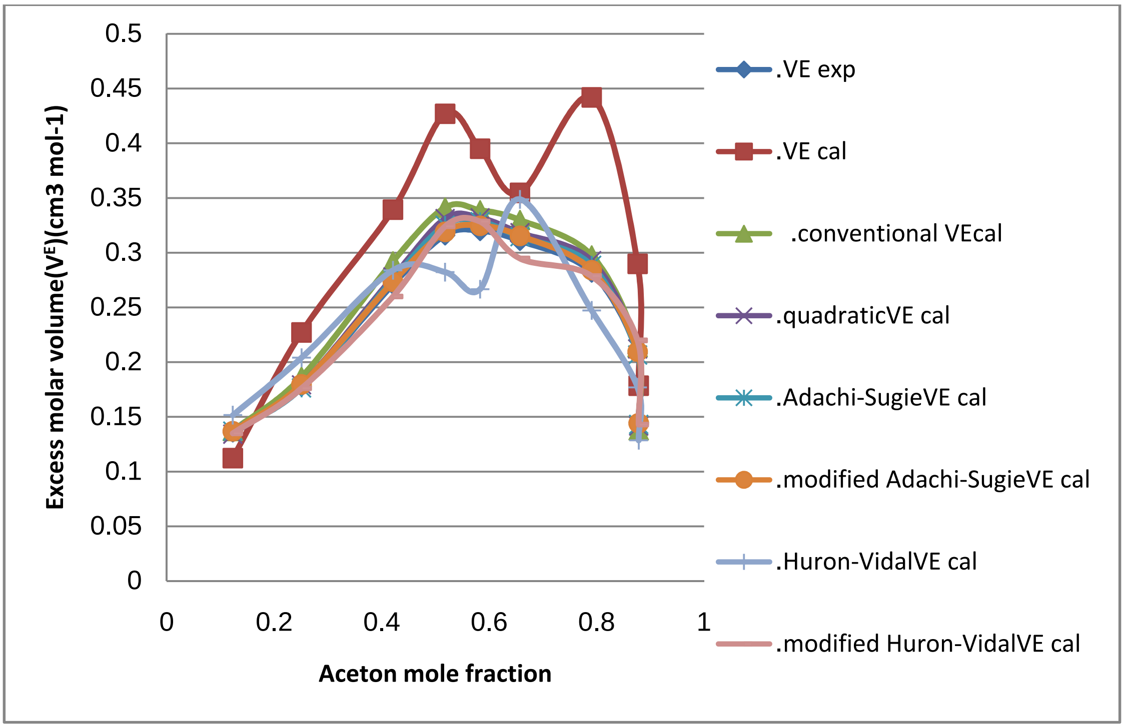

Fig. 4-8 : Excess volume of Aceton Isopropanol system

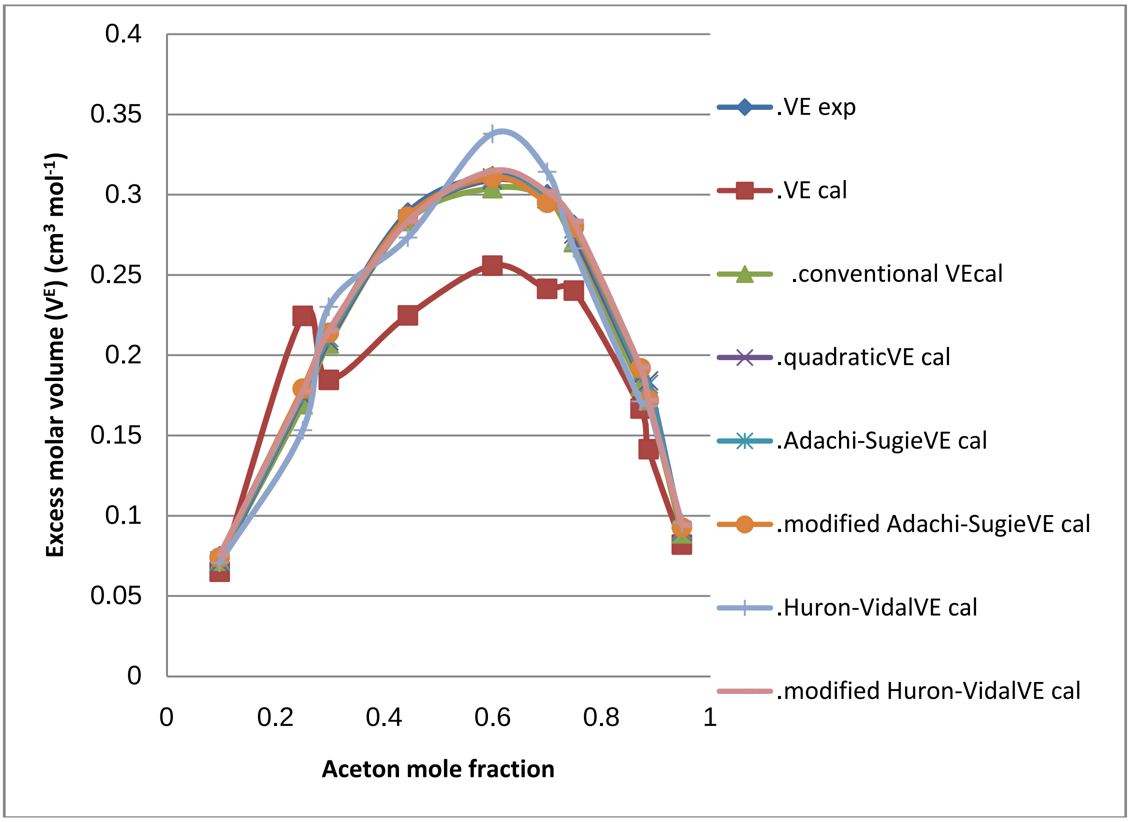

Fig. 4-9 : Excess volume of Aceton Cyclohexane system

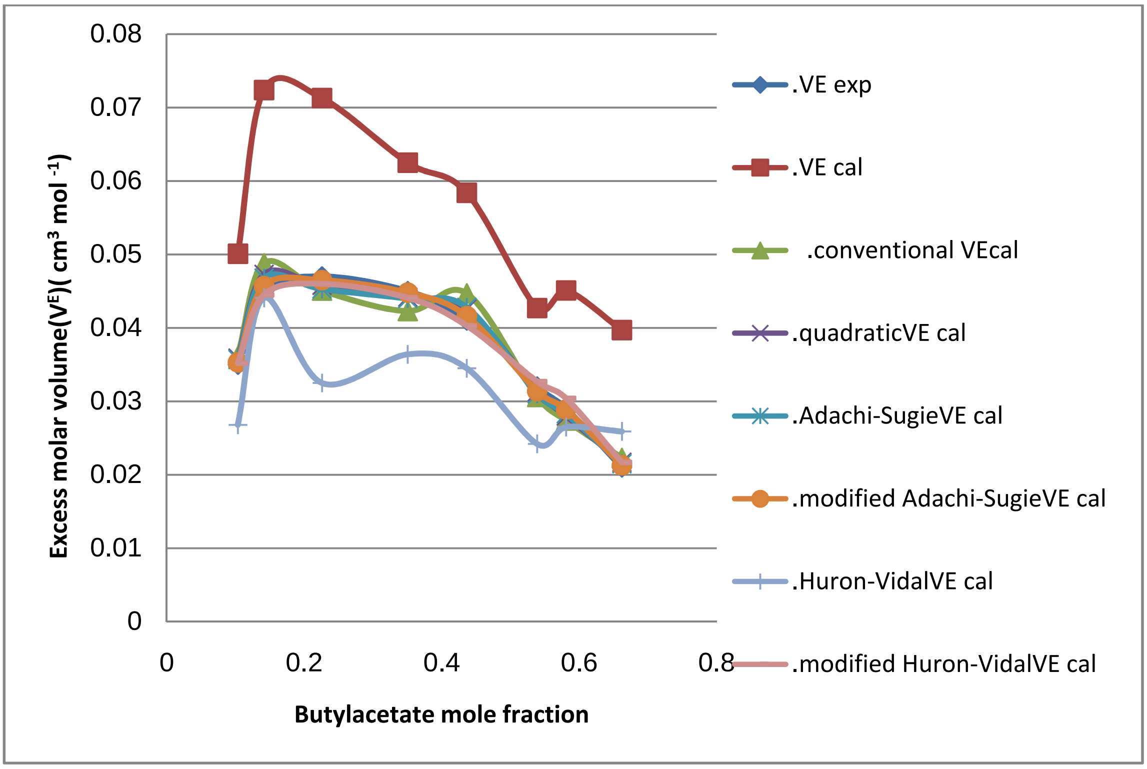

Fig. 4-10 : Excess volume of Butylacetate Benzen system

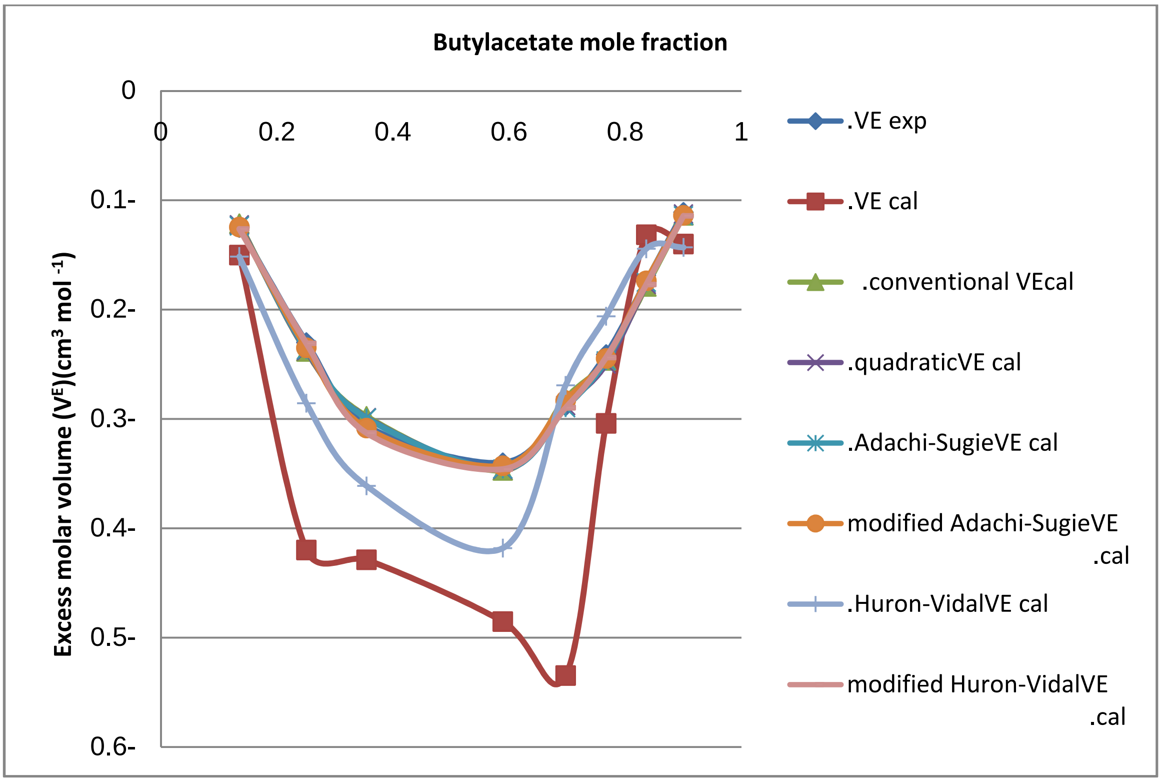

Fig. 4-11 : Excess volume of Butylacetate Bromobenzen system

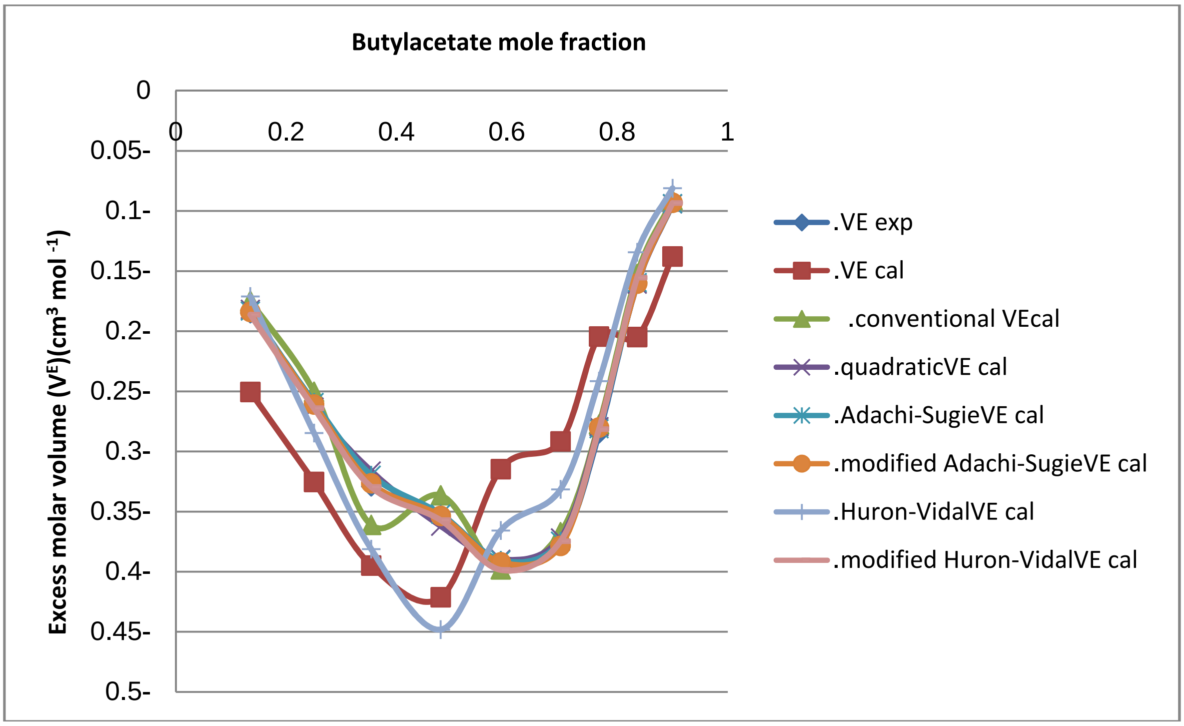

Fig. 4-12 : Excess volume of Butylacetate Chlorobenzen system

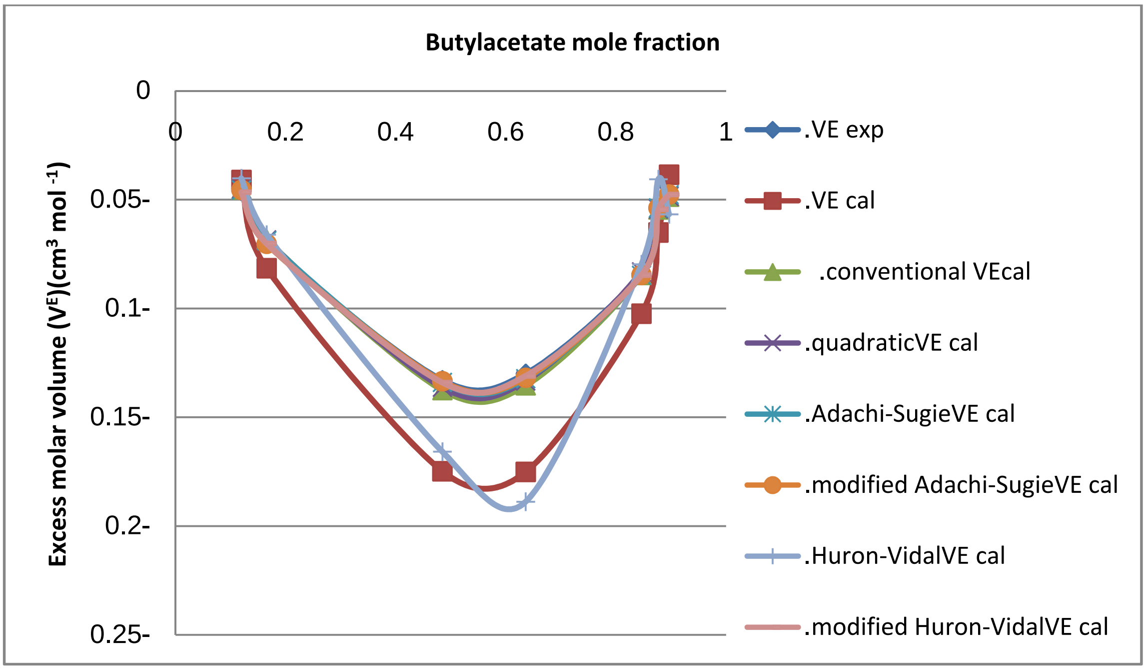

Fig. 4-13 : Excess volume of Butylacetate Tolune system

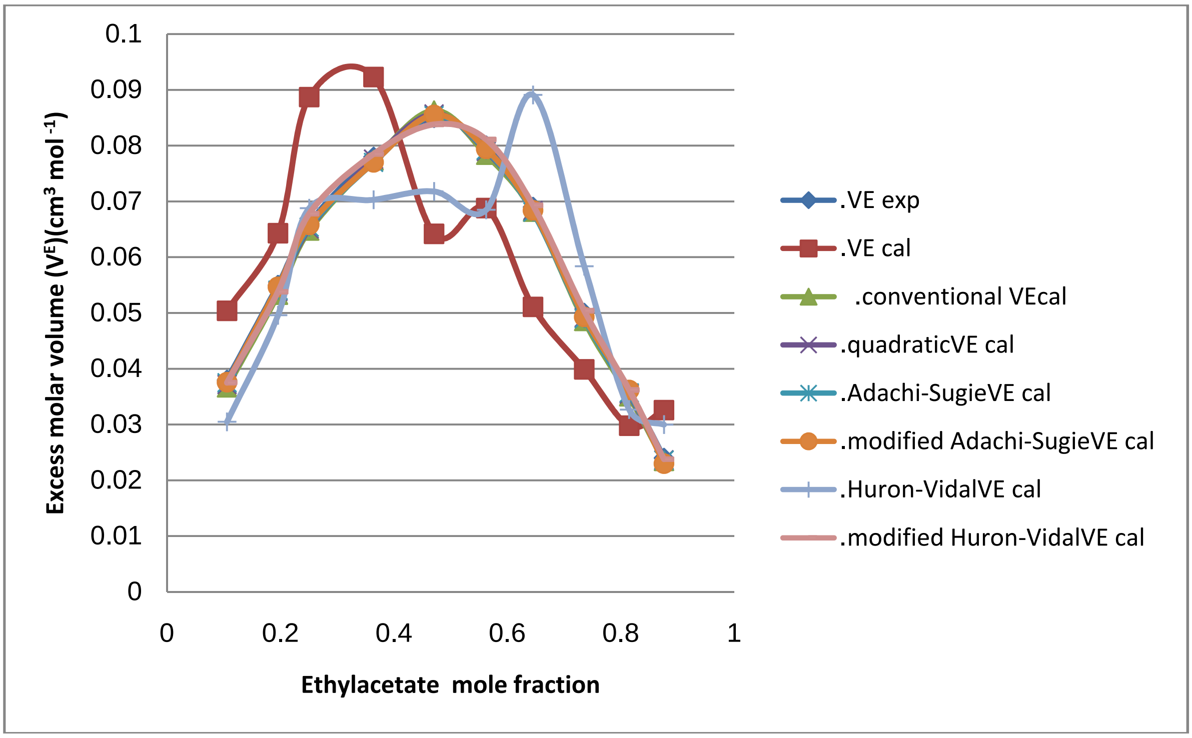

Fig. 4-14 : Excess volume of Ethylacetate Benzen system

It is found from all the previous figures excess molar volume V^E is either positive or negative value . The positive values would indicate that the molecular interaction between different molecules are weaker than interaction between molecules in the same pure liquid and the repulsive forces dominate the behaviour of the solution . The negative values of excess molar volume also means that the mixture is less compressible than the corresponding ideal mixture. Therefore, in the systems a compression in free volume is considered to occur, making the mixtures less compressible than the ideal mixture which ultimately culminates into the negative value of V^E . It is also found the difference between experimental and calculated value and this difference can be reduced to great extend by using suitable mixing rules as shown in this work .

Chapter Five
Conclusions and Recommendations for Future Work

5.1 Conclusions

The following conclusions may be drawn from the present research work:

1. The three equations of state : SRK, PR, and PRSV perform almost equally when correlate the excess molar volumes. The deviations obtained depend largely on the types of mixing and combining rules rather than the type of equation of state. The AAD% are 32.0919, 20.6048, and 18.3203 for SRK-EOS, PR-EOS, and PRSV-EOS respectively for the fourteen binary systems when they are used without any adjustable parameter .
2. It is generally believed that CEOS can be applied successfully to calculate V^E of normal hydrocarbon systems without using any adjustable parameter for light hydrocarbon system as (n-Heptane +n-Hexane). The following AAD% are obtained: for SRK-EOS is 1.29795, for PR-EOS is 0.8555, and for PRSV is 0.5986.
3. The use of the conventional mixing rules with one adjustable parameter led to reduction in the AAD%. Still more accurate results are obtained when applying CEOS with quadratic mixing rule. This is because these mixing rules have two adjustable parameters, the first one eliminates the error in the attraction term of an EOS; and the second one eliminates the error in the covolume term of an EOS. Table 5-1 shows the results of the overall absolute average deviations by using conventional and quadratic mixing rules.
4. The accuracy of correlating VE is further increased when using Adachi and Sugie mixing rules as shown in the table 5-1.
5. New modified method has been used in this work to predict V^E by modifying Adachi-Sugie mixing rules and using three adjustable parameters

L_{ij}, m_{ij}, and h_{ij}. This modification leds to much further reduction the deviations and gave more accurate results. The AAD% are show in table 5-1. These results show a very big difference in deviations obtained with different mixing rules for the same EOS rather than the change of EOS for the same mixing rules.

6. The correlation of V^E data are made with Huron-Vidal method which is based on the excess Gibbs free energy and it is coupled with CEOS. New modification to improve the V^E correlation results, this is by modifying Huron-Vidal method in this work by changing the mixing rules for parameter "b" and using an adjustable parameter h_{ij} . A applying this modification for PRSV-EOS gave more accurate results than other equation of state. These results are show in table 5-1.

7. Good prediction of ternary systems of V^E calculated from its binaries data were obtained by using PRSV-EOS with the same above mixing rules and parameters of binary systems. The overall absolute average deviations results are shown in table 5-2 for two ternary systems.

Table 5-1 : **Summarized overall average absolute deviations for binary V^E data calculation**

Method	AAD% SRK-EOS	AAD% PR-EOS	AAD% PRSV-EOS
kij=0	32.0919	20.6048	18.3203
Conventional mixing rules	9.0096	4.6060	3.3630
Quadratic mixing rules	4.5594	2.6759	1.9972
Adachi-Sugie mixing rules	3.1374	2.1170	1.6020
Modified Adachi-Sugie mixing rules In this work	1.3318	0.9786	0.8357
Huron-Vidal method	-------------	-------------	13.6593
Modified Huron-Vidal method In this work	-------------	-------------	1.5487

Table 5-2: Summarized overall average absolute deviations for ternary V^E data calculation

Method	AAD%
kij=0	18.0718
Conventional mixing rules	6.0137
Quadratic mixing rules	4.1003
Adachi-Sugie mixing rules	3.1728
Modified Adachi-Sugie mixing rules In this work	1.7701
Huron-Vidal method	11.6824
Modified Huron-Vidal method In this work	3.8966

5.2 Recommendations for Future Work

For future work, the following recommendations can be considered :

1.Developement of equation of state and new mixing rules for calculating V^E.

2.Studying the effect of change in temperature and pressure for calculating excess molar volume .

3. Studying the possibility of calculating V^E for more ternary systems and multicomponent systems.

4. Studying the possibility of applying different activity coefficient models to calculate V^E (such as unifac, uniquac).

5. The most important factor is to construct a apparatuse set up experimentally and studying the effect of temperature and pressure and other thermodynamic properties on calculating VE and apply the obtained data of the equation of state.

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Appendix A

Tables of Modification Results in this work

Table A1 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Methylcyclohexane (1)+n Hexane(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
x	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.0506	-0.0321	-0.0323	0.6291	-0.0323	0.6230	-0.0322	0.3115
0.1005	-0.0671	-0.0669	0.2989	-0.0670	0.1490	-0.0669	0.2989
0.1988	-0.1146	-0.1143	0.2617	-0.1149	0.2617	-0.1144	0.1745
0.3015	-0.1462	-0.1474	0.8207	-0.1466	0.2735	-0.1468	0.4103
0.4036	-0.1713	-0.1719	0.3502	-0.1715	0.1167	-0.1716	0.1751
0.5028	-0.1769	-0.1783	0.7914	-0.1774	0.2418	-0.1776	0.3941
0.5945	-0.1663	-0.1670	0.4209	-0.1677	0.8418	-0.1674	0.6571
0.6653	-0.1578	-0.1571	0.4435	-0.1572	0.3801	-0.1570	0.5069
0.7985	-0.1014	-0.1018	0.3944	-0.1019	0.4930	-0.1018	0.3929
0.8508	-0.0900	-0.0901	0.1111	-0.0905	0.5555	-0.0906	0.6666
0.8932	-0.0663	-0.0668	0.7541	-0.0668	0.7541	-0.0667	0.5997
0.9413	-0.0380	-0.0385	1.3157	-0.0382	0.5263	-0.0384	1.0526
AAD%			0.5451		0.4359		0.4687

Table A2 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Methylcyclohexane(1)+n-Heptane(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
x	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.0529	-0.0134	-0.0135	0.7462	-0.0133	0.7462	-0.0133	0.7462
0.1038	-0.0185	-0.0183	1.0810	-0.0186	0.5405	-0.0184	0.5405
0.1958	-0.0220	-0.0218	0.9090	-0.0222	0.9090	-0.0221	0.4545
0.3039	-0.0253	-0.0255	0.7905	-0.0253	1.5564	-0.0254	0.3937
0.3993	-0.0274	-0.0271	1.0948	-0.0273	0.3647	-0.0275	0.3649
0.4611	-0.0281	-0.0282	0.3556	-0.0283	0.7117	-0.0283	0.7067
0.5045	-0.0274	-0.0271	1.0948	-0.0276	0.7299	-0.0278	1.4388
0.5680	-0.0252	-0.0249	1.1904	-0.0251	0.3968	-0.0253	0.3968
0.6280	-0.0224	-0.0223	0.4464	-0.0226	0.8928	-0.0225	0.4444

0.7034	-0.0175	-0.0177	1.1428	-0.0173	1.1542	-0.0176	0.5681
0.8172	-0.0124	-0.0126	1.6129	-0.0123	0.8064	-0.0125	0.8064
0.8650	-0.0093	-0.0092	1.0892	-0.0094	1.0752	-0.0092	1.0869
0.9066	-0.0081	-0.0081	0.0000	-0.0082	1.2134	-0.0083	2.4096
AAD%			0.8894		0.8529		0.7963

Table A3 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for cyclohexane(1)+n-Hexane(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
x	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1222	0.0384	0.0381	0.7812	0.0386	0.5181	0.0383	0.2604
0.1996	0.0533	0.0530	0.5628	0.0532	0.1876	0.0535	0.3752
0.2828	0.0873	0.0806	0.8018	0.0876	0.3424	0.0870	0.3436
0.4375	0.1219	0.1213	0.4922	0.1227	0.6562	0.1222	0.2454
0.5207	0.1340	0.1336	0.2985	0.1348	0.5934	0.1344	0.2976
0.6007	0.1411	0.1408	0.2126	0.1422	0.7795	0.1418	0.4961
0.7657	0.1382	0.1378	0.2849	0.1385	0.2170	0.1390	0.5788
0.8378	0.1237	0.1232	0.4058	0.1241	0.3223	0.1242	0.4042
0.9200	0.0778	0.0773	0.6426	0.0775	0.3856	0.0782	0.5141
0.9611	0.0554	0.0552	0.3610	0.0551	0.5415	0.0557	0.5415
AAD%			0.4870		0.4536		0.4043

Table A4 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for cyclohexane(1)+n-Heptane(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
x	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.0974	0.0748	0.0742	0.8021	0.0751	0.3994	0.0740	1.0810
0.2503	0.1787	0.1805	1.0072	0.1781	0.3358	0.1792	0.2797
0.2982	0.2131	0.2146	0.6989	0.2126	0.2351	0.2140	0.4205
0.4437	0.2889	0.2859	1.0384	0.2872	0.5884	0.2864	0.8653
0.5993	0.3116	0.3096	0.6484	0.3105	0.3550	0.3108	0.2574
0.7000	0.3004	0.2987	0.5691	0.3029	0.8322	0.2950	0.3005
0.7490	0.2814	0.2806	0.2851	0.28	0.5000	0.2796	0.6396
0.8718	0.191	0.1924	0.7276	0.1897	0.6806	0.1920	0.5208
0.8867	0.1701	0.1685	0.9406	0.1751	2.9399	0.1723	1.2933
0.9479	0.0931	0.0934	0.3222	0.0923	0.8592	0.0928	0.3222
AAD%			0.7055		0.7650		0.6933

Table A5: Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Methylcyclohexane(1) + Cyclohexane(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
x	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.0399	-0.0024	-0.0023	4.1678	-0.0025	4.1666	-0.0024	0.0000
0.1202	-0.0072	-0.007	1.3888	-0.0074	2.7027	-0.0073	1.3888
0.2004	-0.0086	-0.0087	1.1162	-0.0087	1.3761	-0.0085	1.1764
0.2820	-0.0056	-0.0058	3.5714	-0.0055	1.8181	-0.0057	1.7543
0.4401	-0.0049	-0.0047	4.0816	-0.0048	2.0833	-0.0050	2.0408
0.5183	-0.0988	-0.0993	0.5035	-0.0990	0.2020	-0.0987	0.1012
0.5511	-0.0134	-0.0133	0.7462	-0.0130	3.0769	-0.0132	1.1492
0.6629	-0.0157	-0.0160	1.9108	-0.0156	0.6410	-0.0155	1.2903
0.7551	-0.0153	-0.0151	1.3245	-0.0154	0.6493	-0.0152	0.6539
0.8334	-0.0120	-0.0124	3.3333	-0.0123	2.4390	-0.1190	0.8333
0.9219	-0.0047	-0.0046	2.1276	-0.0048	2.1276	-0.0049	4.2553
AA%E			2.2238		1.9196		1.3763

Table A6 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Ethanol (1)+ Acetontrile(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.0480	0.0080	0.0081	1.2500	0.0081	1.2500	0.0080	0.0000
0.1474	0.0150	0.0153	2.0000	0.0151	0.6622	0.0151	1.3157
0.4400	0.0200	0.0198	1.0000	0.0198	1.0101	0.0199	0.5251
0.4878	0.0310	0.0312	0.6451	0.0314	1.2738	0.0312	0.6451
0.5929	0.0440	0.0435	1.1494	0.0437	0.6864	0.0445	1.1235
0.6113	0.0530	0.0536	1.1132	0.0527	0.5660	0.0534	0.7547
0.6525	0.0610	0.0619	1.4754	0.0612	0.3267	0.0615	0.8196
0.7842	0.0720	0.0792	0.2700	0.0723	0.4149	0.0718	0.2785
0.8202	0.0690	0.0683	1.0248	0.0701	1.5941	0.0701	1.5942
0.8988	0.0520	0.0528	1.5138	0.0515	0.9615	0.0524	0.7692
0.9478	0.0410	0.0413	0.7317	0.0415	1.2195	0.0406	0.9756
AAD%			0.9886		0.9161		0.8970

Table A7: Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Aceton(1) + Isopropanol(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1231	0.1360	0.1376	1.7647	0.1372	0.8746	0.1368	0.5882
0.2510	0.1780	0.1782	0.1123	0.1793	0.7303	0.1797	0.9460
0.4211	0.2710	0.2776	2.3775	0.2761	1.8471	0.2735	0.9140
0.5181	0.3160	0.3198	1.2025	0.3204	1.3924	0.3191	0.9810
0.5832	0.3200	0.3247	1.4687	0.3251	1.5937	0.3247	1.4474
0.6574	0.3110	0.3175	2.0472	0.3199	2.7821	0.3155	1.7687
0.7908	0.2820	0.2896	2.6950	0.2857	1.3120	0.2841	0.7446
0.8763	0.2080	0.2113	1.5865	0.2108	1.3282	0.2096	0.7632
0.8783	0.1450	0.1452	0.1392	0.1448	0.1379	0.1442	0.5547
AAD%			1.4065		1.3257		0.9308

Table A8: Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Aceton(1) + Cyclohexane(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1688	0.6450	0.6521	1.1007	0.6340	1.7054	0.6532	1.2713
0.3068	0.9300	0.9380	0.8602	0.9341	0.4408	0.9350	0.5347
0.4152	1.0600	1.0532	0.6450	1.0527	0.6886	1.0536	0.6037
0.4745	1.0820	1.0887	0.6192	1.0973	1.3943	1.0958	1.2754
0.6159	1.0430	1.0553	1.792	1.0507	0.7382	1.0347	0.7957
0.6790	0.9740	0.9325	0.1540	0.9711	0.2970	0.9683	0.5852
0.7866	0.7710	0.7834	1.5828	0.7819	1.3940	0.7786	0.9761
0.9294	0.3230	0.3246	0.4953	0.3256	0.8049	0.3252	0.6811
AAD%			0.9548		0.9356		0.8374

Table A9 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Butylacetate(1)+Benzen(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1036	0.0350	0.0354	1.1142	0.0357	2.0000	0.0353	0.8571
0.1416	0.0450	0.0457	1.5555	0.0447	0.6666	0.0457	1.5555
0.2259	0.0470	0.0467	0.6423	0.0481	2.2869	0.0465	1.0752
0.3506	0.0450	0.0442	1.7777	0.0453	0.6622	0.0448	0.4444
0.4365	0.0410	0.0403	1.7073	0.0408	0.4878	0.0416	1.4634
0.5388	0.0320	0.0328	2.439	0.0315	1.5873	0.0314	1.9108
0.5809	0.0290	0.0287	1.0344	0.0286	1.3793	0.0289	0.3448
0.6621	0.0210	0.0212	0.9433	0.0257	1.4492	0.0213	1.4084
0.7456	0.0150	0.0152	1.3333	0.0152	1.3157	0.0149	0.6666
0.8902	0.0050	0.0049	2.0000	0.0049	2.0408	0.0049	2.0000
AAD%			1.4614		1.3872		1.1946

Table A10 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Butylacetate(1)+Bromobenzen(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1352	-0.125	0.1239	0.8800	-0.1244	0.4800	-0.1246	0.3200
0.2506	-0.23	0.2358	2.5217	-0.2369	3.0000	-0.2350	2.1739
0.3542	-0.306	0.3105	1.4492	-0.3093	1.0669	-0.3084	0.7782
0.4801	-0.357	0.3558	0.3361	-0.3562	0.2240	-0.3568	0.5602
0.496	-0.358	0.3600	0.5586	-0.3597	0.4748	-0.3567	0.3631
0.5889	-0.34	0.3311	2.6176	-0.3322	2.2941	-0.3429	0.8529
0.6972	-0.288	0.2821	2.0486	-0.2813	2.3263	-0.2833	1.6311
0.7669	-0.241	0.2432	0.9046	-0.2450	1.6326	-0.2447	1.5120
0.8361	-0.174	0.1722	1.0344	-0.1735	0.2873	-0.1738	0.1149
0.9001	-0.111	0.1134	2.1621	-0.1126	1.4209	-0.1119	0.8181
AAD%			1.4535		1.3231		1.0830

Table A11: Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Butylacetate(1)+Chlorobenzen(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1352	-0.1850	-0.1808	2.2702	-0.1842	0.4343	-0.1840	0.5405
0.2506	-0.260	-0.2699	3.8076	-0.2621	0.8012	-0.2610	0.3831
0.3542	-0.3290	-0.3149	4.4776	-0.3284	0.1827	-0.3265	0.7656
0.4801	-0.3550	-0.3611	1.7183	-0.3512	1.0704	-0.3536	0.3959
0.4960	-0.3900	-0.3700	5.1282	-0.3937	0.9487	-0.3940	1.0256
0.5889	-0.3950	-0.3810	3.6745	-0.4002	1.2993	-0.3922	0.7139
0.6972	-0.3760	-0.3612	3.9361	-0.3791	0.8244	-0.3785	0.6650
0.7669	-0.2850	-0.2701	5.5164	-0.2819	1.0996	-0.2801	1.7192
0.8361	-0.1590	-0.1646	3.5220	-0.1600	0.6289	-0.1604	0.8805
0.9001	-0.0930	-0.0916	0.4301	-0.0935	0.5347	-0.0932	0.2150
AAD%			3.5781		0.7816		0.7284

Table A12 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Butylacetate(1)+Tolune(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1196	-0.046	-0.0466	1.3043	-0.0463	0.6521	-0.0455	1.0869
0.1654	-0.07	-0.0685	2.1428	-0.0709	1.28	-0.0703	0.4285
0.3901	-0.099	-0.0981	0.9090	-0.0988	0.2024	-0.0995	0.5050
0.4847	-0.133	-0.1365	2.6315	-0.1341	0.8202	-0.1335	0.3745
0.5961	-0.136	-0.1314	3.3823	-0.1357	0.2210	-0.1358	0.1470
0.6360	-0.13	-0.1332	2.4615	-0.1315	1.1406	-0.1319	1.2307
0.7589	-0.116	-0.1176	1.3793	-0.1167	0.5998	-0.1168	0.6896
0.8463	-0.084	-0.0829	1.3268	-0.0863	2.6651	-0.0846	0.7092
0.8771	-0.054	-0.0554	2.5292	-0.0537	0.5586	-0.0538	0.3717
0.8965	-0.048	-0.0482	0.4166	-0.0476	0.8333	-0.0478	0.4166
AAD%			1.8287		0.8965		0.6595

Table A13 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Ethylacetate(1)+Benzen(2)

		SRK-EOS		PR-EOS		PRSV-EOS	
X	V^E exp.	V^E cal.	AD%	V^E cal	AD%	V^E cal	AD%
0.1058	0.0380	0.0375	1.3157	0.0378	0.5261	0.0376	1.0526
0.1956	0.0550	0.0544	1.0909	0.0553	0.5454	0.0547	0.5454
0.2506	0.0660	0.0655	0.7575	0.0652	1.2121	0.0658	0.3030
0.3641	0.0780	0.0777	0.3861	0.0775	0.6410	0.0770	1.2820
0.4707	0.0850	0.0856	0.7009	0.0848	0.2358	0.0855	0.5847
0.5626	0.0800	0.0789	1.3750	0.0809	1.1250	0.0794	0.7500
0.6451	0.0690	0.0683	1.0248	0.0695	0.7194	0.0684	0.8771
0.7354	0.0500	0.0494	1.2000	0.0505	1.0000	0.0493	1.4000
0.8146	0.0360	0.0357	0.8333	0.0365	1.3888	0.0362	0.5555
0.8759	0.0240	0.0237	1.2500	0.0238	0.8333	0.0230	0.8403
AAD%			0.9936		0.8211		0.8243

Table A14 : Comparison between experimental and calculated excess molar volume when applying Modified Adachi-Sugie mixing rules for Ternary Systems

Methylcyclohexane+Cyclohexane+n-Hexane				Methylcyclohexane+Cyclohexane+n-Heptane			
x	V^E exp.	V^E cal.	AD%	x	V^E exp.	V^E cal	AD%
0.2025	0.0522	0.0518	0.7662	0.2051	0.1058	0.1042	1.5122
0.1901	0.0778	0.0772	0.7712	0.1862	0.1633	0.1654	1.2859
0.1536	0.0841	0.0825	1.9024	0.1511	0.2414	0.2448	1.4084
0.1337	0.0790	0.0779	1.3924	0.1336	0.2439	0.2349	3.6900
0.1148	0.0676	0.0671	0.7396	0.1157	0.2378	0.2336	1.7661
0.1005	0.0567	0.0555	2.1164	0.0988	0.2221	0.2251	1.3327
0.0810	0.0428	0.0423	1.1682	0.0798	0.1991	0.1996	0.25
0.0645	0.0333	0.0328	1.5015	0.0562	0.1710	0.1670	2.3791
0.0479	0.0252	0.0241	4.3650	0.0464	0.0749	0.0738	1.4686
0.0285	0.0140	0.0138	1.4492	0.0112	0.0121	0.0123	1.6528
AAD%			1.6188				1.9215

Table A15 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Methylcyclohexane(1)+n Hexane(2)

x	V^E exp.	V^E cal.	AD%
0.0506	-0.0321	-0.0324	0.9345
0.1005	-0.0671	-0.0678	1.0432
0.1988	-0.1146	-0.1140	0.5235
0.3015	-0.1462	-0.1457	0.3431
0.4036	-0.1713	-0.1728	0.8756
0.5028	-0.1769	-0.1760	0.5087
0.5945	-0.1663	-0.1648	0.9019
0.6653	-0.1578	-0.1584	0.3802
0.7985	-0.1014	-0.1009	0.4930
0.8508	-0.0900	-0.0906	0.6666
0.8932	-0.0663	-0.0671	1.2066
0.9413	-0.0380	-0.0382	0.5263
AAD%			0.6974

Table A16 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Methylcyclohexane(1)+ n-Heptane(2)

X	V^E exp.	V^E cal.	AD%
0.0529	-0.0134	-0.0135	0.7462
0.1038	-0.0185	-0.0187	1.0810
0.1958	-0.0220	-0.0225	2.2272
0.3039	-0.0253	0.0258	1.9762
0.3993	-0.0274	-0.0268	2.218
0.4611	-0.0281	-0.0286	1.7793
0.5045	-0.0274	-0.0279	1.8948
0.5680	-0.0252	-0.0247	1.9841
0.6280	-0.0224	-0.0219	2.2132
0.7034	-0.0175	-0.0179	2.2846
0.8172	-0.0124	-0.0121	2.4193
0.8650	-0.0093	-0.0092	1.0752
0.9066	-0.0081	-0.0078	3.7037
AAD%			1.9770

Table A17 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for cyclohexane (1)+ n-Hexane(2)

X	V^E exp.	V^E cal.	AD%
0.1222	0.0384	0.0380	1.0416
0.1996	0.0533	0.0535	0.37
0.2828	0.0873	0.0876	0.3464
0.4375	0.1219	0.1228	0.7383
0.5207	0.1340	0.1349	0.671
0.6007	0.1411	0.1425	0.9922
0.7657	0.1382	0.1376	0.4341
0.8378	0.1237	0.1246	0.7275
0.9200	0.0778	0.0783	0.6426
0.9611	0.0554	0.0537	3.0685
AAD%			0.9113

Table A18 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for cyclohexane(1) + n-Heptane(2)

X	V^E exp.	V^E cal.	AD%
0.0974	0.0748	0.0755	0.9358
0.2503	0.1787	0.1776	0.6193
0.2982	0.2131	0.2153	1.0323
0.4437	0.2889	0.2835	1.8691
0.5993	0.3116	0.3148	1.0269
0.7000	0.3004	0.3018	0.4660
0.7490	0.2814	0.2833	0.6751
0.8718	0.191	0.1926	0.8307
0.8867	0.1701	0.1720	1.1169
0.9479	0.0931	0.0942	1.1815
AAD%			0.9726

Table A19 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Methylcyclohexane(1) + Cyclohexane(2)

X	V^E exp.	V^E cal.	AD%
0.0399	-0.0024	-0.0025	4.1666
0.1202	-0.0072	-0.0070	2.777
0.2004	-0.0086	-0.0084	2.3809
0.2820	-0.0056	-0.0055	1.8181
0.4401	-0.0049	-0.0051	4.0816
0.5183	-0.0988	-0.0981	0.7135
0.5511	-0.0134	-0.0138	2.9850
0.6629	-0.0157	-0.0156	0.6369
0.7551	-0.0153	-0.0151	1.3245
0.8334	-0.0120	-0.0116	3.3333
0.9219	-0.0047	-0.0046	2.1276
AAD%			2.3636

Table A20 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Ethanol (1)+ Acetontrile(2)

X	V^E exp.	V^E cal.	AD%
0.0480	0.0080	0.0084	5.0000
0.1474	0.0150	0.0152	1.3333
0.2461	0.0100	0.0103	3.0000
0.4400	0.0200	0.0205	2.4390
0.4878	0.0310	0.0318	2.5806
0.5929	0.0440	0.0446	1.3636
0.6113	0.0530	0.0534	0.7547
0.6525	0.0610	0.0617	1.1475
0.7842	0.0720	0.0725	0.6896
0.8202	0.0690	0.0696	0.8620
0.8988	0.0520	0.0548	5.3846
0.9478	0.0410	0.0418	1.9151
AAD%			2.4969

Table A21 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Aceton(1) + Isopropanol(2)

x	V^E exp.	V^E cal.	AD.%
0.1231	0.0136	0.1350	0.7407
0.2510	0.1780	0.1762	1.0112
0.4211	0.2710	0.2600	4.0590
0.5181	0.3160	0.3241	2.4992
0.5832	0.3200	0.3285	2.5632
0.6574	0.3110	0.2948	5.4952
0.7908	0.2820	0.2787	1.1840
0.8763	0.2080	0.2193	5.4325
0.8783	0.1450	0.1430	1.3793
AAD%			2.7298

Table A22: Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Aceton(1) + Cyclohexane(2)

X	V^E exp.	V^E cal.	AD%
0.1688	0.6450	0.6581	2.0310
0.3068	0.9300	0.9254	0.4946
0.4152	1.0600	1.0773	1.6325
0.4745	1.0820	1.0836	0.1478
0.6159	1.0430	1.0481	0 .4889
0.6790	0.9740	0.9813	0.7439
0.7866	0.7710	0.7785	0.9079
0.9294	0.3230	0.32 68	1.1764
AAD%			0.9495

Table A23: Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Butylacetate(1)+Benzen(2)

X	V^E exp.	V^E cal.	AD%
0.1036	0.0350	0.0352	0.5714
0.1416	0.0450	0.0445	1.1235
0.2259	0.0470	0.0460	2.1276
0.3506	0.0450	0.0441	2.0000
0.4365	0.0410	0.0403	1.7369
0.5388	0.0320	0.0327	2.1875
0.5809	0.0290	0.0304	4.6052
0.6621	0.0210	0.0217	3.0000
0.7456	0.0150	0.0153	1.9607
0.8902	0.0050	0.0048	40000
AAD%			2.3742

Table A24: Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Butylacetate(1)+Bromobenzen(2)

X	V^E exp.	V^E cal.	AD%
0.1352	-0.1250	-0.1263	1.0460
0.2506	-0.2300	-0.2308	0.3478
0.3542	-0.3060	-0.3038	0.7189
0.4801	-0.3570	-0.3684	3.194
0.496	-0.3580	-0.3528	1.4525
0.5889	-0.3400	-0.3458	1.5348
0.6972	-0.2880	-0.2897	0.5902
0.7669	-0.2410	-0.2438	1.1684
0.8361	-0.1740	-0.1771	1.7504
0.9001	-0.1110	-0.1153	3.8738
AAD%			1.5949

Table A25 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Butylacetate(1)+Chlorobenzen(2)

X	V^E exp.	V^E cal.	AD%
0.1352	-0.1850	-0.1863	0.7027
0.2506	-0.260	-0.2641	1.5769
0.3542	-0.3290	-0.3296	0.1820
0.4801	-0.3550	-0.3572	0.6197
0.4960	-0.3900	-0.3934	0.8642
0.5889	-0.3950	-0.3985	0.8782
0.6972	-0.3760	-0.3747	0.3457
0.7669	-0.2850	-0.2815	1.1355
0.8361	-0.1590	-0.1555	2.2012
0.9001	-0.0930	-0.0935	0.5363
AAD%			0.8857

Table A26 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Butylacetate(1)+Tolune(2)

x	V^E exp.	V^E cal.	AD%
0.1196	-0.0460	-0.0466	1.304
0.1654	-0.0700	-0.0702	0.2857
0.3901	-0.099	-0.0996	0.606
0.4847	-0.1330	-0.1341	0.8202
0.5961	-0.1360	-0.1355	0.3676
0.6360	-0.1300	-0.1310	0.7692
0.7589	-0.1160	-0.1168	0.6896
0.8463	-0.0840	-0.0847	0.8333
0.8771	-0.0540	-0.0545	0.9174
0.8965	-0.0480	-0.0477	0.6250
AAD%			0.7164

Table A27 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Ethylacetate(1)+Benzen(2)

x	V^E exp.	V^E cal.	AD%
0.1058	0.0380	0.0375	1.3157
0.1956	0.0550	0.0538	2.2304
0.2506	0.0660	0.0678	2.7272
0.3641	0.0780	0.0785	0.6410
0.4707	0.0850	0.0838	1.4319
0.5626	0.0800	0.0811	1.3563
0.6451	0.0690	0.0693	0.4349
0.7354	0.0500	0.0504	0.8000
0.8146	0.0360	0.0362	0.5555
0.8759	0.0240	0.0238	0.8333
AAD%			1.4650

Table A28: Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Ternary System Methylcyclohexane(1)+Cyclohexane(2)+n-Hexane(3)

x_1	x_2	V^E exp.	V^E cal.	AD%
0.2025	0.7117	0.0522	0.0531	1.724
0.1901	0.6502	0.0778	0.0761	2.2339
0.1536	0.5304	0.0841	0.0893	6.1831
0.1337	0.4737	0.0790	0.0782	1.0131
0.1148	0.4055	0.0676	0.0664	1.8072
0.1005	0.3475	0.0567	0.0538	5.1146
0.0810	0.2829	0.0428	0.0436	1.8348
0.0645	0.2247	0.0333	0.0348	4.5045
0.0479	0.1590	0.0252	0.0263	4.1825
0.0285	0.0961	0.0140	0.0143	2.142
AAD%				3.0397

Table A29 : Comparison between experimental and calculated excess molar volume when applying modified Huron Vidal Method for Ternary System Methylcyclohexane(1)+Cyclohexane(2)+n-Heptane(3)

x_1	x_2	V^E exp.	V^E cal.	AD%
0.2051	0.7165	0.1058	0.1183	10.8693
0.1862	0.6539	0.1633	0.1689	3.4290
0.1511	0.5295	0.2414	0.2316	4.2314
0.1336	0.4102	0.2439	0.2382	2.3370
0.1157	0.4701	0.2378	0.2328	2.1477
0.0988	0.3471	0.2221	0.2410	8.5096
0.0798	0.2845	0.1991	0.2050	2.4610
0.0562	0.2250	0.1710	0.1931	11.4448
0.0464	0.1595	0.0749	0.0752	0.4005
0.0112	0.0326	0.0121	0.0124	2.4788
AAD%				4.7536

Appendix B

MATLAB Programing

Ethanol-Acetontrile system

```
clear
clc
Vexp=[0.008  0.0150  0.002  0.0021  0.031  0.044  0.053  0.061 0.072  0.069  0.0520  0.0410]*0.001;
T=298.15;
R=8.314;
P=101.325;
Tc1=513.9;
Tc2=545.5;
Pc1=6140;
Pc2=4833;
W1=.664;
W2=.327;
p1=786.65;
p2=785.25;
Mwt1=46.069;
Mwt2=40.053;
Tr1=T/Tc1;
Tr2=T/Tc2;
V1=Mwt1/p1;
V2=Mwt2/p2;
x1=[0.0480 0.1474 0.2461 0.3008 0.3523 0.4009 0.4400 0.4878 0.5929 0.6113 0.6525 0.7842 0.8202 0.8988 0.9478];
x2=1-x1;
b1=.08664*(R*Tc1)/Pc1;
b2=.08664*(R*Tc2)/Pc2;
b=x1*b1+x2*b2;
m1=0.48+1.574*W1-0.176*(W1^2);
m2=0.48+1.574*W2-0.176*(W2^2);
alpha1=[1+m1*(1-Tr1^.5)]^2;
alpha2=[1+m2*(1-Tr2^.5)]^2;
ac1=.42748*((R*Tc1)^2)/Pc1;
```

```
ac2=.42748*((R*Tc2)^2)/Pc2;
a1=alpha1*ac1;
a2=alpha2*ac2;
k=1;kkk=1;
k12value=-1.5:.001:1.5;
l12value=-1.5:.001:1.5;
m12value=-1.5:.001:1.5;
for k12=-1.5:.001:1.5
bb(kkk,:)=x1.^2*b1+2*x1.*x2*((b1+b2)/2).*(1-k12)+x2.^2*b2;
kk=1;
    for l12=-1.5:.001:1.5
        k=1;
     for m12=-1.5:.001:1.5
     aa(k,:)=x1.^2*a1+2*x1.*x2.*(a1*a2)^.5.*(1-l12-m12*(x1-x2))+x2.^2*a2;
     k=k+1;
     end
        k=k-1;
        Videal=(x1*V1+x2*V2);
          for j=1:k
          b=bb(kkk,:);
            a=aa(j,:);
A=a*P/R^2*T^2;
B=b*P/R*T;

            V(1,:)=b;
            error=1;%any value
            i=1;
                while(max(error)>.0001)
                          F(i,:)=V(i,:).^3*(P/(R*T))^3-(P/(R*T))^2.*V(i,:).^2+(A-B-
B.^2)*(P/(R*T)).*V(i,:)-A.* B;
Fd(i,:)=3*V(i,:).^2*(P/(R*T))^3-2*(P/(R*T))^2.*V(i,:)+(A-B-B.^2)*(P/(R*T));
                 V(i+1,:)=V(i,:)-(F(i,:)./Fd(i,:));
                   error=V(i+1,:)-V(i,:);
                  i=i+1;
                  end
          Vcal=V(end,:)-Videal;
          error1=abs((Vexp-Vcal)./ Vexp);
          er(kkk,kk,j,:)=error1;
          VV(kkk,kk,j,:)=V(end,:);
         FF(kkk,kk,j,:)=F(end,:);
```

```
      end
% [k1,k2]=min(er);
% sol(kk,:)=VV(k2);
% solK(kk,:)=k12(k2);
%
     kk=kk+1;
    end
   % kk=kk-1;
    kkk=kkk+1;
 end
 kkk=kkk-1;
 kk=kk-1;

% mm(1:12)=10;
% for i=1:12
%    xx=er(:,:,:,i);xx2=xx(:);
%    yy=VV(:,:,:,i);yy2=yy(:);
%    [bb(i) cv(i)]=min(xx(:));
%    err(i)=xx2(cv(i));
%    sol(i)=yy2(cv(i));
% end
  for i=1:12
  xx=er(:,:,:,i);
  ma=xx(1,1,1);
  for j=1:kkk
    for g=1:kk
      for z=1:k
       if xx(j,g,z)<ma
        ma=xx(j,g,z);
         qqq(i)=j;www(i)=g;eee(i)=z;

       end
      end
    end
  end
  pos(i,:)=[k12value(qqq(i)),l12value(www(i)),m12value(eee(i))];
sol(i)=er(qqq(i),www(i),eee(i),i);
yy(i)=VV(qqq(i),www(i),eee(i),i);

end
```

```
disp('      k12                  l12                  m12           error')
disp('------------------------------------------------------------------------')
disp([pos sol'])
disp('      Vexp       Vcal     error')
disp([Vexp' Vcal'])
```

الخلاصة

ان وجود قيم دقيقه للحجم الفائض لمزيج السائل ضروري جدا في حساب التصاميم الهندسية والصناعية المختلفة , ولكي نحصل على قيم دقيقة تولد السعي في قياس هذه القيم من معادلات الحالة مع العلم ان هذه المعادلات قد تم اشتقاقها وتطويرها لغرض حساب توازن السائل مع البخار. وتم استعمالها في هذه الدراسة لغرض قياس هذه القيم من معادلات الحالة مع العلم ان هذه المعادلات قد تم اشتقاقها وتعديل قيم معاملها لغرض قياس الحجم الفائض ولغرض التغلب على هذه المشكلة توجهت الجهود نحو تطوير معادلة الحالة وقوانين الخلط التابعة لها بحيث تصبح ملائمة لحساب الحجم الفائض.

وفي هذه الدراسة استعملت ثلاث معادلات تكعيبية لغرض حساب الحجم الفائض وهي Soave Relich Kwong (SRK)و Peng Robinson (PR) و Peng Robinson(PRSV) Stryjek Vera . وكان معدل الانحراف عن القيم المختبرية لأربعة عشر خليط ثنائي وبأستعمال مئه وثمانية وخمسون نقطة مختبرية بدون استخدام اي متغير توليفي($k_{ij}=0$) لكل منSRK 32.091% و PR 20.6048% و.PRSV 18.3203%

خمسة قوانين للخلط قد استخدمت لحساب الحجم الفائض . conventional الذي يحتوي على متغير توليفي واحد (k_{ij}) وتستعمل هذه الطريقة لأزالة الخطأ في فرضية القوى المسببة للجاذبية بين المتشابه والمختلف من الجزيئات في كل مكون فردي الخليط , وكان معدل الانحراف لكل من SRK9.0096% و PR4.6060% و PRSV 3.3630% . استخدم قانون الخلط من الدرجة الثانية quadratic الذي استعمل لألغاء وتقليل الأنحراف في معادلات الحالة عن طريق الثابت "b" وقد تم أستخدم متغير توليفي (h_{ij}) لكي يلغي تأثير الشكل وحجم الجزيئات وانحرافاتهم من فرضية امتلاك نوع شكل كروي وقد تم الحصول على معدل انحراف منخفض SRK4.5594% و PR2.6759% وPRSV1.9972%. وقد انخفض معدل الانحراف لكل من SRK وPR و PRSV الى 3.1374% و2.1170% و1.6020% على التوالي, وذلك عند استخدام قانون الخلط Adachi-Sugie التي تحتوي على متغيرين توليفين (L_{ij} و m_{ij}). وفي هذا البحث تم تطوير قانون الخلط Adachi-Sugie بأستخدام ثلاث متغيرات توليفية (L_{ij} و m_{ij} و h_{ij}) وكانت نتائج الأنحراف منخفضة جدا مقارنة بقوانين الخلط السابقة وكان معدل الأنحراف لكل من SRK1.3318% وPR0.9786% و PRSV0.8357% .

في طريقة اخرى تم استخدام معادلة الحالة PRSV التي اعطيت دقة بالنتائج أفضل من المعادلتين

الاخرى و تم استخدامها مع Huron-Vidal method وهي طريقه لربط الثوابت a و b في معادلة الحالة عن طريق Gibbs free energy وكانت معدل الانحراف 13.6593% . في هذا البحث تم تطوير Huron-Vidal method بأستخدام متغير توليفي(h_{ij}) ادى الى تقليل معدل الانحراف الى 1.5487%.

طبقت جميع قوانين الخلط السابقة على نظامين ثلاثيين وبأستخدام المتغيرات التوليفية التي أستعملت في الأنظمة الثنائية وكان معدل الانحراف كالأتي: (1) عند استخدام معادلة الحالة PRSV بدون اي متغير توليفي 18.0718%, (2) عند استخدام قانون الخلط conventional 6.0137%, (3) عند استخدام قانون الخلط quadratic 4.1003%,(4) عند استخدام قانون الخلط Adachi-Sugie 3.1728%, (5) عند استخدام تطوير Adachi-Sugie في هذا البحث 1.7701%, (6) عند استخدام Huron-Vidal method 11.6824%, (7) عند استخدام تطوير Huron-Vidal method في هذا البحث 3.8966%.

شكر و تقدير

ابدأ بشكر الله عز وجل الذي وفقني لإكمال مستلزمات هذا البحث. وإنا انهي بحثي لا يسعني واعترافا بالفضل آلا ان أتقدم بوافر الشكر والامتنان لكل من الأستاذ المشرف الدكتور محمود عمر عبد الله و الدكتورة ڤينوس مجيد حميد لإشرافهما على الرسالة و متابعتهما العلمية المستمرة للبحث وما ترتب على ذلك من توجيهات قيمة و أراء سديدة.

كما أتقدم بجزيل الشكر إلى رئيس قسم الهندسة الكيمياوية، و جميع أساتذة قسم الهندسة الكيمياوية, وأتقدم بشكري وامتناني إلى عمادة جامعة النهرين وأدعو من الله إن يوفقهم جميعا لخدمة المسيرة العلمية.

كما أتقدم بالشكر الجزيل إلى كافة العاملين في المكتبة المركزية بجامعة النهرين، وذلك لمساعدتهم لي في الحصول على بعض المصادر المستعملة في البحث.

وشكري الجزيل إلى جميع زملائي و زميلاتي الذين مدوا يد العون عند حاجتي إليها في البحث.

ولا أنسى إن أتقدم بجزيل الشكر والتقدير إلى من ساندني وساعدني على تخطي الصعوبات خلال فترة البحث إلى الذين لا مثيل لهم في الدنيا الى أبي وأمي الأعزاء، وزوجي العزيز وأختي واخي الاعزاء والشكر والامتنان الى الدكتور جمعه المياحي والدكتورة بلقيس محمد جواد على دعمهم ومساندتهم لي في تخطي هذه الصعوبات .

المهندسة فاطمه ضيف علي

دراسة الأرتباط وتنبؤ الحجم المولي الفائض بأستخدام معادلات الحالة المختلفة

رسالة
مقدمة إلى كلية الهندسة في جامعة النهرين
وهي جزء من متطلبات نيل درجة ماجستير علوم
في الهندسة الكيمياوية

من قبل

فاطمه ضيف علي
(بكالوريوس علوم في الهندسة الكيمياوية 2005)

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