Isobaric Vapor - Liquid Equilibria of Gasoline Additives Systems At 101.3 kPa

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Abstract

   In this study, isobaric vapor-liquid equilibrium of gasoline additives for three ternary systems: "*MTBE + Ethanol + 2-Methyl-2-propanol*", "*Ethanol + 2-Methyl-2-propanol + Octane*", and "*MTBE + Ethanol + Octane*" at 101.3 kPa are studied. Furthermore three binary systems: "*ethanol + 2-Methyl-2-propanol*", "*MTBE + Ethanol*", and "*MTBE + Octane*" at 101.3 kPa have been studied.

   The binary system "*MTBE + Ethanol*" forms minimum boiling azeotrope. The azeotrope data are $x_1(AZ) = 0.955$ mole fraction and $T(AZ) = 327.94$ K. The other ternary systems and the other binary systems do not form azeotrope.

   All the literature data used passed successfully the test for thermodynamic consistency using McDermott-Ellis test method.

   In this study the calculation of VLE K–values is done by using three methods, the first method uses modified Soave Redlich and Kwong (SRK), modified Peng and Robinson (PR) equations of state for two phases. The second method uses SRK-EOS for vapor phase with (NRTL, UNIQUAC and UNIFAC activity coefficient models) for liquid phase and using PR-EOS for vapor phase with (NRTL, UNIQUAC and UNIFAC activity coefficient models) for liquid phase. The third method uses the Wong- Sandler mixing rules and the PRSV- EOS based on GE of (NRTL and UNIQUAC activity coefficient models).

   The non ideality of both vapor and liquid phases for the literature data for the ternary and binary systems have been accounted for predicting VLE K-values using the *maximum likelihood principle* for parameter estimation which provides a mathematical and computational guarantee of global optimality in parameters estimation.

The Wong- Sandler mixing rules and the PRSV- EOS based on excess Gibbs free energy G^E of NRTL activity coefficient model give more accurate results for correlation and prediction of the K-values than other methods for the ternary and binary systems which contain asymmetric and polar compounds.

Keywords: VLE, Gasoline Additives, Equations of State, Activity Coefficient Model, Mixing Rule.

إتزان بخار - سائل تحت ضغط جوي ثابت لأنظمة مضافات الكازولين عند ضغط 101.3كيلو باسكال

الخلاصة

في هذا البحث تمت دراسة إتّزان بخار – سائل لمضافات الكازولين تحت ظروف ضغط جوي ثابت لثلاثة من الأنظمة الثلاثية وهي: "2-ميثوكسي-2-مثيل بروبان+ ايثانول+2-ميثل-2-بروبانول" ، "ايثانول+2-ميثوكسي-2-مثيل بروبان+ اوكتان" و" 2-ميثوكسي-2-مثيل بروبان+ ايثانول+ اوكتان" تم قياسهم في ضغط 101,3 كيلو باسكال .

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وثلاثة من الانظمة الثنائية وهي:" ايثانول+2-ميثل-2-بروبانول " ، " 2-ميثوكسي-2-مثيل بروبان+ ايثانول "و " 2-ميثوكسي-2-مثيل بروبان+ اوكتان" تم قياسهم في ضغط 101,3 كيلو باسكال. النظام الثنائي "2-ميثوكسي-2-مثيل بروبان+ ايثانول" يكون ظاهرة الإيزوتروب (minimum azeotrope) نقاط الايزوتروب هي (AZ)x_1=0.955 جزء مولي و   (AZ)T = 327.94 أما الانظمة الثلاثية والانظمة الثنائية الباقية لا تكون ظاهرة الإيزوتروب.

كل النقاط اجتازت بنجاح اختبار الدقة والصحة من الناحية الثرموديناميكية (thermodynamic consistency) باستخدام طريقة الاختبار لـــ (McDermott-Ellis method).

تمت في هذه الدراسة الحسابات لثابت الإتزان(K–values) لإتزان بخار – سائل (VLE) بواسطةثلاثة طرق: الطريقة الاولى بواسطة معادلة الحالة لـ (modified Soave Redlich and Kwong (SRK) المطورة و معادلة الحالة لـ (modified Peng and Robinson (PR) المطورة لكلا الطورين البخاري والسائل. الطريقة الثانية استخدمت معادلة الحالة لـ (modified Soave Redlich and Kwong (SRK) المطورة للطور البخاري مع نماذج معامل الفعالية لـ (NRTL,UNIQUAC and UNIFAC) للطور السائل ومعادلة الحالة لـ(modified Peng and Robinson (PR)) المطورة للطور البخاري مع نماذج معامل الفعالية لـ (NRTL,UNIQUAC and UNIFAC) للطور السائل. الطريقة الثالثة استخدمت معادلة الحالة PRSV مع قاعدة خلط جديدة لـ(Wong-Sandler) لكلا الطورين البخاري والسائل . قاعدة الخلط هذه اشتقت من معادلة Gibbs للطاقة الحرة الذي يعتمد على نموذجي معامل الفعالية لـ NRTL and UNIQUAC.

الخواص اللامثالية لكلي الطورين الـبخار والسـائل للأنظمة الثنائية و الثلاثية قد أخذت بالاعتبار للتنبؤ بثابت الإتزان (K–values) باستخدام طريقة (*maximum likelihood principle*) لتقدير افضل قيم للمعاملات وان هذه الطريقة تعطي ضمانة من الناحية الرياضية والحسابية لحساب افضل قيم للمعاملات.

الطريقة الثالثة التي تعتمد على قاعدة الخلط لـ (Wong-Sandler) ومعادلة الحالة لـ (PRSV) مبنية على معادلة الطاقة الحرة الزائدة (G^E) لمعادلة معامل الفعالية لـ (NRTL) أعطت نتائج اكثر دقة للتنبؤ بقيم ثابت (K-values) من الطرق الاخرى للانظمة الثلاثية والثنائية والتي تحتوي على مركبات لامتماثلة وقطبية.

استخدمنا في هذا البحث نظام النمل للامثليه لإيجاد حلول تقريبية لمسائل البرمجة الخطية كمــا استخدمنا نظريه الثنائية لمعرفه ما إذا كان الحل التقريبي المقترح هو الحل المثالي أيضا وان لم يكن فكم هو قريب من الحل المثالي ، تم مناقشه الفوائد المتوقعة لهذا الأسلوب في حل مســـائل البرمجة الخطية وتحديد نقاط الضعف كذلك وتم التركيز على الفوائد المتوقعة في جانب إجراء الحسابات المتوازية والامثليه الانيه ، من الجدير بالذكر هنا أيضا إن الأسلوب المقترح لايحتاج إلى أضافه متغيرات مصطنعه فقد كانت المتغيرات الفائضة كافيه لإيجاد الحل التقريبــي ممــا يعطي الأسلوب المقترح ميزه اضافيه بالنسبة لعدد المتغيرات التي يجب التعامل معها لإيجـــاد الحل.

Nomenclature

Abbreviations		
Abbreviation	*Meaning*	
AAD	Average Absolute Deviations.	
CEOS	Cubic equation of	
EOS	Equation of State.	
K-Value	Equilibrium Constant.	
Mean D %	Percentage of Mean Overall Deviation.	

State.

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NRTL	Non-Random Two Liquid activity coefficient model.	K_i	K-values or equilibrium constant of component i.
PR	Peng and Robinson equation of state.	M	Intensive property; $M = K\text{-}value$ or T.
PRSV	Stryjek and Vera modification of Peng and Robinson Equation of state.	n_i	Number of moles of component i.
		P	Equilibrium pressure of the system. MPa
SRK	Soave – Redlich and Kwong equation of State.	P_C	Critical Pressure. MPa
		P_i	Vapor pressure of pure component i. MPa
UNIFAC	UNIQUAC Functional Group Activity Coefficients Model.	P_i^s	Vapor pressure at saturation of component i . MPa
		S	Objective function.
UNIQUAC	Universal Quasi-Chemical activity coefficient model.	T	Temperature. K
		T_C	Critical temperature. K
VLE	Vapor – Liquid Equilibrium.	x_i	Mole fraction of component i in liquid phase.
WS	Wong and Sandler mixing rules.	y_i	Mole fraction of component i in vapor phase.

Symbols

Symbol	Meaning	Unit
A	Vapor pressure coefficient of Antoine equation.	
B	Vapor pressure coefficient of Antoine equation.	
C	Vapor pressure coefficient of Antoine equation.	
D	Local deviation.	
D_{cd}	Deviation of pair of points c and d.	
D_{max}	Local maximum Deviation.	
G^E	Excess Gibbs free energy model kJ / kmol	
k_{ij}	Binary interaction parameter for components i and j.	

Greek Litters

Symbol	Meaning
α	NRTL Parameter
γ	Activity coefficient
$\Im$	Poynting factor of equation (3.47)
σ	Standard deviation
σ^2	Estimated variance
Φ	Fugacity coefficient
ω	Acentric factor

Subscript

Symbol	Meaning
c	Critical property
cal.	Calculated value

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cd	Pair of points *c* and *d*
lit.	Literature value
i	Component *i* in the mixture
ij	Binary interaction between *i* and *j*
j	Component *j* in the mixture
max	Maximum value

Superscript

Symbol	*Meaning*
c	Calculated value
cal	Calculated value
E	Excess property
ig	Ideal gas
lit.	Literature value
L	Liquid phase
obs	Observed value
s	Saturation condition
VVapor phase	

Introduction

Ethers and alcohols used as gasoline additives have excellent antiknock properties and are environmentally acceptable substances. Gasoline blended with about 7-15 % 2-methoxy-2-methyl propane (MTBE) has been used for high-performance premium gasoline. On the other hand, recommendations for gasoline additives include not only pure MTBE but also mixtures with alcohols for high-octane gasoline [1].

The study of gasoline + alcohol and ether mixtures using the methods of physical-chemical analysis is considered at the present time as a difficult goal as gasoline is an extremely complex mixture of hydrocarbons of varying composition. Accordingly, a more

appropriate approach would seem to be to study model hydrocarbon + alcohol and ether mixtures composed of a small number of individual compounds [2].

The reasons for studying mixtures of hydrocarbons and oxygen-containing compounds relating to the use of oxygen-containing compounds in motor fuels [3].

For MTBE + ethanol, one set of isobaric VLE at 101.3 kPa is reported by Arce et al. [4]. VLE for the system MTBE + octane at 94 kPa has been measured by Wisniak et al. [5].

For the ethanol + 2-methyl-2-propanol system, one set of isobaric VLE data at 101.3 kPa is reported by Suska et al. [6] and one set of isothermal data at 313.15 K have been measured by Oracz [7].

In this research, isobaric the vapor-liquid equilibrium data found in literature for Three ternary systems: "*MTBE + Ethanol + 2-Methyl-2-propanol*", "*Ethanol + 2-Methyl-2-propanol + Octane*", and "*MTBE + Ethanol + Octane*" And three binary systems: "*Ethanol + 2-Methyl-2-propanol*", "*MTBE + Ethanol*", and "*MTBE + Octane*" were studied at 101.3 kPa.

The literature data were correlated using activity coefficient models for the liquid phase and equation of state (EOS) for the vapor phase and some time with the liquid phase too, and study their abilities to predict vapor-liquid equilibria *K-values* for binary and ternary systems accurately.

Many proposed activity coefficient models used to correlate the literature data for the liquid phase

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for binary and ternary systems. Among these models are Non-Random Two-Liquid (NRTL) model, the Universal quasi-chemical equations (UNIQUAC), and the Uniquac functional group activity coefficients (UNIFAC).

An important advance in the description of phase equilibria is to combine the strengths of both EOS and activity coefficient approaches by forcing the mixing rule of an EOS to behave with composition dependence like the G^E model. These are called G^E mixing rules and generally include the direct use of activity coefficient parameters fitted to VLE data[8].

System Selection:

Ethers and alcohols used as gasoline additives have excellent antiknock qualities and are considered environmental protection substances. Gasoline including 2-methoxy-2-methylpropane (MTBE) has been used for a high performance premium gasoline. In recent years, mixtures of ethers with alcohols have been considered for blending with gasoline to reduce carbon monoxide that is created during the burning of the fuel.

Binary Systems: Three binary systems are used in this study.
1- binary system(I) consists of *Ethanol + 2-methyl-2-propanol* [1]
2- binary system(II) consists of *MTBE + Ethanol* [9]
3- binary system(III) consists of *MTBE + Octane* [9]

Ternary Systems : Three ternary systems are used in this study:
1- ternary system(I) consists of *MTBE + Ethanol + 2-methyl-2-propanol* [1].

2- ternary system(II) consists of *Ethanol + 2-methyl-2-propanol + Octane* [1].
3- ternary system(III) consists of *MTBE + Ethanol + Octane* [9].

Thermodynamic Consistency Test:

One of the greatest arguments in favor of obtaining redundant data is the ability to assess the validity of the data by means of a thermodynamic consistency test. The consistency of the experimental data was examined to provide information on the thermodynamic plausibility or inconsistency and to recognize any deviations of the measured values.

According to McDermott-Ellis test method [10], two experimental points *a* and *b* are thermodynamically consistent if the following condition is fulfilled:

$$D < D_{max} \qquad \textbf{...(1)}$$

The local deviation D is given by

$$D = \sum_{i=1}^{N} (x_{ia} + x_{ib})(\ln g_{ib} - \ln g_{ia}) \textbf{ ...(2)}$$

In this method, it is recommended using of a fixed value of 0.01 for D_{max} [10], If the accuracy in the measurement of the vapor and the liquid mole fraction is within 0.001. The local maximum deviation, D_{max}, due to experimental errors, is not constant, and is given by

$$D_{max} = \sum_{i=1}^{N} (x_{ia} + x_{ib}) \left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}} \right) \Delta y$$

$$+ 2 \sum_{i=1}^{N} \left| \ln g_{ib} - \ln g_{ia} \right| \Delta x + \sum_{i=1}^{N} (x_{ia} + x_{ib}) \frac{\Delta P}{P}$$

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$$+ \sum_{i=1}^{N} (x_{ia} + x_{ib}) \left(\frac{1}{t_a} + \frac{1}{t_b} \right) \Delta t \qquad ...(3)$$

The conclusion can be drawn that all the data are thermodynamically consistent.

Improvement of Equation of State and Activity Coefficients Models:

The almost infinite number of possible mixtures and wide range of temperature and pressure encountered in process engineering are such that no single thermodynamic model is ever likely to be applicable in all cases. Consequently, knowledge and judgment are required to select the most appropriate methods by which to estimate the conditions under which two phases will be in equilibrium [11].

The first method was rigorously tested using two various mixing rules for vapor-liquid equilibria calculation [12]. The first mixing rules tested for the PR equation of state [13]. The second mixing rules tested are for the SRK equation of state [14].

The second method is obtained for properties of vapor liquid equilibria when fugacity of the component in the liquid phase is estimated from an activity coefficient mode.

The activity coefficients are correlated with the UNIQUAC model [15], UNIFAC model [16, 17] and NRTL model [18, 19]. The non random two liquid (NRTL) equation using the α term as either a fitting parameter or a fixed value. In the

case of the systems containing an alcohol with a hydrocarbon or an ether, it was acceptable to correlate using the fixed value of 0.47 as the α term [20].

The parameters in the equation were obtained by using maximum-likelihood principle method. The sum of squares of relative deviations in the activity coefficients was minimized during optimization of the parameters [21].

The third method for the vapor liquid equilibrium calculations with the Wong-Sandler mixing rules and the Peng-Robinson Stryjek-Vera PRSV-EOS based on excess Gibbs free energy G^E models [22, 23].

Discussion of Results

Phase Equilibrium Calculations (K-values)

The basic conditions for equilibrium between vapor and liquid phases in a system of n components, which are required, equality of temperature and pressure and the fugacity coefficient of both phases.

In terms of fugacity coefficient, these equations become

$$x_i \hat{\Phi}_i^L = y_i \hat{\Phi}_i^V \quad (i = 1, 2, \dots n)..(4)$$

Φ_i^L and Φ_i^V are liquid and vapor fugacity coefficients.

We have an equation of state from which we may calculate the fugacity coefficients of all components in both phases.

The activity coefficients g_i are calculated with the equation [11]

$$P y_i = g_i P_i^s x_i \qquad ...(5)$$

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In most cases it is preferable to calculate the activity coefficients by including fugacity coefficients and the Poynting factor correction.

In cases where it is preferable to obtain the fugacity of components in the liquid phase from an activity coefficient model, we write Eq.(4) as

$$x_i g_i \Phi_i^s P_i^s \Im_i = y_i \Phi_i^V P \qquad ...(6)$$

The state of the vapor and liquid phases in contact at a given temperature and pressure may be conveniently specified by the vaporization equilibrium ratio $K_i = y_i / x_i$. When the two phases are in thermodynamic equilibrium, Ki is given by

$$K_i = \frac{\Phi_i^L}{\Phi_i^V} \qquad ...(7)$$

Or, in term of an activity coefficient model instead of Φ_i^L, by

$$K_i = \frac{g_i \Phi_i^s P_i^s \Im_i}{\Phi_i^V P} \qquad ...(8)$$

The concept of ideality in vapor and liquid mixtures is often useful as a means of obtaining an initial approximation to the solution of VLE problem. For an ideal vapor mixture, all fugacity coefficients are unity, while for an ideal liquid mixture, all activity coefficients and poynting factors are unity. Eq.(6)then reduces to Raoult's law.

$$y_i P = x_i P_i^s \qquad ..(9)$$

Consequently, the total pressure in an isothermal ideal vapor-liquid system is a linear function of the mole fractions in the liquid phase; alternatively, the inverse of the total pressure is a linear function of the mole fraction in vapor phase.

All the required physical property data are available for MTBE to calculate these terms accurately [20]. The activity coefficients were therefore calculated on the assumption of an ideal vapor phase. The vapor pressures of the pure components, P_i^s, were obtained using the Antoine equation.

$$\ln P^s = A - \frac{B}{T + C} \qquad ...(10)$$

Values of the constants A, B and C which appear in this equation are shown in Table (B-1) in Appendix B [11, 24].

In order to test accurately the suitability of the G^E method [22, 23], the three binary and ternary systems that have been chosen encompassing compounds of a wide different molecular weights and mixtures of various types of non ideality (ideal, nearly ideal, highly not ideal) including polar mixture.

The predicted value for the equilibrium constants (K-values) are compared with the literature value and good agreement is obtained for all method used.

It appears from table (2) and table (3) that the calculated equilibrium K-values using the Wong- Sandler mixing rules and the PRSV EOS based on G^E models method gave the best results. Because this method is capable of accurate and consistent predictions of the equilibrium K-values it is applied

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applicability to mixture containing heavy hydrocarbons and polar substances as compared with the other method used in this research.

It appears from tables (B2-B15) in Appendix B that the calculated VLE is sensitive to the type of cubic EOS and activity coefficients models used and to the value of the adjustable parameters, particularly when the EOS are coupled with the modified mixing rules. In addition, it can be observed that the type of cubic EOS significantly changes the results when the number of parameter is increased.

With the effect of the number of adjustable parameters (two, three or more) on the VLE calculations, including mixtures with polar compounds as one component or systems containing dissimilar constituents, as more parameters are used the accuracy of calculated results is increased. It is evident that the more constants in an equation of state, the more flexibility in fitting experimental data but it is also clear that to obtain more constants, one requires more experimental information.

The literature and calculated data of VLE for the ethanol +2-methyl-2-propanol system is shown graphically in figures (1) and (2).

To measure the Azeotropic point, a method is introduced for graphical determination of the binary Azeotropic point on the basis of experimental binary vapor – liquid equilibrium data. Also, a method is evolved for determination of the binary and ternary Azeotropic points by using the extended Redlick – Kister equation applicable to the

condition of constant pressure [25]. The agreement between prediction and experimental data is good.

The MTBE + ethanol system forms minimum boiling azeotrope. The azeotrope data are $x_l(AZ)$ =0.955 mole fraction and T(AZ)=327.94K. The literature on VLE for the MTBE + Ethanol system is shown in Figures (3) and (4).

The tendency of a mixture to form an azeotrope depends on two factors [26]:

- The difference in the pure component boiling points.
- The degree of non ideality.

The closer the boiling points of the pure components and the less ideal mixture, the greater the likelihood of an azeotrope.

The literature and calculated VLE for the binary system MTBE +Octane is shown graphically in Figures (5) and (6).

The tie lines and isotherms based on the literature data for this ternary system (I) MTBE(1) +Ethanol(2) + 2-methyl-2-propanol(3) at 101.3KPa are shown in Figures (7) and (8) respectively. The system forms non azeotropic mixture.

The ternary system (II) of Ethanol (1) + 2-methyl-2-propanol (2) + Octane (3) at 101.3KPa are shown graphically in Figures (9) and (10) This system forms non azeotropic mixture.

The tie lines and isotherms based on data for the ternary system(III) MTBE (1) + Ethanol (2) + Octane (3) at 101.3KPa do not form azeotropic mixture shown in Figures (11) and (12).

Conclusions

Based on this study, the following conclusions can be made:

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1- All literature data are thermodynamically consistent because they passed the thermodynamic consistency test of McDermott-Ellis test method.

2- The success of correlating vapor-liquid equilibrium data using a cubic equation of state primarily depends on the mixing rule upon which the accuracy of predicting mixture properties relies An important advance in the description of phase equilibria is to combine the strengths of both EOS and activity coefficient approaches by forcing the mixing rule of an EOS to behave with composition dependence like the G^E model. These are called G^E mixing rules and generally include the direct use of activity coefficient parameters fitted to VLE data.

3- In dealing with VLE of asymmetric and polar compounds, the composition dependence mixing rules must be used rather the conventional mixing rule. The G^E method is appreciably good when applied to the most difficult case of polar mixture of highly different molecular weight.

4- The VLE calculation of K-values uses the *maximum likelihood principle* for parameter estimation which provides a mathematical and computational guarantee of global optimality in parameter estimation because all the measured variables are subject to errors.

5- The Wong- Sandler mixing rules and the PRSV EOS with G^E models method in this work gives more accurate results in

evaluating K-values than other methods for binary system and ternary system

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Table (1) Results of Thermodynamic Consistency Test.

System		D	D_{max}	Thermodynamic Consistency Test
Binary systems	Ethanol + 2-methyl-2-propanol	0.0271	0.029	Pass
	MTBE +Ethanol	0.0241	0.025	Pass
	MTBE + Octane	0.0159	0.020	Pass
Ternary systems	MTBE+Ethanol+2-methyl-2-propanol	0.0316	0.035	Pass
	Ethanol+2-methyl-2-propanol+Octane	0.0242	0.026	Pass
	MTBE+Ethanol+Octane	0.0197	0.021	Pass

Table (2) The overall error for three binary systems by comparison between literature K-values and those calculated by various methods.

BINARY SYSTEMS		
NO. of Data		71
K- value		Overall Error
(SRK) Φ^V and Φ^L	AAD	0.0426
	Mean D%	1.9696
(PR) Φ^V and Φ^L	AAD	0.0375
	Mean D%	1.8068
(SRK) Φ^V (NRTL) g^L	AAD	0.0341
	Mean D%	1.6390
(SRK) Φ^V (UNIQUAC) g^L	AAD	0.0903
	Mean D%	2.7895
(SRK) Φ^V (UNIFAC) g^L	AAD	0.1576
	Mean D%	3.6200
(PR) Φ^V (NRTL) g^L	AAD	0.0312
	Mean D%	1.1303
(PR) Φ^V (UNIQUAC) g^L	AAD	0.0609
	Mean D%	2.3464
(PR) Φ^V (UNIFAC) g^L	AAD	0.1179
	Mean D%	3.1120
WS and PRSV Based on UNIQUAC G^E	AAD	0.0269
	Mean D%	1.0155
WS and PRSV Based on NRTL G^E	AAD	0.0232
	Mean D%	0.8368

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Table (3) the overall error for three ternary systems by comparison between literature K values and those calculated by various methods.

| TERNARY SYSTEMS		
NO. of Data		298
K- value		Overall Error
(SRK) Φ^V and Φ^L	AAD	0.025
	Mean D%	2.629
(PR) Φ^V and Φ^L	AAD	0.021
	Mean D%	2.256
(SRK) Φ^V (NRTL) g^L	AAD	0.018
	Mean D%	1.921
(SRK) Φ^V (UNIQUAC) g^L	AAD	0.037
	Mean D%	3.703
(SRK) Φ^V (UNIFAC) g^L	AAD	0.048
	Mean D%	4.679
(PR) Φ^V (NRTL) g^L	AAD	0.016
	Mean D%	1.787
(PR) Φ^V (UNIQUAC) g^L	AAD	0.031
	Mean D%	3.037
(PR) Φ^V (UNIFAC) g^L	AAD	0.042
	Mean D%	4.254
WS and PRSV Based on UNIQUAC G^E	AAD	0.013
	Mean D%	1.565
WS and PRSV Based on NRTL G^E	AAD	0.011
	Mean D%	1.387
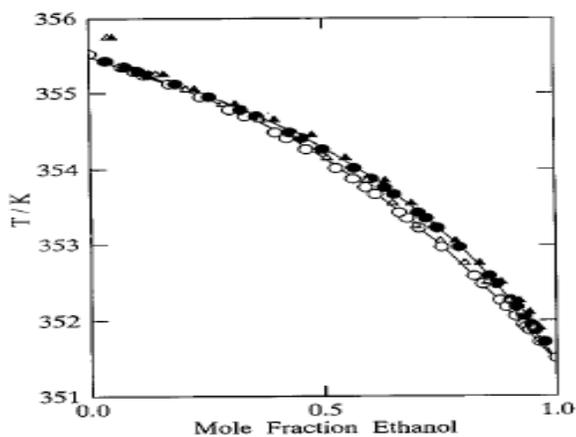
Figure (1) Temperature-composition diagram for ethanol (1) +2-methyl-2-propanol (2) at 101.3 kPa: O, x_1; ●, y_1. literature data [3] and △, x_1; ▲, y_1. -, PRSV-EOS with WS mixing rules and NRTL model.

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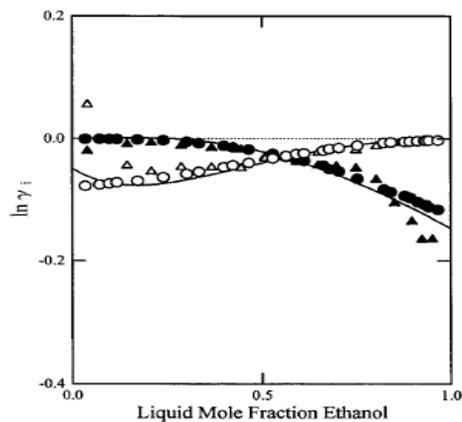of Gasoline Additives Systems At
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Figure (2) Activity coefficient-liquid composition diagram for ethanol (1) + 2-methyl-2-propanol (2) at 101.3 kPa.: O, lnγ_2; ●, lnγ_2. literature data [3], $\triangle$,lnγ_1; ▲,lnγ_2. -, NRTL model.
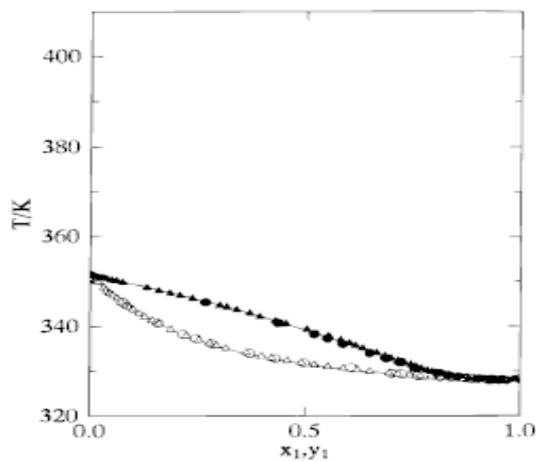

Figure (3) Temperature-composition diagram for MTBE (1) +ethanol (2) at 101.3 kPa: (O) x_1, (●) y_1 litreature data [9]; ($\triangle$) x_1, (▲) y_1, (-) PRSV-EOS and WS mixing rules and NRTL model.

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**Figure (4) Activity coefficient-liquid composition diagram for MTBE (1) +
ethanol (2) at 101.3 kPa: (O) ln γ_1,(●) ln γ_2 literature data [9]; ($\triangle$) ln γ_1, (▲)
ln γ_2, (-) NRTL model.**

**Figure (5) Temperature-composition diagram for MTBE (1) +octane (2) at
101.3 kPa: (O) x_1, (●) y_1; literature data [9] ;($\triangle$) x_1, (▲) y_1, (-) PRSV-EOS with
WS mixing rules and NRTL model.**

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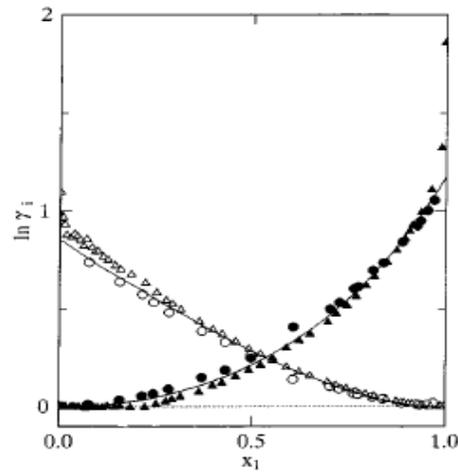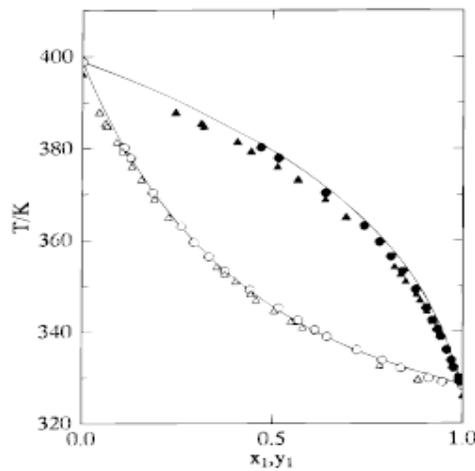of Gasoline Additives Systems At
101.3 Kpa

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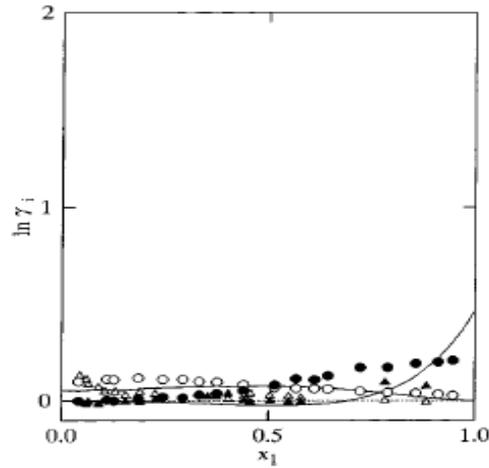**Figure (6) Activity coefficient-liquid composition diagram for MTBE (1) +
octane (2) at 101.3 kPa: (O) ln γ_1, (●)ln γ_2 literature data [9]; (Δ) ln γ_1, (▲) ln
γ_2, (-)NRTL model.**

**Figure (7) Tie lines for the ternary system MTBE (1) + ethanol(2) + 2-methyl-
2-propanol (3) at 101.3 kPa: (O), liquid composition;(Δ),vapor composition.**

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                                                 101.3 Kpa

Figure (8) Isotherms for the ternary system MTBE (1) + ethanol (2) + 2-methyl-2-propanol (3) at 101.3 kPa.

Figure (9) Tie lines for the ternary system ethanol (1) + 2-methyl-2-propanol (2) + octane (3) at 101.3 kPa:(O), liquid composition;(Δ), vapor composition.

**Figure (10) Isotherms for the ternary system ethanol (1) +2-methyl-2-propanol
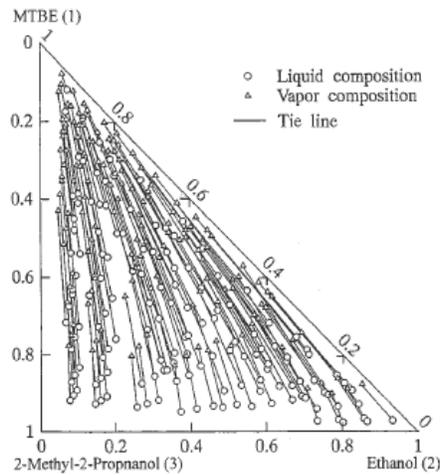(2) + octane (3) at 101.3 kPa.**

**Figure (11) Tie lines for the ternary system MTBE (1) + ethanol (2) + octane
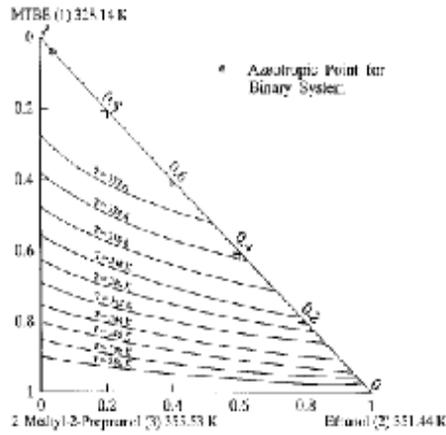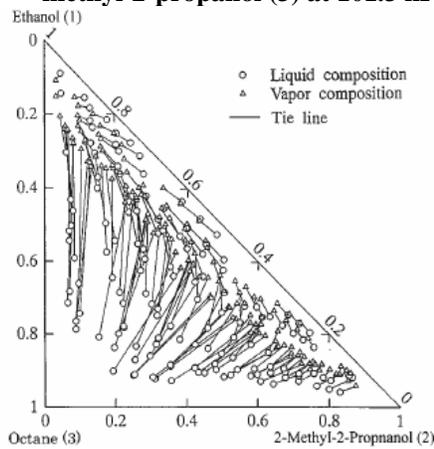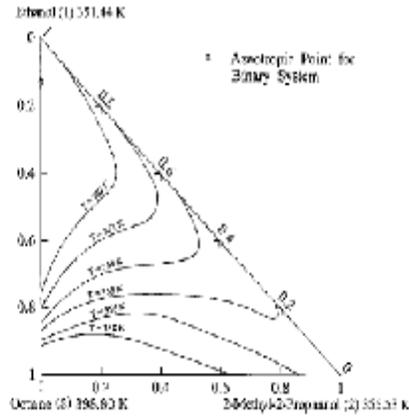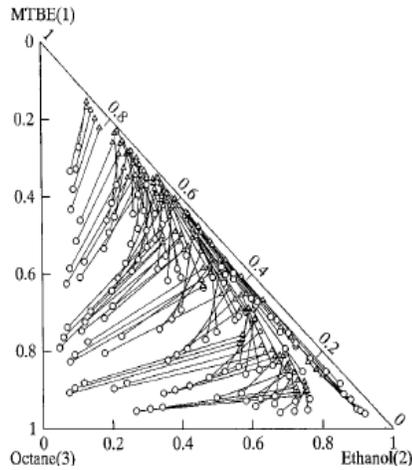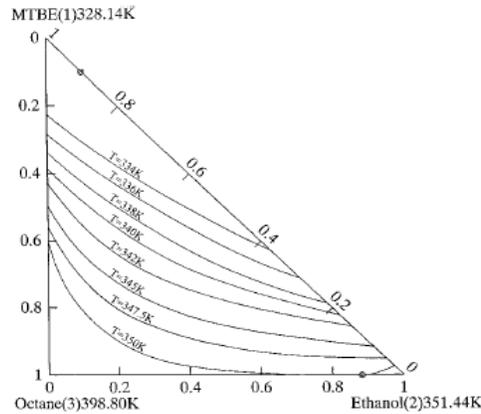(3) at 101.3 kPa: (O) liquid composition; (Δ) vapor composition.**

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Figure (12) Isotherms for the ternary system MTBE (1) + ethanol (2) + octane (3) at 101.3 kPa.

APPENDIX A
Parameters Estimation

Statistical Measurement and Analysis of Dispersion

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 various measurement of dispersion or variation are available, the most common being the *Mean Overall Deviation* and *Average Absolute Deviation.*

The *Mean Overall Deviation* "*mean D %*" is a more tangible element indicating the overall goodness of the fit of the data by the correlation and it reads [27]:

$$mean\ D\ \% = \frac{\sum_{i=1}^{n} \left| \frac{M_i^{exp.} - M_i^{calcd}}{M_i^{exp.}} \right|}{n} \times 100 \quad ...(\text{A-1})$$

And the *Average Absolute Deviation* "*AAD*" is given as

$$AAD = \frac{\sum_{i=1}^{n} \left| M_i^{exp.} - M_i^{calcd} \right|}{n} \quad ...(\text{A-2})$$

Where *M* is an intensive property and *n* is the number of data point [27].

These equations are used to calculate *Mean Overall Deviation* "*mean D%*" and *Average Absolute Deviation* "*AAD*" of literature results of binary and ternary systems.

Maximum-Likelihood Principle

The estimation of parameters in theoretical and semi-empirical mathematical models from experimental data is an important requirement in many fields of science and engineering. In the maximum-likelihood analysis, it is assumed that all measured data are subject to

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random errors. If each experiment were replicated, the average value for each replicated experimental point would approach some true value. Usually the distribution of a measured variable about its true value is approximated by the normal distribution, characterized by an associated variance. The variances are ideally obtained from replicated experiments, but they may be estimated from experience associated with a particular type of experimental apparatus. It is customary to assume that the random errors in different experiments are uncorrelated.

For each experiment, the true values of the measured variables are related by one or more constraints. Because the number of data points exceeds the number of parameters to be estimated, all constraint equations are not exactly satisfied for all experimental measurements. Exact agreement between theory and experiment is not achieved due to random and systematic errors in the data and to "lack of fit" of the model to the data. Optimum parameters and true values corresponding to the experimental measurements must be found by satisfaction of an appropriate statistical criterion.

If this criterion is based on the maximum-likelihood principle, it leads to those parameter values that make the experimental observations appear most likely when taken as a whole. The likelihood function is defined as the joint probability of the observed values of the variables for any set of true values of the variables, model parameters, and error variances. The best estimates of the model parameters and of the true

values of the measured variables are those which maximize this likelihood function with a normal distribution assumed for the experimental errors.

The parameter estimation algorithm based on the maximum likelihood principle, converges rapidly for almost any initial estimates of the parameters. The rapid convergence is due in part to the similarity to Gauss-Newton iteration method and in part to the successful application of a step-limiting procedure that assures superior convergence behavior [21].

The maximum likelihood principle method provides a mathematical and computational guarantee of global optimality in parameter estimation that provides the best fit to measured data. The objective function in nonlinear parameter estimation problems is given below:

$$S = \sum_{i=1}^{M} \left\{ \frac{\left(P_i^c - P_i^{lit}\right)^2}{\sigma_P^2} + \frac{\left(T_i^c - T_i^{lit}\right)^2}{\sigma_T^2} + \sum_{j=1}^{N} \frac{\left(x_{j_i}^c - x_{j_i}^{lit}\right)^2}{\sigma_x^2} + \frac{\left(y_{j_i}^c - y_{j_i}^{lit}\right)^2}{\sigma_y^2} \right\}$$

$$...(A-3)$$

Where the superscripts c and lit indicate calculated and literature values, respectively, the σ^2 are the estimated variances of the corresponding variables, and the sum is taken over all M literature data, and N is the number of compounds in the mixtures. The standard deviations assumed are:

$\sigma_P = 0.5$ mmHg
$\sigma_T = 0.1$ ^{o}C

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σ_x = 0.001 mole fraction
σ_y = 0.005 mole fraction

The assumed standard deviations had been based on the results of duplicated analyses of samples, and then this inconsistency could indicate either systematic error in the data or lack of fit of the model to the data. In this case, however, they are a priori estimates, and the results of the parameter estimation

procedure serve merely to provide best estimates of the standard deviations [21].

APPENDIX B
CALCULATED RESULTS

Table (B-1) Antoine equation constants of the components

Material	A	B	C
MTBE	6.120 19	1190.420	-39.040
Ethanol	7.242 22	1595.811	-46.702
2-methyl-2-propanol	6.352 72	1105.198	-101.256
Octane	6.043 94	1351.938	-64.030

Where:

$$\log P^s = A - \frac{B}{C+T}$$

, P^s in KPa, T in K [11, 24].   **...(B-1)**

Table (B-2): Physical properties of pure components [24].

Material	T_c,K	P_c,bar	V_c,cm3/mol	ω
MTBE	500.60	32.50	339.00	0.328
Ethanol	513.92	61.48	167.00	0.649
2-methyl-2-propanol	506.21	39.73	275.00	0.613
octane	568.70	24.90	492.00	0.399

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Table (B-3) m and *n* factors for SRK and PR equation of state

Compound	SRK – EOS		PR – EOS	
	m	*n*	*m*	*n*
MTBE	0.6207	0.2285	0.6671	0.4112
Ethanol	0.7446	0.3125	1.1505	0.8077
2-methyl-2-propanol	0.6943	0.6958	0.7939	0.5723
Octane	0.5563	0.2476	0.7563	0.3114

**Table (B-4) Optimized interaction parameters for binary systems for modify
PR-EOS &SRK-EOS.**

Binary system	No. of data point	Modify SRK – EOS		Modify PR – EOS			
		k_{12}	h_{12}	ka_{12}	ka_{21}	kb_{12}	kb_{21}
Ethanol + 2-methyl-2-propanol	30	0.0237	0.2132	-0.1431	-0.1040	-0.0512	-0.1598
MTBE + Ethanol	22	0.0175	0.1822	-0.2462	-0.1695	-0.0213	-0.0851
MTBE + Octane	19	0.1102	0.4252	-0.3116	-0.2201	-0.2456	-0.0268

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**Table (B-5) Optimized interaction parameters for ternary systems for modify
PR-EOS &SRK-EOS .**

Ternary systems		System (I) MTBE+Ethanol+2-methyl-2-propanol	System(II) Ethanol+2-methyl-2-propanol+Octane	System(III) MTBE+Ethanol+Octane
Modify SRK-EOS	k_{12}	0.0231	0.0143	0.0229
	k_{13}	0.1115	0.0153	0.1093
	k_{23}	0.0182	0.0175	0.0177
	h_{12}	0.2243	-0.2483	0.2157
	h_{13}	0.6076	-0.1573	0.5974
	h_{23}	0.1857	-0.1071	0.1955
Modify PR -EOS	ka_{12}	-0.1398	-0.3601	-0.1427
	ka_{21}	-0.1128	-0.2121	-0.1035
	ka_{13}	-0.3181	-0.2914	-0.3059
	ka_{31}	-0.2304	-0.1926	-0.2174
	ka_{23}	-0.2397	-0.1718	-0.2471
	ka_{32}	-0.1864	-0.2682	-0.1726
	kb_{12}	-0.0565	-0.0316	-0.0523
	kb_{21}	-0.1705	-0.2238	-0.1672
	kb_{13}	-0.2195	-0.5198	-0.2386
	kb_{31}	-0.0289	-0.1734	-0.0273
	kb_{23}	-0.0228	-0.2118	-0.0211
	kb_{32}	-0.0912	-0.0845	-0.0844
No. of data point		88	88	122

**Table(B-6): NRTL parameters (g_{ij} (J mol^{-1})) and (a_{ij}) for the binary systems at
101.3 kPa.**

BINARY SYSTEMS	g_{11}	g_{22}	g_{12}	a_{12}
Ethanol+2-methyl-2-propanol	1745.000	14.885	5465.000	0.290
MTBE+Ethanol	1188.000	961.639	5598.000	0.206
MTBE+Octane	1878.000	76.276	5401.000	0.261

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Table(B-7): NRTL parameters (g_{ij} (J mol^{-1})) and (a_{ij}) for the ternary systems at 101.3 kPa.

Ternary systems	g_{11}	g_{22}	g_{33}	g_{12}	g_{13}	g_{23}	α_{12}	α_{13}	α_{23}
MTBE+Ethanol+2-methyl-2-propanol	1076.000	810.669	1878.000	5607.000	8824.000	9699.000	0.462	0.412	0.401
Ethanol+2-methyl-2-propanol+Octane	1077.000	1117.000	4676.000	5547.000	7220.000	5026.000	0.367	0.332	0.345
MTBE+ethanol+Octane	776.118	189.003	3075.000	5604.000	7895.000	6176.000	0.466	0.402	0.336

Table(B-8): UNIQUAC parameters (u_{ij} (J.mol^{-1})) for the binary systems at 101.3KPa.

Binary systems	u_{11}	u_{22}	u_{12}	u_{21}
Ethanol+2-methyl-2-propanol	579.172	2249.000	2691.000	3481.000
MTBE+Ethanol	866.000	912.999	5477.000	2092.000
MTBE+Octane	1085.000	1143.000	5971.000	2738.000

Table(B-9): UNIQUAC parameters (u_{ij} (J.mol^{-1})) for the ternary systems at 101.3KPa.

Ternary systems	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
MTBE+Ethanol+2-methyl-2-propanol	897.569	1214.000	259.684	2842.000	1957.000	1480.000
Ethanol+2-methyl-2-propanol+Octane	1294.000	1741.000	4654.000	3571.000	1855.000	1423.000
MTBE+Ethanol+Octane	1718.000	1765.000	938.861	2632.000	2746.000	2167.000

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Table (B-10) The R_i and Q_i values for the UNIFAC groups and the r_i and q_i for the UNIQUAC compounds

UNIFAC model			UNIQUAC model		
Group	R_i	Q_i	*component*	r_i	q_i
CH_3	0.9011	0.848	MTBE	4.0678	3.632
CH_2	0.6744	0.540	Ethanol	2.5755	2.588
C	0.2195	0.000	2-methyl-2-propanol	3.9228	3.744
OH	1.0000	1.200	Octane	5.847	4.936
CH_3O	1.1450	1.088			

Table(B-11) UNIFAC Group-Group interaction parameters, a_{mn} in Kelvin

Group	CH_3 CH_2 C	OH	CH_3O
CH_3 CH_2 C	0.0	986.50	251.50
OH	156.40	0.00	28.06
CH_3O	83.36	237.70	0.00

Table (B-12): Adjustable parameters value when applying WS mixing rule with UNIQUAC model on PRSV-EOS to binary systems at101.3KPa

Binary Systems	No. of data	Temp.(K)	k_{ij}	C
Ethanol+2-methyl-2-propanol	30	351-356	0.375	-0.431
MTBE +ethanol	22	328-352	0.421	-0.501
MTBE +octane	19	328-399	0.256	-0.322

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**Table (B-13): Adjustable parameters value when applying WS mixing rule
with UNIQUAC model on PRSV-EOS to ternary systems at101.3KPa**

Ternary systems	No. of data	Temp.(K)	C	k_{12}	k_{13}	k_{23}
MTBE+ethanol+2-methyl-2-propanol	88	328-351	-0.411	0.455	0.467	0.301
Ethanol+2-methyl-2-propanol+octane	88	350-360	-0.624	0.333	0.587	0.516
MTBE+ethanol+octane	122	332-351	-0.650	0.394	0.369	0.521

**Table (B-14): Adjustable parameters value when applying WS mixing rule
with NRTL model on PRSV-EOS to binary systems at101.3KPa**

Binary Systems	No. of data	Temp.(K)	k_{ij}	C
Ethanol+2-methyl-2-propanol	30	351-356	0.364	-0.401
MTBE +ethanol	22	328-352	0.401	-0.498
MTBE +octane	19	328-399	0.259	-0.276

**Table (B-15) Adjustable parameters value when applying WS mixing rule
with NRTL model on PRSV-EOS to ternary systems at101.3KPa**

Ternary systems	No. of data	Temp.(K)	C	k_{12}	k_{13}	k_{23}
MTBE+ethanol+2-methyl-2-propanol	88	328-351	-0.476	0.479	0.505	0.301
Ethanol+2-methyl-2-propanol+octane	88	350-360	-0.562	0.301	0.622	0.570
MTBE+ethanol+octane	122	332-351	-0.651	0.479	0.248	0.622