

Investigation of Correlation and Prediction of Excess Molar Volume Using Different Equations of States

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Received on: 2/4/2012 & Accepted on: 11/6/2013

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 theoretical purpose. Soave RedlichKwong (SRK-EOS), Peng-Robinson (PR-EOS), and Peng-Robinson-Stryjek-Vera (PRSV-EOS) are selected. Five Mixing Rules are applied on different groups systems of different polarity which are: Conventional Mixing Rules, Quadratic Mixing Rules, Adachi and Sugie Mixing Rules, a modified Adachi and Sugie mixing rules. Another tried method to extend the applicability of CEOS by using the best applicable EOS from the three selected EOS with the PRSV-EOS with a new correlation method that uses Excess Gibbs free energy (G^E) and Huron-Vidal Method. Also by means of using Huron-Vidal Mixing Rules (HV), the Huron-Vidal Method is developed by using an adjustable parameter h_{ij} . The developed applied method gave very acceptable results for binary mixtures. To find the applicability of the gated constant for different group families; same constants of the binaries which confirm the ternary system are quite well applicable to calculate V^E data for ternary system with very reasonable accuracy.

Keywords: excess volume, equation of state, mixing rules

دراسة الارتباط و تنبؤ الحجم الفائض باستخدام معادلات الحالة المختلفة

الخلاصة

ان وجود قيم دقيقة للحجم الفائض لمزيج السوائل ضروري جدا في حساب التصميم الهندسية والصناعية المختلفة. في هذه الدراسة استعملت ثلاثة معادلات تكعيبية لغرض حساب الحجم الفائض وهي:

Soave RedlichKwong-EOS, Peng Robinson-EOS, Peng Robinson Stryjek Vera-EOS

ايضا" استخدمت خمس قوانين للخلط وهي:

Conventional, quadratic, Adachi-Sugie mixing rules وفي هذا البحث تم تطوير قانون الخلط لـ Adachi-Sugie باستخدام ثلاثة متغيرات توليفية L_{ij} , m_{ij} , h_{ij} . وقد تم الحصول على افضل النتائج مع معادلة الحالة التكعيبية PRSV-EOS وقد اعطت دقة عالية وتم استخدامها مع طريقة Huron-Vidal وهي طريقة لربط الثوابت a , b في معادلة الحالة عن طريق Gibbs

free energy. في هذا البحث تم تطوير طريقة بربط Huron-Vidal مع متغير توليفي h_{ij} وقد اعطت نتائج جيدة للانظمة الثنائية. وطبقت جميع قوانين الخلط على نظامين ثلاثيين باستخدام متغيرات توليفية التي استعملت في الانظمة الثنائية واعطت نتائج جيدة ودقيقة في حساب الحجم الفائق.

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].

Excess volume is 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 functions are zero.

$$= V - \dots (1)$$

Where V^{id} is the molar volume of an ideal solution?

Excess molar volume has been measured experimentally by using the vibrating-tube densimeter and the flow calorimeter device. Since it is difficult to get accurate measurements, researchers tried to find another suitable way. To calculate molar excess volume (V^E) by making a mathematical models, to fit experimental data. Those mathematical models may not be supported by any theoretical arguments. 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. Therefore, attention has been turned into modifying EOS and EOS-Mixing Rules [5].

Cubic Equation of State

Wide range of applicability of Equation of State in industrial operation conditions explains the rapid improvement of EOS. Recently, CEOS become very powerful in correlating and predicting phase equilibrium behavior for either non polar or/ and polar systems. Three types of CEOS were used to calculate V^E of binary mixture and these equations are (SRK) equation [12, 13], (PR) equation, and (PRSV) equation [14, 15] while the PRSV-EOS was used to calculate V^E for the ternary mixtures. In order to improve the accuracy of V^E results, mixing rules have to be modified by introducing one or more adjustable parameters, Table 1 indicates the overall absolute average percent deviation of using SRK, PR and PRSV are 32.0919, 20.6048 and 18.3203 respectively by using conventional mixing rules without any adjustable parameter i.e. ($k_{ij}=0$).

**Table (1) Percentage of average absolute deviations of excess molar
Volume by using different EOS, with $k_{ij}=0$.**

<i>System</i>	<i>Np.</i>	<i>SRK AAD%</i>	<i>PR AAD%</i>	<i>PRSV AAD%</i>
n-Heptane +n-Hexane ^[9]	23	1.2979	0.8555	0.5986
Methylcyclohexane +n- Hexane ^[8]	12	22.2803	16.1283	14.1354
Methylcyclohexane + n-Heptane ^[8]	13	22.4074	18.0327	16.4921
Cyclohexane +n-Hexane ^[8]	10	20.8733	14.8004	12.8980
Cyclohexane + n- Heptane ^[8]	10	25.4975	19.2928	17.7669
Methylcyclohexane+Cyclohexane ^[8]	11	22.8341	18.0201	15.6199
Ethanol+Acetonitrile ^[3]	12	38.9029	33.7668	30.0441
Aceton +Isopropanol ^[11]	9	39.5962	25.2413	21.7456
Aceton +Cyclohexane ^[11]	8	40.9559	23.6669	20.1580
Butylacetate +Benzene ^[7]	10	51.4665	36.2130	33.4363
Butylacetate + Bromobenzene ^[7]	10	43.2673	30.9373	28.7295
Butylacetate + Chlorobenzene ^[7]	10	49.5700	26.6494	24.2225
Butylacetate + Toluene ^[7]	10	59.2195	22.2179	20.0593
Ethylacetate + Benzene ^[7]	10	58.1057	28.6894	23.6356
Overall AAD%	158	32.0919	20.6048	18.3203

Mixing rules

Different forms of mixing rules were applied to binary and ternary mixtures. Investigation of the ability of these forms of mixing and combining rules to predict V^E data 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 applicability of success 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 [4]. These forms of mixing and combining rules are:

1. Conventional Mixing Rules
2. Quadratic Mixing Rules.
3. Adachi-Sugie (AS) Mixing Rules [2].
4. Modification of Adachi –Sugie(AS) Mixing Rules.
5. Huron and Vidal Mixing Rules [6].
6. Modification Huron and Vidal Mixing Rules.

EVALUATION OF EOS WITH DIFFERENT MIXING RULES

Four types of mixing rules are applied on SRK, PR, and PRSV-EOS to ensure the accuracies with different mixing rules in order to select the best one with its suitable mixing rules.

- a. SRK with conventional, quadratic, Adachi-Sugie and its modified mixing rules. Table (2) will show the results of applying these mixing rules.

Table (2) Application of conventional, quadratic, Adachi-Sugie and its modified mixing rules on SRK-EOS for binary systems.

<i>Systems</i>	<i>N_P</i>	<i>Conventional AAD%</i>	<i>Quadratic AAD%</i>	<i>(AS) AAD%</i>	<i>Modified (AS) AAD%</i>
Methylcyclohexane+n-Hexane ^[8]	12	5.0173	2.5896	2.0258	0.5451
Methylcyclohexane+n-Heptane ^[8]	13	6.8089	3.4037	2.8897	0.8894
Cyclohexane+n-Hexane ^[8]	10	6.2888	2.7675	2.3854	0.4870
Cyclohexane+n-Heptane ^[8]	10	4.8562	2.2256	1.9035	0.7055
Methylcyclohexane+Cyclohexane ^[8]	11	8.4432	4.8428	3.8645	2.2238
Ethanol+Acetonitrile ^[3]	12	11.8979	6.3305	4.0696	0.9886
Acetone+Isopropanol ^[11]	9	12.0946	7.6830	3.6997	1.4065
Acetone+Cyclohexane ^[11]	8	7.1855	4.2835	3.0124	0.9548
Butylacetate+Benzene ^[7]	10	7.6135	4.9728	4.8404	1.4614
Butylacetate+Bromobenzene ^[7]	10	15.2250	3.8267	3.0762	1.4535
Butylacetate+Chlorobenzene ^[7]	10	9.0925	4.9728	1.3768	3.5781
Butylacetate+Toluene ^[7]	10	14.6661	7.4528	4.1238	1.8287
Ethylacetate+Benzene ^[7]	10	8.8178	4.5405	3.5874	0.9936
Overall AAD%	135	9.0096	4.5594	3.1374	1.3318

b. PR with conventional, quadratic, Adachi-Sugie and its modified mixing rules. The results of application of these mixing rules are appeared in the following table

Table (3) Application of conventional, quadratic, Adachi-Sugie and its modified mixing rules on PR-EOS for binary systems.

<i>Systems</i>	<i>N_P</i>	<i>Conventional AAD%</i>	<i>Quadratic AAD%</i>	<i>(AS) AAD%</i>	<i>Modified (AS) AAD%</i>
Methylcyclohexane+n-Hexane ^[8]	12	1.9846	0.9652	0.9212	0.4359
Methylcyclohexane+n-Heptane ^[8]	13	4.4807	2.3370	2.2611	0.8529
Cyclohexane+n-Hexane ^[8]	10	3.2801	1.9596	1.6987	0.4536
Cyclohexane+n-Heptane ^[8]	10	6.5613	3.2356	2.1045	0.7650
Methylcyclohexane+Cyclohexane ^[8]	11	6.0123	3.5586	3.2262	1.9196
Ethanol+Acetonitrile ^[3]	12	6.3625	3.7895	2.6384	0.9161
Acetone+Isopropanol ^[11]	9	6.6837	4.2100	2.8026	1.3257
Acetone+Cyclohexane ^[11]	8	3.2095	2.7074	1.7388	0.9356
Butylacetate+Benzene ^[7]	10	7.0990	4.0817	3.3629	1.3862
Butylacetate+Bromobenzene ^[7]	10	3.6075	2.2464	1.9612	1.3231
Butylacetate+Chlorobenzene ^[7]	10	5.5148	2.8985	1.8983	0.7816
Butylacetate+Toluene ^[7]	10	2.3589	1.3841	1.4406	0.8965
Ethylacetate+Benzene ^[7]	10	2.7223	1.7117	1.4409	0.8211
Overall AAD%	135	4.6060	2.6759	2.1170	0.9786

C. PRSV EOS is applied with with different mixing rules which are conventional, quadratic, Adachi-Sugie and its modified mixing rules on PRSV-EOS for binary systems. The following table will shows the results when they applied.

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

<i>Systems</i>	N_P	<i>ConventionalA</i> <i>AD%</i>	<i>QuadraticA</i> <i>AD%</i>	<i>Adachi-</i> <i>Sugie</i> <i>(AS)</i> <i>AAD%</i>	<i>Modified</i> <i>AS AAD%</i>
Methylcyclohexne+n-Hexane ^[8]	12	1.6855	0.8450	0.8797	0.4687
Methylcyclohexne+n-Heptane ^[8]	13	3.9342	1.8643	1.5609	0.7963
Cyclohexane+n-Hexane ^[8]	10	1.9891	1.0691	0.9693	0.4043
Cyclohexane+n-Heptane ^[8]	10	3.1699	2.7958	1.9036	0.6933
Methylcyclohexne+Cyclohexane ^[8]	11	4.0408	3.0765	2.2981	1.3763
Ethanol+Acetontrile ^[3]	12	4.9417	2.5955	2.0142	0.8970
Acetone+Isopropanol ^[11]	9	4.9950	2.5563	1.6213	0.9308
Acetone+Cyclohexane ^[11]	8	2.3130	1.2328	0.9637	0.8374
Butylacetate+Benzene ^[7]	10	5.7667	3.3711	3.4109	1.1946
Butylacetate+Bromobenzene ^[7]	10	2.5454	1.8386	1.8518	1.0830
Buylacetate+Chlorobenzene ^[7]	10	4.0926	1.7886	1.1157	0.7284
Buylacetate+Tolune ^[7]	10	1.8167	1.5549	0.8636	0.6595
Ethylcetate+Benzene ^[7]	10	2.1650	1.3349	1.2588	0.8243
Overall AAD%	135	3.3630	1.9972	1.6020	0.8357

The results of Table(2, 3, and 4) proved that PRSV-EOS with modify AS mixing rules is the best. PRSV is the more applicable EOS to different binary systems with different polarities of different groups. But this result required three adjustable parameters. So, attention is turn on calculating V^E with less number of adjustable parameters.

HV- mixing rules is selected to correlate "a" and "b" parameters of EOS with G^E with and without adjustable parameter. HV is used with PRSV-EOS since it is the more accurate EOS. The results will be shown below in table 5:

**Table (5) Application of Huron-Vidal method on PRSV-EOS
for binary systems.**

<i>Systems</i>	<i>N_p</i>	<i>Without adjustable parameter AAD%</i>	<i>With adjustable parameter AAD%</i>
Methylcyclohexane + n- Hexane ^[8]	12	6.8744	0.6974
Methylcyclohexane + n-Heptane ^[8]	13	9.8120	1.9770
Cyclohexane + n-Hexane ^[8]	10	5.5196	0.9113
Cyclohexane + n- Heptane ^[8]	10	8.9580	0.9726
Methylcyclohexane + Cyclohexane ^[8]	11	8.7351	2.3636
Ethanol+Acetonitrile ^[3]	12	18.1226	2.4969
Aceton +Isopropanol ^[11]	9	12.9460	2.7298
Aceton +Cyclohexane ^[11]	8	17.7197	0.9495
Butylacetate +Benzene ^[7]	10	19.6862	2.3742
Butylacetate + Bromobenzene ^[7]	10	23.2031	1.5949
Butylacetate + Chlorobenzene ^[7]	10	13.6704	0.8857
Butylacetate + Toluene ^[7]	10	16.9654	0.7164
Ethylacetate + Benzene ^[7]	10	15.6589	1.4650
Overall AAD%	135	13.6593	1.5487

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 results 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 modification of Huron-Vidal method is used in this work the overall average percent deviations are reduced to 3.8966.

The results of using PRSV equations with this different type of mixing rules for ternary systems are shown in tables 6 and 7 respectively.

Table (6) Application of Conventional, Quadratic, Adachi-Sugie and its modified mixing rules on PRSV-EOS on ternary systems.

<i>Systems</i>	<i>N_P</i>	<i>Conventional AAD%</i>	<i>Quadratic AAD%</i>	<i>(AS) AAD%</i>	<i>Modified (AS) AAD%</i>
Methycyclohexane+Cyclohexane+n-Hexane ^[8]	10	5.5184	3.8255	2.7640	1.6188
Methycyclohexane+Cyclohexane+n-Heptane ^[8]	10	6.5090	4.3751	3.5817	1.9215
Overall AAD%	20	6.0137	4.1003	3.1728	1.7701

Table (7) Application of Huron-Vidal method for prediction of excess volume of ternary systems using PRSV-EOS.

<i>Systems</i>	<i>N_P</i>	<i>h_{ij}=0 AAD%</i>	<i>This work AAD%</i>
Methycyclohexane+Cyclohexane+n-Hexane ^[8]	10	10.5239	3.0397
Methycyclohexane+Cyclohexane+n-Heptane ^[8]	10	12.8409	4.7536
Overall AAD%	20	11.6824	3.8966

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 prevail 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.

V^E calculated by using EOS without any adjustable parameter the errors are 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 PRSV-EOS with $k_{ij}=0$ gives the more applicable with the most accurate EOS to calculate V^E between the three selected EOS. So, the attention was focused on modified EOS mixing and combining rules in order 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 binary interaction parameter (k_{ij}) is obtained from experimental data using Matlab optimization program prepared 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.

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 that 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 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. Also, 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. This phenomenon indicates 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 with k_{ij} which is 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 now is used depending on the required accuracy of the calculation and design purpose.

Quadratic Method

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 a percent deviation 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 has the following form:

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

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 improvements 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 [10].

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 cannot 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 was 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.

It is generally believed 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 Figure (1).

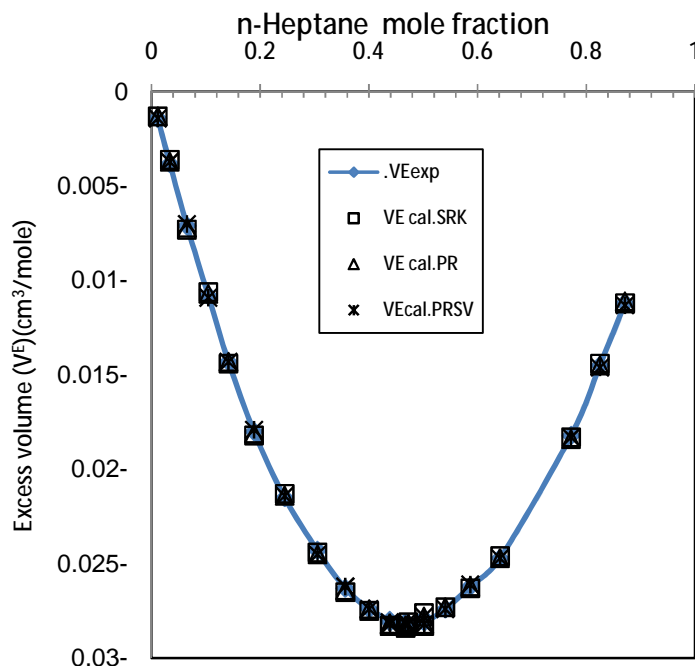


Figure (1) Excess volume of n-Heptane + n-Hexane system.

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 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 equilibrium at high pressure and temperature.

The connection of EOS with Gibbs free energy, allows EOS to become predictive tools. This method 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 are reduced to 1.5487.

Ternary System

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.

It is a fact that any successful correlation for prediction of V^E or other thermodynamic property must satisfy two points. The first point 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 the modification.

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% is 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% is 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 because those mixing rules suitable for various component families or groups (polar and non-polar). Table 8 shows the results of the overall absolute average deviations by using conventional and quadratic mixing rules.
4. The accuracy of correlating V^E is further increased when using Adachi and Sugie mixing rules as shown in the table 8. The result shows the large effect of any slight change in "a" parameter of CEOS. Also, table 8 shows that composition is a very important affecting factor in any adjusting that improve accuracy.
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 led to much further reduction the deviations and gave more accurate results. The AAD% is shown in table 8. 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} . Applying this modification for PRSV-EOS gave more accurate results than other equations of state since the effect of polarity of component is decreased for the selected type of CEOS which is originally derived for saturated hydrocarbons. These results are shown in table 8.

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 9 for two ternary systems. The results of table show this method is very predictive tools for V^E calculation of ternary systems without a need to do an experiment to get a ternary experimental V^E data.

Table (8) Summarized overall average absolute deviations for binary V^E data calculation.

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

Table (9) Summarized overall average absolute deviations for ternary V^E data calculation.

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

ABBREVIATION

AAD	Average Absolute Deviation
AS	Adachi-Sugie
CEOS	Cubic Equation of State
EOS	Equation of State
PR	Peng Robinson
RK	RedlichKwong
SRK	Soave RedlichKwong
V	Volume
HV	Huron-Vidal
h	covolume term adjustable parameter
k	Equation of state interaction parameter
m and L	Binary Adachi-Sugie interaction parameters

5. SUPERSSCRIPTS

E	Excess
id	Ideal solution

SUBSCRIPTS

i, j	Refer to component i and j in the mixture
cal	Calculated
id	Ideal solution

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