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PREDICTION OF PHYSICAL & THERMODYNAMICAL PROPERTIES FOR BINARY SYSTEMS USING EQUATION OF STATE

Karima M. Putrus
University of Technology
Chemical Engineering Department
*E-mail: Karima_Marogi@yahoo.com

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ABSTRACT:– A single equation of state (EOS) such as Soave – Redlich Kwong EOS can accurately describe both the liquid and vapour phase, therefore it is used for binary systems to predict some physical and thermodynamical properties. Two methods, which are Soave- Redlich Kwong and Generalized Compressibility Factor Correlation are compared and adopted for the cubic equation of state to calculate molar volume, density, viscosity, thermal conductivity, specific heat and compressibility factor.

In this paper a computer program is developed requiring critical properties to perform these calculations. The results are compared with some available literature data, and we find that the computer programs are shown to be adequately reliable for this purpose, with deviation in some properties equal to (3.6%) as other predictive programs and procedures. Also from this comparison we notice that the Generalized Compressibility Factor Correlation method is better and more general than the Soave- Redlich Kwong.

Keywords: equation of state; prediction of physical & thermodynamic properties; binary mixtures.

INTRODUCTION

The process of obtaining accurate value for the physical and thermodynamical properties for hydrocarbon is most important in all the different chemical industries, especially for non-ideal multicomponent systems and those for which no experimental values are available.

There are two traditional classes of thermodynamic models for phase equilibrium calculations: one is liquid activity coefficient and the other is equation-of-state models. Activity coefficient models can be used to describe mixtures of any complexity, but only as a liquid well below its critical temperature. Any mathematical relation between volume, pressure, temperature, and composition is called the equation of state. Many equations of state have been proposed, but most all of them are essentially empirical in nature.

The viral equation is appropriate only for the description of properties of gases at low to moderate densities. The viral equations of state are polynomials in density. The simplest useful polynomial equation of state is cubic, for such an expression is capable of yielding the ideal gas equation as volume goes to infinite and of representing both liquid-like and vapor-like molar volumes at low temperatures(1).

A cubic equation of state (CEOS) usually contains 2 or 3 parameters. These parameters in the CEOS are constrained to satisfy the critical point conditions. As a result, the cubic equations of state provide an exact duplication of the critical temperature and critical pressure which is the end point of the vapor pressure curve. These constraints also layout a foundation for the alpha (α) function (2, 3).

Peng & Robinson proposed another two- constant equation of state which had been used for predicting the vapor pressure and volumetric behavior of single component systems. The phase behavior and volumetric behavior of binary, ternary and multicomponent systems were also given. The proposed equation combined simplicity and accuracy (4).

A modification at Peng–Robinson equation of state was proposed by Heyen (5), where a third parameter added to reproduce experimental critical compressibility factor and excluded volume was made temperature dependent to match predicted saturation liquid volume.

All the forgoing equations of state are empirical or at best semi-theoretical, the viral equation of state has a theoretical basis from statistical mechanics, but the form of an infinite power series of volume is not convenient for practical use (6).

A great number of cubic equations were proposed for better representation of the phase equilibria and/or the volumetric properties of fluids. Most of them aimed at the improvement in liquid volumes, such as the equations developed by Trebble and Bishnoi (7).

The cubic EOS's can be formulated to predict phase equilibria, but they are normally poor in yielding correct volumes. The complex EOS's in general have many terms including viral terms and the terms based on certain assumption of molecular shape, size, and electric charges, such as the EOS's of Anderko and Pitzer (8).

Marc Assael, Marten Truselr and Thomas Tsolakis state these properties in their book "Thermo Physical Properties of Fluids" (9).

Nasrifar and Moshfeghian put forward a new two-term, cubic equation (NM), whose co-volume b has a linear dependence on temperature. Compared with RKS and PR in the range from about Tr=0.5 to 0.98, this equation is slightly better in vapor pressures and remarkably better in saturated liquid volumes (10).

Sun reported a new totally inclusive cubic equation, which has better performance in saturated liquid volumes, but no obvious advantage over RKS or PR in vapor pressures (11).

Equations of state (EOS) formulate the relationship between the pressures (P), temperatures (T), volumes (V) and compositions (x) of components, offering a theoretically strict way to calculate various thermodynamic properties, such as phase equilibrium and PVTx properties, which are important in a wide range of geochemical applications (12).

Recently, there is a software allows the prediction of multicomponent vapor-liquid equilibria (VLE), vapor-liquid-liquid equilibria (VLLE) and gas solubility (GLE) with the group contribution equation of state models PSRK (Predictive Soave-Redlich-Kwong) and VTPR Volume-Translated Peng-Robinson). The program Predictive EOS allows to specify the components of the desired system, to enter necessary data like compositions and temperatures and pressures and it will display the result in tables and plots. The results can be copied to the Windows clipboard, saved and printed (13).

Techniques are available for prediction of most physical properties with sufficient accuracy for use in process and equipment design. The criterion used for selecting a particular method is to choose the most easily used simplest, method that had sufficient accuracy for general use by Reid et al. (14).

Group contribution techniques (15); which are based on the concept that a particular physical property of compound can be considered to be made up of contributions from the constituent atoms, groups and boards, the contributions being determined from experimental data. Also useful, and convenient, are the prediction methods based on the use of reduced conditions: temperature, pressure and volume providing values for the critical constants are available.

Bazmi, Ghanbari, and Alaei, (16) presents vapour-liquid equilibrium calculations for a binary system, which is based on a computer program. For this purpose Patel and Teja equation of state has been used for the measurement of equilibrium data, which has high efficiency for polar systems. By using this program, various equilibrium datum such as bubble and dew point temperature/ pressure, flash calculations, and equilibrium coefficient (k value) could been calculated.

Therefore, the aim of the present work is to predict the physical and thermodynamical properties of binary system using the equation of state requiring critical properties and a centric factor

THEORTICAL COMPUTATION OF PROPERTIES

Cubic Equation of State

Equation of state was applied to calculate the compressibility factor by using the following methods:

A. Soave- Redlich Kwong

TheSoave- Redlich Kwong equation may be written in the following form(3):

$P = (R * T / (V – b)) – (a / V (V + b)$ (1)

Where:

$a = 0.42747 * \alpha (T) * (R * Tc)^2 / Pc$ (2)

$b = 0.0866 * R * Tc / Pc$ (3)

$\alpha(T) = (1 + m * (1 – Tr^{0.5})^2$ (4)

$m = 0.48 + 1.574 * \omega - 0.176 * \omega^2$ (5)

Replacing V in Equation (1) with (Z* R * T / P) gives:

$Z^3 – Z^2 + (A – B – B^2) Z – A * B = 0$ (6)

The general form of Cubic Equation is:

$C_3 * Z^3 – C_2 * Z^2 + C_1 * Z – C_0 = 0$ (7)

Where:

$C_3 = 1 \quad C_2 = -1 \quad C_1 = A – B – B^2 \quad C_0 = - A * B$

$A = a * P / (R * T) 2$ (8-A)

$B = b * P / R * T$ (8-B)

$V= Z * R * T / P$ (9)

B. Generalized Compressibility Factor Correlation

The simplest form of the viral Equation may be written (17):

$Z = 1 + B * P /R * T = 1+ (B * Pc / R *Tc) Pr /Tr$ (10)

Thus, Anderko and Pitzer, (8) proposed a second correlation, which expresses the quantity (B * Pc/ R*Tc) as:

$(B * Pc / R *Tc) = B_o + \omega * B'$ (11)

Combination of equation (9) and (10) gives:

$$Z = 1 + [B_0 + \omega' B'] \frac{\Pr}{Tr} \qquad (12)$$

Second viral coefficients are functions of temperature only and similarity B_o & B_1 functions of reduced temperature only. They are well represented by the following simple equation.

$B_o = 0.083 – 0.422/ Tr^{1.6}$ (13-A)

$B' = 0.139 - 0.172 / Tr^{4.2}$ (13-B)

$V= Z * R * T / P$ (14)

Mixing Rule for Cubic Equation

In general equation of state is developed first for pure substance then extended to mixtures through the use of mixing rule for combining the pure component parameters.

For Soave Redilch Kwong equation(20):

$a = \Sigma_i \Sigma_J x_I x_J (a_I a_J)^{0.5} (1- k_{iJ})$ (15)

$b = \Sigma_i x_i b_i$ (16)

$a_I = 0.42747 * \alpha(T) * (R * Tci)^2 / Pci$ (17)

$\alpha(T) = (1 + mi * (1 - Tri^{0.5})^2$ (18)

$mi = 0.48 + 1.574 * \omega_i - 0.176 * \omega_i^2$ (19)

$bi = 0.0866 * R * Tci / Pci$ (20)

Where Kij = binary interaction coefficient. This binary interaction coefficient for all hydrocarbon-hydrocarbon equal to zero and in the range (0 – 0.15) for others.

For Generalized Compressibility Factor correlation (19):

$Tc' = \Sigma_i Tci * x_i$ (21)

$Pc' = \Sigma_i Pci * x_i$ (22)

$Pr = P/Pc'$ (23)

$Tr = T/Tc'$ (24)

$\omega' = \Sigma_i \omega_i x_i$ (25)

$Z= 1+ (B_0 + \omega' B') Pr'/Tr'$ (26)

Properties

Saturated liquid properties and binary mixture at any temperature based on the following correlation (15, 18):

$\rho_L = A * B^{-(1-Tr)^{2/7}}$ (35)

$$\rho_m = \frac{1}{\sum_{i=1}^{N} (\frac{x_i}{\rho_{Li}})} \quad (36)$$

$\text{Log}\ \mu_L = A + B / T + C * T + D * T^2$ (37)

$$\mu_m = \frac{1}{\sum_{i=1}^{N} (\frac{w_i}{\mu_{Li}})} \quad (38)$$

$K_L = A + B * T + C * T^2$ (39)

$$K_m = \sum K_i w_i \quad (40)$$

$p = A + B * T + C * T^2 + D * T$ (41)

$$Cp_m = \sum x_i Cp_i \quad (42)$$

COMPUTER PROGRAM

The program implement by using Visual basic version 6.0 because it is a good language, modern, easy in used, & it has plenty of futures that make it the most recommended language at this time . The Program makes you to calculate each of properties as a lone. It calculates the Compressibility Factor (Z) and Molar volume depending on two methods:

A – Soave-Redlich Kwong**.**
B – Generalized Compressibility Factor Correlation.

Where in this part of the program, it is required temperature, pressure & mole fractions for each compounds, also it is required critical temperature & pressure, centric factor and molecular weight which be given for some compounds in appendix (E).

In Soave-Redlich Kwong method, the equation of Compressibility Factor (Z) is third order, so we used Newton Raphson method to solve equation of (Z). It may be derived from Taylor series expansion of f(x) =0 around x_0, the first estimation of x.

$$F(x) = f(x_0) + (x - x_0)\, f'(x_0) + 0.5*(x - x_0)^2\, f''(x_0) + (1/6)\,(x - x_0)^3 f'''(x_0) \qquad (43)$$

RESULT AND DISSCUSION

The computer program is used to calculate the compressibility factor, molar volume, density, viscosity, thermal conductivity, & specific heat. The equation of state used to predict the compressibility factor, molar volume for mixtures that contain compounds below their critical point, utilizing *Soave- Redlich Kwong & Generalized Compressibility Correlation equations*. They included two binary systems composed of light hydrocarbon. The experimental physical properties for each component in the mixture were obtained from Carl Yaws (18) for pure components.

The results are listed in Tables (1-4) while Table (5) represents the critical properties, a centric factor and molecular weight for some compounds. The relationships are plotted for those results and shown in Figures (1-12) for Methane – Ethane & Ethylene – Propylene system. The calculations of compressibility factor & molar volume are performed using Soave- Redlich Kwong at different temperature, with zero interaction (k_{ij}), because interaction coefficient for hydrocarbon - hydrocarbon systems equal to zero.

A comparison for calculations from two methods (Soave-Redlich Kwong and Generalized Compressibility Correlation) is made by computing the overall Average Absolute Deviation (AAD) which obtained by:

$$AAD\,\% = 1/N\ \{\Sigma_{I=1}\,(\ A_I - B_I\,|\,/\,B_{I})\ *100\%\} \qquad (44)$$

The (AAD) ratio of compressibility factor for Methane – Ethane system =3.72 %, and AAD for molar volume for same system = 3.11% when the temperature range (200 – 500) K. The (AAD) ratio of compressibility factor for Ethylene – Propylene system =3.4%, and AAD for molar volume for same system =3.34%, when the temperature range (300 – 700) K. See for this purpose Tables (1 to 56) for Ethylene – Propylene system and Tables (7 to 12) for Methane – Ethane system. Plots of those results are shown in Figures (1 to 6) & (7 to 12) respectively.

In Methane – Ethane system the minimum Absolute Deviation for Compressibility factor = 1.3%, and maximum Absolute Deviation = 8.2%, while the Molar volume for same system, the minimum Absolute Deviation = 1.44%, and maximum Absolute Deviation = 6.37%. In Ethylene – Propylene system the minimum Absolute Deviation for Compressibility factor = 1.63%, and maximum AAD =7.1%, and Molar volume for same system, the minimum Absolute Deviation = 1.5%, and maximum Absolute Deviation = 6.01%.

One of notes should be taken is that when the temperature increase, the AAD ratio will decrease at constant low pressure. The other note is the difference of (ADD) among mixtures, because the Generalized Compressibility Correlation method is better and more general than the Soave- Redlich Kwong. The same conclusion was given by Dr. Binous (22) who, has also performed with his student, similar computations using Matlab. The result agrees with the experimental work of Carl Yaws (18) as shown in Tables (1 to 4). The critical properties (Tc, Pc) and a centric factor were taken from literature (21).

CONCLUSIONS

1. The benefit of the use of computer in prediction of physical & thermodynamical properties can be listed as follows:
   A – Minimize the prediction time.
   B – Maximize the reliability and flexibility.
2. In this work, Visual Basic 6.0 technique is used in which the capabilities of modern personal computers appear clearly and the implementation is faster.
3. Generalized Compressibility Correlation method is better and more general than the Soave-Redlich Kwong.

NOMENCLATURE

a,b - Parameters of Soave- Redilch Kwong & Generalized Correlation
A,B - Dimensionless Parameters
A,B,C,D - correlation constants in equation (41)
AAD - Average Absolute Deviation
C0,C1,C2,C3 - coefficients of cubic Equation of state
k_{ij} - interaction coefficient
K - Thermal conductivity, (watt/m. °C)
Mw - molecular weight
μ - Viscosity, (centipoises)
ρ - Density, (g/cm^3)
Cp - Specific heat, (cal/g.K)
P - Total Pressure, (bar)
Pc - Critical Pressure, (bar)
Pr - Reduced Pressure
R - Gases constant ((kJ/kmol K)
T - Temperature, (K)
Tc - Critical Temperature, (K)
Tr - Reduced Temperature
V - Volume, (m^3)
V_m - Molar Volume, (m^3/kmol)
ω - a centric factor
w_1, w_2 - mass fraction of compounds
x_1, x_2 - mole fractions for the components
Z - Compressibility factor

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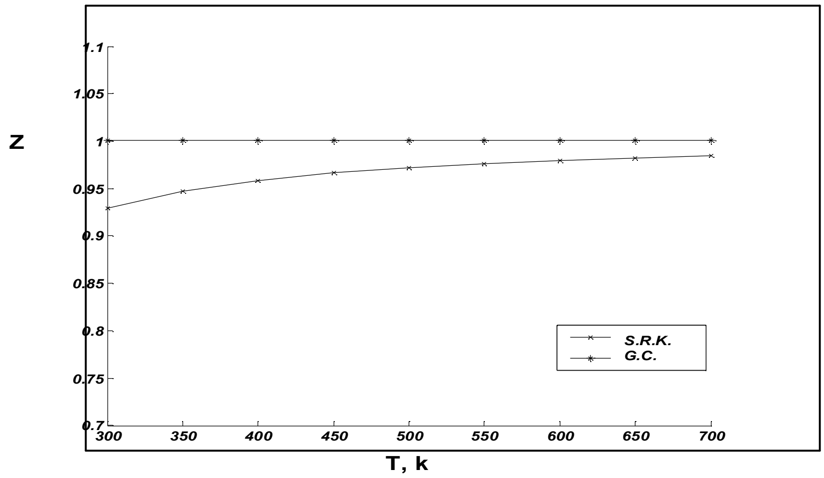

Fig.(1): Calculated COMPRESSIBILITY FACTOR for the system Ethylene - Propylene by S.R.K. & G.C. methods at 1 atm.

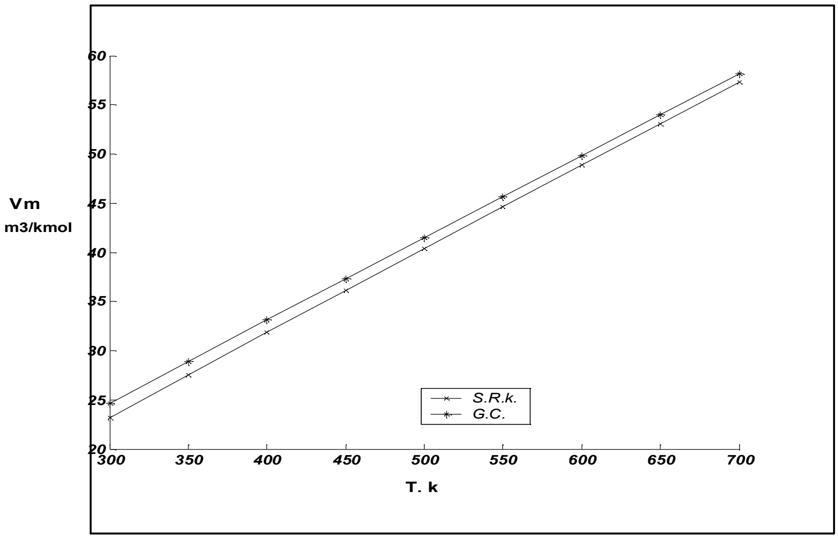

Fig.(2): Calculated MOLAR VOLUME for the system *Ethylene - Propylene* by S.R.K. & G.C. methods at 1 atm.

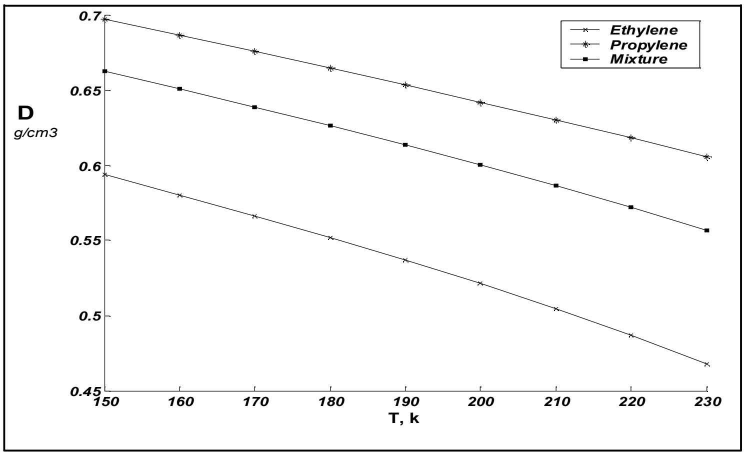

Fig.(3): Calculated THE DENSITY for the system *Ethylene - Propylene* at 1 atm.

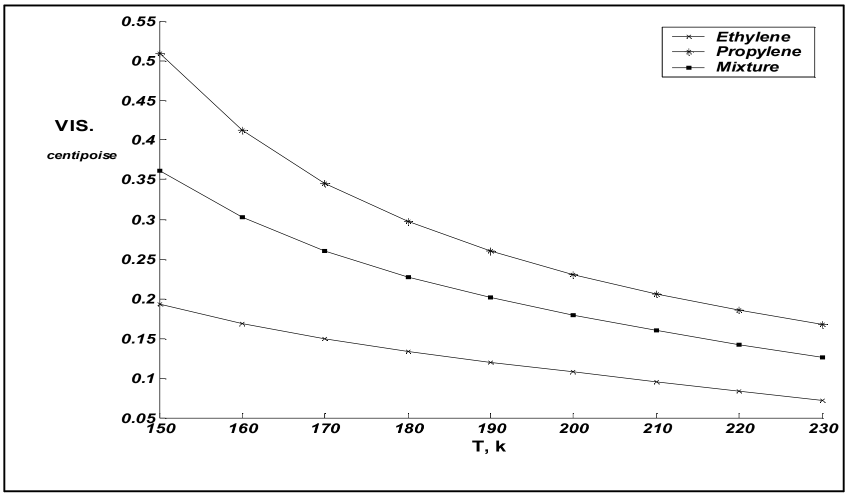

Fig.(4): Calculated THE VISCOSITY for the system *Ethylene* - *Propylene* at 1 atm.

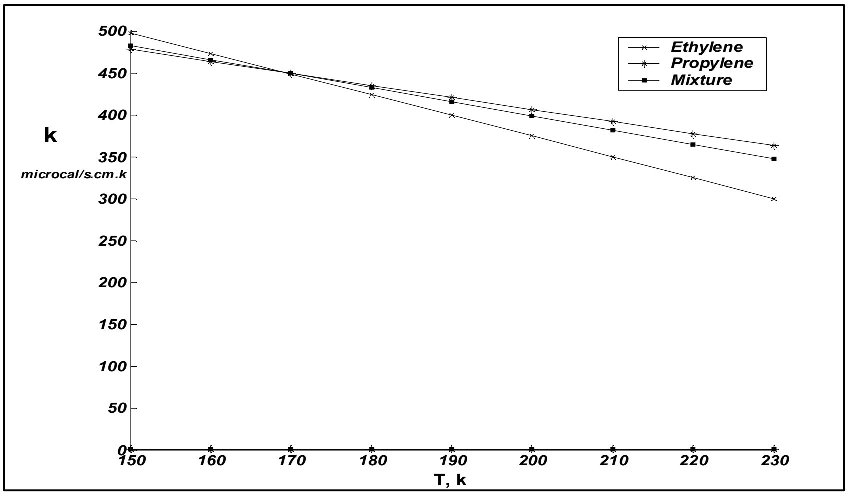

Fig.(5): Calculated THERMAL CONDUTIVITY for the system *Ethylene* - *Propylene* at 1 atm.

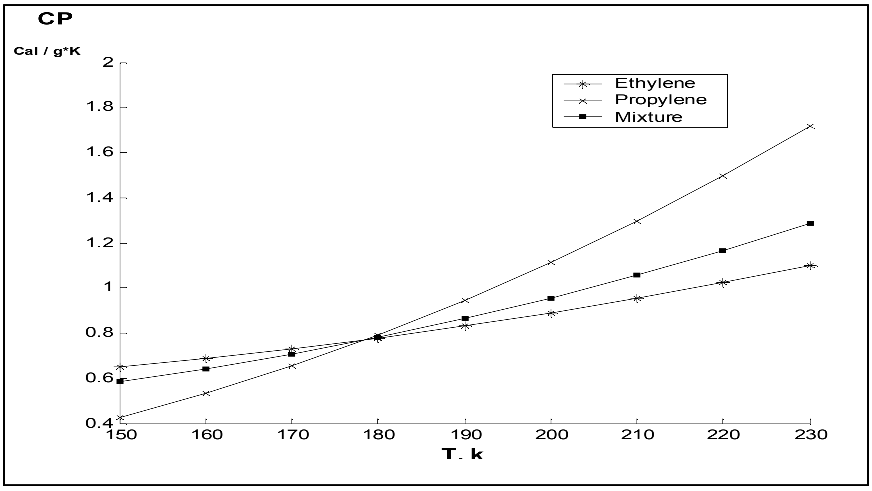

Fig.(6): Calculated SPESFIC HEAT for the system *Ethylene* - *Propylene* at 1 atm.

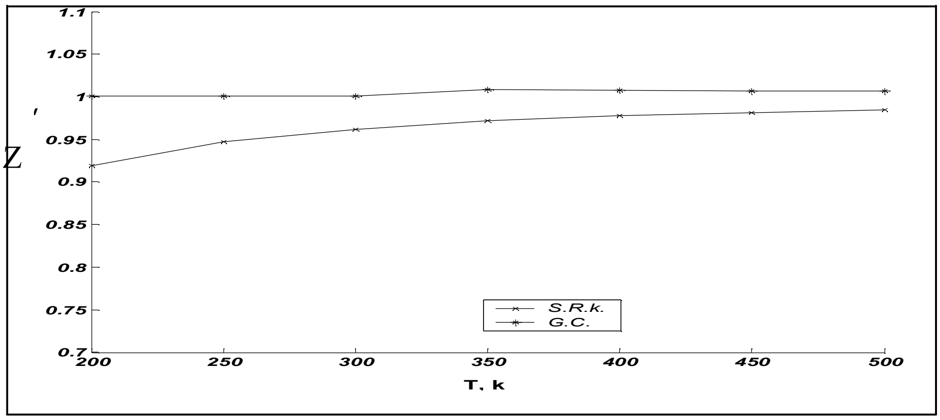

Fig.(7): Calculated COMPRESSIBILITY FACTOR for the system *Methane – Ethane* by S.R.K. & G.C. methods at 1 atm.

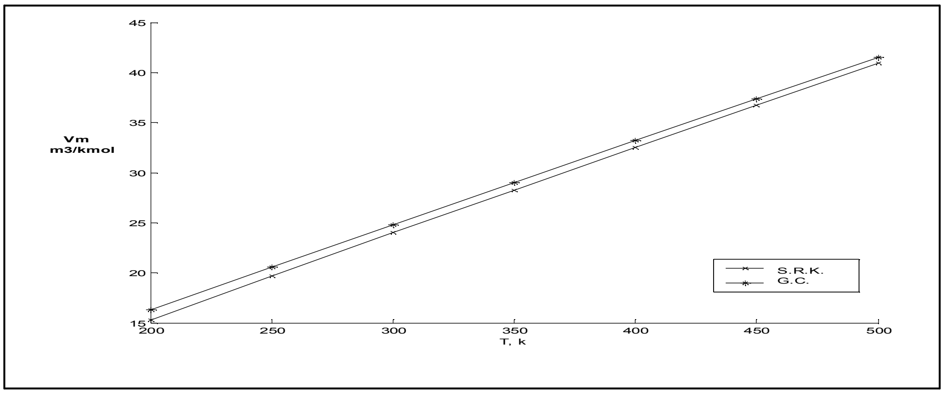

Fig.(8): Calculated MOLAR VOLUME FOR the system *Methane – Ethane* by S.R.K. & G.C. methods at 1 atm.

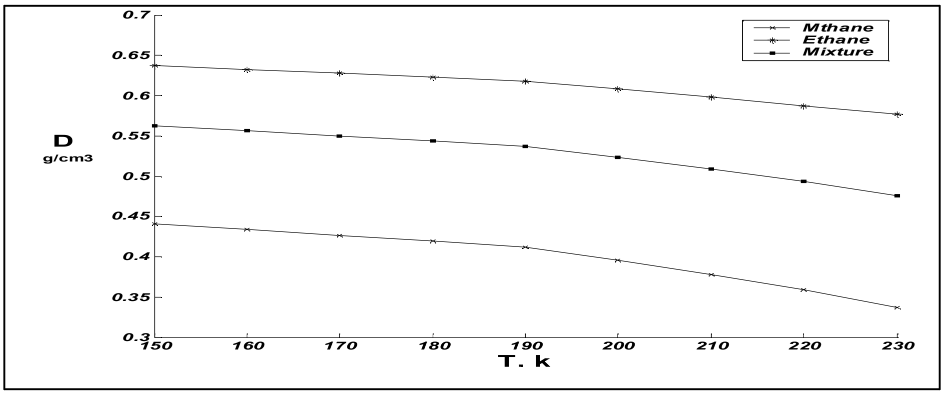

Fig.(9): Calculated THE DENSITY for the system *Methane – Ethane* at 1 atm.

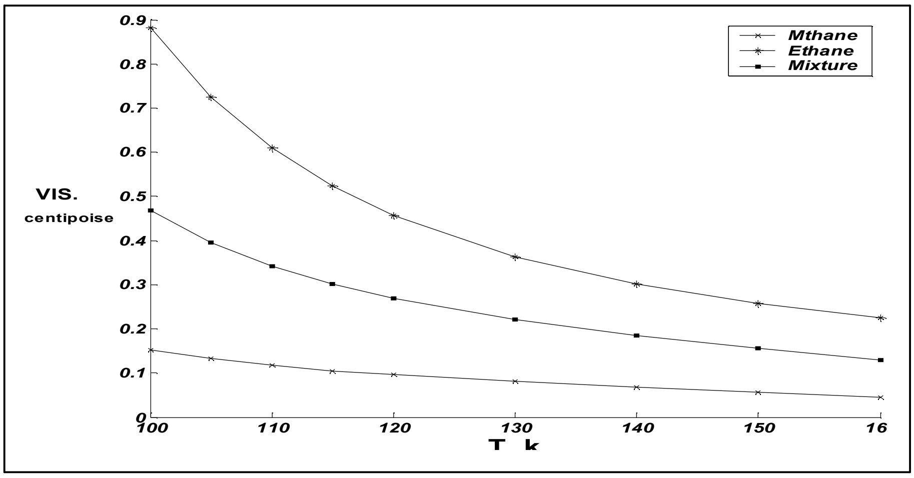

Fig.(10): Calculated THE VISCOSITY for the system *Methane – Ethane* at 1 atm.

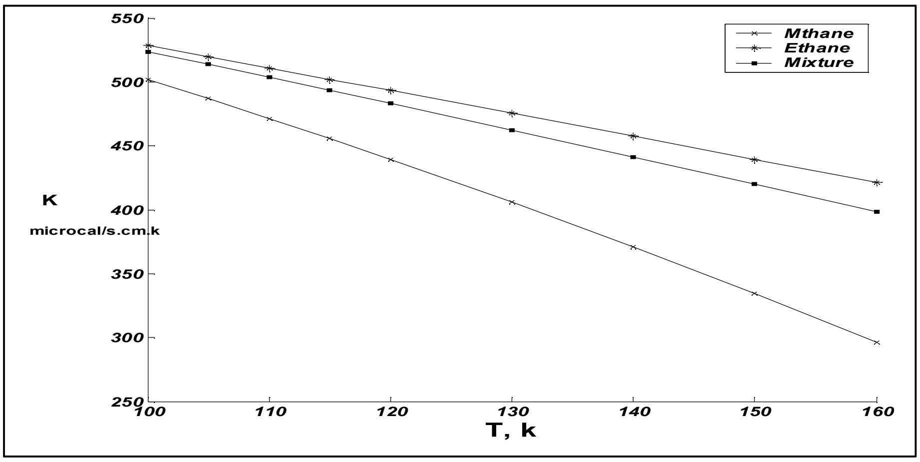

Fig.(11): Calculated THERMAL CONDUTIVITY for the system *Methane – Ethane* at 1 atm.

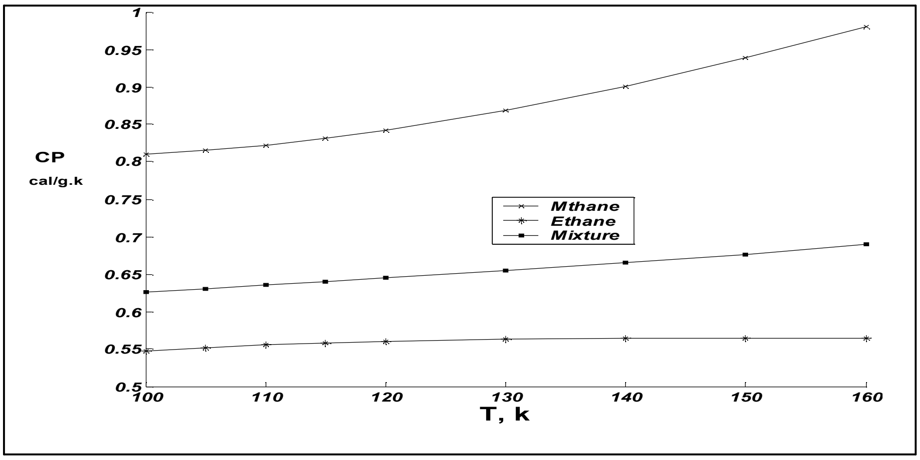

Fig.(12): Calculated SPESFIC HEAT for the system *Methane – Ethane* at 1 atm.

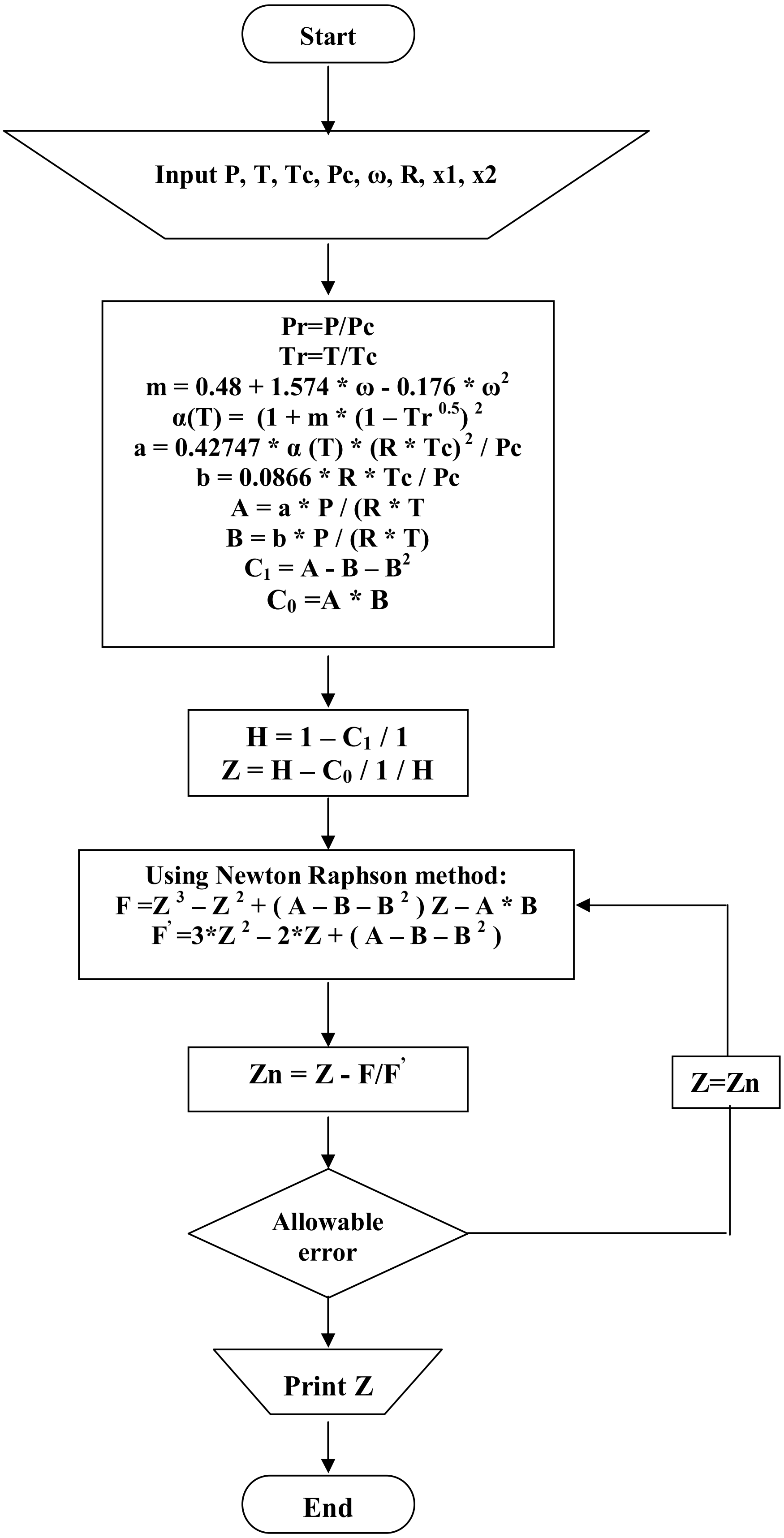

Fig.(13): Flowchart of Compressibility factor (Soave R. K.) Calculations**.**

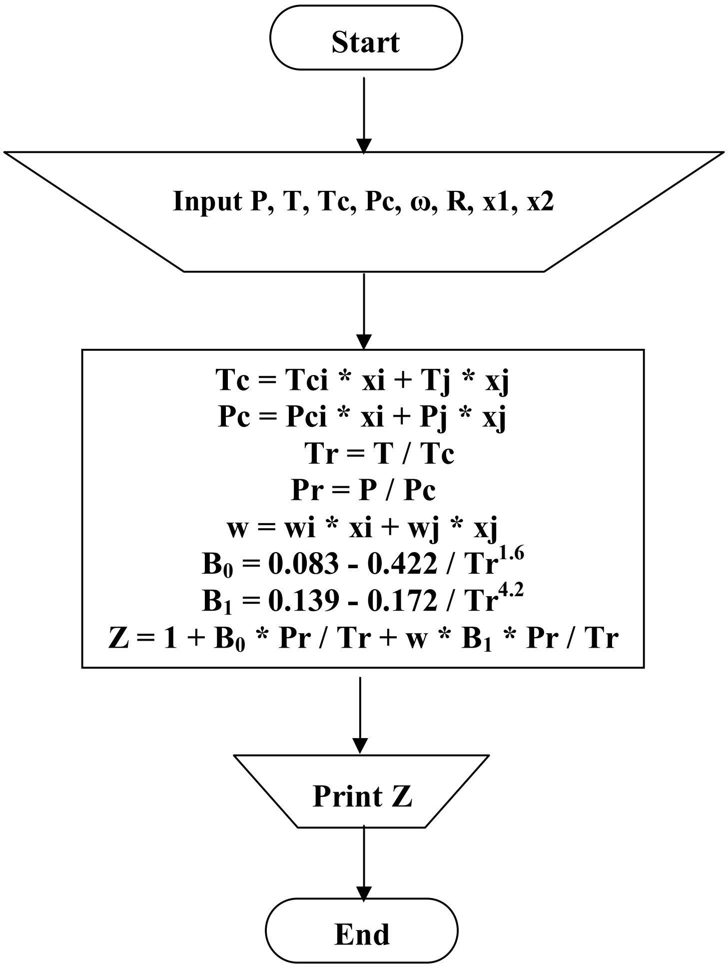

Fig.(14): Flowchart of Compressibility factor (Generalized Correlation) Calculations.

Table (1): The experimental (18) and calculated data of Density.

Compound	Density, (g/cm^3)		
	T, c	Calc.	Exp.
Methane	-161.5	0.424	0.422
Ethane	25	0.331	0.331
Propane	25	0.494	0.493
Ethylene	-103.8	0.567	0.567
Propylene	-47.7	0.61	0.61
1-Butene	25	0.589	0.59
Benzene	25	0.872	0.87
Naphthalene	217	0.862	0.86
Toluene	25	0.861	0.86
Ethyl benzene	25	0.861	0.86
Cumene	25	0.86	0.86
Chlorobenzene	25	1.12	1.1
Phenol	60	1.039	1.04
Methanol	25	0.79	0.79
Ethanol	25	0.788	0.79
n-Propanol	25	0.81	0.8
n-Butanol	25	0.8	0.8
Chloroform	25	1.481	1.48

Table (2) : The experimental (18) and calculated data of Viscosity.

Compound	Viscosity, (centipoises)		
	T, c	Calc.	Exp.
Methane	-170	0.1398	0.14
Ethane	25	0.032	0.032
Propane	25	0.091	0.091
Ethylene	0.0	0.031	0.031
Benzene	25	0.61	0.61
Naphthalene	100	0.78	0.78
Toluene	25	0.55	0.55
Ethyl benzene	25	0.64	0.64
Chlorobenzene	25	0.76	0.76
Methanol	25	0.53	0.53
Ethanol	25	1.04	1.04
Chloroform	25	0.52	0.52

Table (3): The experimental [(18)] and calculated data of Thermal Conductivity.

Compound	Thermal Conductivity, (cal/s.cm)		
	T, c	*Calc.*	*Exp.*
Methane	-120	323	324
Ethane	20	171	170
Propane	20	233.82	234
Ethylene	-63	351	351
Propylene	20	275.2	275
Benzene	20	350	350
Naphthalene	120	311	311
Toluene	20	322	322
Ethyl benzene	20	310.7	311
Chlorobenzene	20	310.2	310
Methanol	20	459.18	459.2
Ethanol	20	404	404
Chloroform	20	286.8	287

Table (4): The experimental [(18)] and calculated data of Specific Heat.

Compound	Specific Heat , (cal/g.K)		
	T, c	*Calc.*	*Exp.*
Methane	-161.5	0.824	0.824
Ethane	-88.2	0.532	0.53
Propane	-42.1	0.531	0.532
Ethylene	-103.7	0.57	0.572
Propylene	-47.7	0.5	0.51
Benzene	25	0.41	0.41
Toluene	25	0.40	0.40
Ethyl benzene	25	0.419	0.418
Chlorobenzene	25	0.32	0.31
Phenol	60	0.534	0.535
Methanol	25	0.608	0.608
Ethanol	25	0.58	0.58
n-Propanol	25	0.57	0.57
Chloroform	*25*	*0.225*	*0.225*

Table (5): Physical properties for some compounds (21).

Compound	Properties			
	Tc , k	Pc , bar	ω	Mw
Methane	190.55	46.0	0.008	16.043
Ethane	305.45	48.8	0.098	30.07
Propane	396.85	42.5	0.152	44.097
Ethylene	283.05	50.4	0.085	28.054
Propylene	364.9	46.2	0.148	42.081
1-Butene	419.35	40.2	0.187	56.108
Benzene	562.09	48.9	0.212	78.114
Toluene	591.7	41.1	0.257	92.141
Chlorobenzene	632.35	45.2	0.249	112.559
ethanol	512.55	81.0	0.559	32.042
Ethanol	516.25	63.8	0.635	46.069
Chloroform	536.4	55.0	0.216	119.378

حساب الخواص الفيزياويه والثرموديناميكيه لأنظمه ثنائيه باستخدام معادلة الحاله

د. كريمة مروكي بطرس
مدرس
الجامعة التكنولوجية / قسم الهندسه الكيمياويه

الخلاصة

ان معادلة الحاله (Soave – Redlich Kwong) يمكن ان توصف الطور السائل والغازي بدقه لذلك تم استخدامها للانظمه ألثنائيه لحساب الخواص الفيزياويه والثرموديناميكيه. تم استخدام ومقارنة طريقتين وهما (Soave-Redlich Kwong و Generalized Compressibility Factor Correlation) لحساب الحجم المولي، الكثافه، اللزوجه، معامل التوصيل الحراري، محتوى الحراري، ومعامل الانضغاط .

في هذه المقاله تم تطوير برنامج حاسبه يتطلب الخواص ألحرجه لتنفيذ هذه الحسابات والنتائج قورنت مع بيانات الادبيات المتوفرة ووجدنا ان معدل الانحراف المطلق (AAD) هو (3.6%) عن بقية البرامج والطرق الحسابيه. كذلك من مقارنة النتائج لاحظنا ان Generalized Compressibility Factor Correlation افضل واكثر عموميه من الطريقه الاخرى.