Diyala Journal
of Engineering
Sciences

ISSN 1999-8716
Printed in Iraq

Vol. 03 , No. 01 , pp. 91-106 , June 2010

GAS-LIQUID EQUILIBRIUM PREDICTION OF CO_2-ETHANOL SYSTEM AT MODERATE PRESSURES AND DIFFERENT TEMPERATURES

Arkan Jasim Hadi

Engineering College , Tikrit University

(Received:17-11-2009 ; Accepted:22-3-2010)

ABSTRACT - In this work, a thermodynamic model for the prediction of gas-liquid equilibrium at moderate pressures (up to 19 bar) and different temperatures (288-323 K) for the binary system of carbon dioxide (1)-ethanol (2) is established using Soave-Redlich-Kwong equation of state (SRK-EOS), Peng-Robenson equation of state (PR-EOS), and HYSYS program with same equations of state. Three different mixing rules were used to show the effect of the type of mixing rule.

A comparison of experimental phase equilibrium data in the literature with the predicted results showed very good representation for some mixing rules and good for the others, also the comparison with the results obtained using simulation on HYSYS program exhibits good agreement up to 11 bar with a deviation of $4*10^{-4}$ - $2*10^{-4}$ %.

KEY WORDS:- Gas-liquid equilibrium, Carbon dioxide, Ethanol, Moderate pressure, Mixing rules, SRK-EOS, PR-EOS, HYSYS program.

NOTATIONS

a, b	parameters in the equation of state
A, B	dimensionless parameters
f	fugacity, bar
k_{ij}, L_{ij}	adjustable parameters
n	number of components
n_i	number of moles of component i, mole

N	number of data points
P	pressure, bar
R	universal gas constant, 0.08314 lit. bar/ mole K
T	temperature , K
x, y	liquid and gas mole fractions, respectively
Z	compressibility factor
$\underline{V}$	total system volume, lit
¬	total system molar volume , lit./mole

GREEK SYMBOLS

$\overset{\frown}{\text{¤}}$	fugacity coefficient in mixture
μ	a centric factor

SUBSCRIPTS AND SUPERSCRIPTS

c	critical condition
Exp	experimental value
calc	calculated value
g	gas phase
ℓ	liquid phase
i,j	component
m	mixture
r	reduced property

1- INTRODUCTION

The solubility of gases in liquids has been under intense investigation over the past three decades since the knowledge of gas solubility data in pure liquids and in mixed solvents plays an important role in several industrial processes, such as the carbonation of alcoholic beverages and soft drinks, gas absorption, stripping columns, wastewater treatment, etc. (2)

From theoretical point of view, the solubility of gases in liquids, especially in the dilute region, is also a matter of great interest. Experimental solubility data can be used to test molecular theories. It is also used to elucidate intermolecular interactions and microscopic structure. According to Wilhelm et al(1)., the advantages of low-pressure gas solubility over high-pressure equilibrium data relies on the fact that inaccuracies introduced by possible necessary semi-empirical relations (for example, for the partial molar volume of solute at infinite dilution in the solvent) have essentially no effects on the final results and the thermodynamic treatment is much facilitated by well-defined assumptions.(2)

Accurate thermodynamic data such as volumetric properties and phase equilibria of pure compounds and mixtures (i.e.CO_2 + alkanes, CO_2 + alkanols) are of great significance in the chemical, oil and biotechnology areas, and for the development and validation of thermodynamic models. In this context, it is especially important to know the global phase behavior of systems within the range of working pressures and temperatures.(3)

Dalmolin et al. (2). Studied the gas solubility data and Henry's constants for carbon dioxide in pure water and ethanol and in their mixtures. The experiments were performed in the temperature range of 288–323 K, up to 6 atm in pure solvents and at various ethanol–water mixture compositions.

Elizalde-Solis et al.(3) measured the vapor–liquid equilibria for CO_2 + alkanol systems. Equilibrium measurements for the CO_2 + 1-propanol system were performed from 344 to 426 K. For the case of the CO_2 + 2-propanol system, measurements were made from 334 to 443 K, and for the CO_2 + 1-butanol were obtained from 354 to 430K.

Minqiang Hou et.al.(4) Studied the solubility of CO_2 in polyethylene glycol200 (PEG200, PEG with an average molecular weight of 200 g/ mol), 1-pentanol, and1-octanol.

Elizalde and Galicia-Luna,(5). measured the solubility of thiophene in CO_2 and in CO2 + 1-propanol mixtures. Vapor–liquid equilibria (VLE) data of binary mixtures were fitted to the Peng–Robinson equation of state (EOS) with classical mixing rules.

Chemical plants are never truly at steady state. Feed and environmental disturbances, heat exchanger fouling, and catalytic degradation continuously upset the conditions of a smooth running process. The transient behavior of the process system is best studied using a dynamic simulation tool like HYSYS. With dynamic simulation , you can confirm that the plant can produce the desired product in a manner that is safe and easy to operate. Dynamic analysis provides feedback and improves the steady state model by identifying specific areas in a plant that have difficulty achieving the steady state objectives. In HYSYS, the dynamic analysis of a process system can provide insight into the process system when it is not possible with steady state modeling(6).

The HYSYS dynamic model shares the same physical property packages as the steady state model. The dynamic model simulates the thermal, equilibrium, and reactive behaviour of the chemical system in a similar manner as the steady state model. By using a degrees of freedom approach, calculations in HYSYS are performed automatically. HYSYS performs calculations as soon as unit operations and property packages have enough required in formation(6).

The design of the HYSYS interface is consistent, if not integral, with this approach to modeling. Access to information is the most important aspect of successful modeling, with accuracy and capabilities accepted as fundamental requirements(7).

In modeling operations, HYSYS uses a Degrees of Freedom approach which increases the flexibility with which solutions are obtained. For most operations , you are not constrained to provide information in a specific order , or even to provide a specific set of information(7).

In the present work, theoretical results is obtained using mathematical model for SRK-EOS and PR-EOS for different mixing rules. The effect of mixing rules on theoretical results is found by comparing theoretical and experimental data.

The results for SRK-EOS and PR-EOS for CO_2(1)-ethanol(2) at moderate pressure and different temperature is compared with the experimental data obtained by Dalmolin, et sl.(2), then after these results are compared with that obtained from simulation program (HYSYS) using same equations of state and two mixing rules.

2- EQUATION OF STATE

Cubic equations of state in fact is the simplest equation capable of representing both liquid and vapor behavior. Yet it must be not complex to present excessive numerical or analytical difficulties in application. (8). Table (1) shows the general forms of SRK-EOS, and PR-EOS. Replacing v in the general form of SRK-EOS, and PR-EOS in term of ZRT/P, gives the cubic equation of compressibility factor as shown in Table (2), where Z is the compressibility factor of the liquid mixture and may be calculated from the cubic equation by an iteration method such as Newton-Raphson method.

The useful relation for finding fugacity coefficients(11) is,

$$\ln \hat{\phi}_i = \frac{1}{RT} \int_{v}^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,v,nj} - \frac{RT}{\underline{V}} \right] d\underline{V} - \ln Z \qquad \ldots..(1)$$

When the SRK-EOS is introduced into Eq. (1), the following closed-form for fugacity coefficient is obtained in the liquid phase,

$$\ln\hat{\phi}_i^{\ell} = \frac{b_i}{b_m}(Z-1) - \ln\left[Z\left(1-\frac{b_m}{v}\right)\right] + \frac{a_m}{RTb_m}\left(\frac{b_i}{b_m} - \frac{2}{a_m}\sum_j x_i a_{ij}\right)\ln\left(1+\frac{b_m}{v}\right) \qquad \text{.....(2)}$$

Introducing PR-EOS into Eq. (1) gives the following closed-form expression for fugacity coefficient is obtained in the liquid phase,

$$\ln\hat{\phi}_i^{\ell} = \frac{b_i}{b_m}(Z-1) - \ln\left[Z\left(1-\frac{b_m}{v}\right)\right] + \frac{a_m}{2.828RTb_m}\left(\frac{b_i}{b_m} - \frac{2}{a_m}\sum_j x_i a_{ij}\right)\ln\left(\frac{1+2.414\frac{b_m}{v}}{1-0.414\frac{b_m}{v}}\right) \qquad (3)$$

The fugacity coefficients of the components in the gas phase are also calculated with Eqs.(2,3) with, y_i and all the (SRK, PR) a and b values for the gas replacing their corresponding terms. Most of simple equations of state are evolved from the van der Waal's mixing rules with or without modifications and the mixing rules for equation of state calculate the mixture parameters am and b_m for the equation of state according to the one-fluid mixing rules (Eqs. 4 and 5) and the only difference between them is the combining rule that determines how the cross coefficients a_{ij} and b_{ij} are calculated.

$$a_m = \sum_i^n \sum_j^n x_i x_j a_{ij} \qquad \text{.....(4)}$$

and

$$b_m = \sum_i^n \sum_j^n x_i x_j b_{ij} \qquad \text{.....(5)}$$

Equations for three mixing rules using in this work are listed on Table (3).

3- RESULTS AND DISCUSSION

Theoretical solubility of CO$_2$ in ethanol is calculated using SRK-EOS and PR-EOS with different mixing rules. Calculations included the mole fraction of CO$_2$ in liquid phase (x) and the mole fraction of CO$_2$ in vapor phase (y). Each equation of state includes one or more mixing rules. Calculated data of mole fraction of CO$_2$ in liquid phase are compared with experimental data obtained by Dalmolin, et al.(2) while the comparison of data concerning mole fraction of CO$_2$ in gas phase is not performed since there is no experimental data available in literature.

Adjustable parameter (k_{12}) is obtained from experimental data by fitting these data using SRK-EOS and PR-EOS. Adjustable parameter (L_{12}) which is used in MR3 is found by trail and error. Acceptable values of (k_{12}, L_{12}) that values which gives minimum mean absolute deviation (%MAD) which is calculated by the following equation:

$$\%MAD = \frac{100}{N}\sum\left|x_{\exp.} - x_{calc.}\right| \qquad \ldots..(6)$$

where N is the number of data points. The steps of the calculations and the computer program in basic language are described in flow chart below.

Adjustable parameter used in MR1 and MR2 are the same used in simulation program HYSYS. Table (4) includes the values of k_{12}, and L_{12}. The values of adjustable parameter k_{12} in MR2 and MR3 increased as the temperature is increased, for the tow equation of state (SRK, PR). The values of L_{12} in MR3 decreased with the temperature increased.

The values of MAD for all mixing rules at different temperatures using SRK, PR EOS, and HYSYS for CO_2-ethanol system are lists on Table5.

The results shown graphically on Figs (2-13). These Figures indicated that the mixing rules MR3 gave %MAD smaller than the mixing rules MR1 and MR2 for SRK, PR -EOS. Thus, the MR3 with two adjustable parameter k_{12} and L_{12} can be used to calculate the gas-liquid equilibrium of CO_2 (1)-ethanol (2) at moderate pressures and different temperatures adequately.

It is obvious that there is good agreement between calculated data using SRK and PR -EOS for MR3 and experimental data. This means that the two equations of state can be used to calculate gas-liquid equilibrium of CO_2 (1)-ethanol (2) system.

Regarding the results obtained from fitting of the experimental data which are compared with the results obtained from the simulation on HYSYS program using MR1 and MR2, it is found that there is an exact matching at 11 bar or less, whereas a small deviation of $4*10^{-4}$ - $2*10^{-4}$ % is realized at operating pressure of 11-19 bar. It is worth to mention that the results obtained from BASIC program, especially at low and medium pressure is better than that of simulation on HYSYS program.

4- CONCLUSOINS

1. It is possible to collate gas-liquid equilibrium of CO_2 – ethanol system using PR and SRK-EOS with the mixing rules of two adjustable parameters.
2. Mixing rule MR3 includes two adjustable parameter k_{12} and L_{12} can be employed to find the gas -liquid equilibrium data of CO_2 (1)-ethanol (2) at moderate pressures and

different temperatures since it gives good agreement compared with the other mixing rules.

3. It is acceptable to use MR2 that contain one adjustable parameter k_{12} to calculate gas - liquid equilibrium data of CO_2 (1)-ethanol (2) at moderate pressures and different temperatures since it gives good agreement.
4. The adjustable parameter $k_{12,}$ increase with increase the temperature, note that the increment is very slight compare with the increases of the temperature in this system.
5. In this system the adjustable parameter $L_{12,}$ decrease with increase the temperature.

5- REFERENCES

1. E. Wilhelm, R. Battino, and R.J. Wilcock, Chem. Rev. 1977, vol. 77, pp:219–262.
2. I. Dalmolin, E. Skovroinski, A. Biasi, M.L. Corazza, C. Dariva, and J. Vladimir Oliveira; 2006, "Solubility of carbon dioxide in binary and ternary mixtures with ethanol and water". Fluid phase Equilibria, vol.245, pp:193-200.
3. Octavio Elizalde-Solis, Luis A. Galicia-Luna, and Luis E. Camacho-Camacho; 2007 "High-pressure vapor–liquid equilibria for CO2 + alkanol systems and densities of *n*-dodecane and *n*-tridecane" Fluid phase Equilibria, vol.259, pp:23-32.
4. Minqiang Hou, Shuguang Liang, Zhaofu Zhang, Jiyuan Song, and Tao Jiang, Buxing Han.;2007, "Determination and modeling of solubility of CO2 in PEG200 + 1-pentanol and PEG200 + 1-octanol mixtures" Fluid phase Equilibria, vol.258, pp:108-114.
5. O. Elizalde-Solis, and L.A. Galicia-Luna.; 2005, "Solubility of thiophene in carbon dioxide and carbon dioxide + 1-propanol mixtures at temperatures from 313 to 363K" Fluid phase Equilibria, vol.230, pp:51-57.
6. Hyprotech Ltd.; 2002. Dynamic Modeling, HYSYS 3. pp:1-3.
7. Hyprotech Ltd.; 2002. Operations Guids, HYSYS 3.pp:1-3.
8. J. M. Smith, H. C.,Van Ness, and M. M. Abbott; 2005. Introduction to Chemical Engineering Thermodynamics, 7th Edn., McGraw. Hill Book Company, Cha.3, pp:90
9. Soave, G, 1972; "Equilibrium constants from a modified Redlich-Kwong equation of state" Chem.Eng.Science, vol.27, pp:1197-1203.
10. Peng, D.-Y., and Robinson, D.B; 1976, "A new two-constant equation of state" Ind. Eng. Chem. Fundamen., vol.15, pp:59-64.

11. Walas, S. M., 1985. Phase Equilibria in Chemical Engineering. Butterworth Publishers, USA.
12. Adachi, Y., and Sugie, H. A; 1986. New Mixing Rule - Modified Conventional Mixing Rule. Fluid Phase Eq., vol.28, pp:103.

Table (1):- General form for SRK-EOS, and PR-EOS(11)

SRK- EOS	PR-EOS
$P = \frac{RT}{(v-b)} - \frac{a}{v(v+b)}$	$P = \frac{RT}{(v-b)} - \frac{a}{v(v+b)+b(v-b)}$
$a = 0.42747 \frac{R^2 T_c^2}{P_c} \sim (T_r, \mu)$	$a = 0.45724 \frac{R^2 T_c^2}{P_c} \sim (T_r, \mu)$
$b = 0.08664 \frac{RT_c}{P_c}$	$b = 0.0778 \frac{RT_c}{P_c}$
$(\alpha)^{0.5} = 1 + (1 - T_r^{0.5})(0.48508 + 1.55171\omega - 0.15613\omega^2)$	$(\alpha)^{0.5} = 1 + (1 - T_r^{0.5})(0.37464 + 1.5422\omega - 0.2699\omega^2)$

Table (2):- Cubic equation of compressibility factor for SRK-EOS, and PR-EOS(11)

SRK-EOS	PR-EOS
$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$	$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0$
$A = \frac{aP}{R^2 T^2} = 0.42747 \frac{P_r}{T_r^2}$, $B = \frac{bP}{RT} = 0.08664 \frac{P_r}{T_r}$	$A = \frac{aP}{R^2 T^2} = 0.45724 \frac{P_r}{T_r^2}$, $B = \frac{bP}{RT} = 0.07780 \frac{P_r}{T_r}$

Table(3):- Mixing Rules Equations.

No	Mixing rules	Adjustable parameters
1- van der Waal's mixing rules (MR1)$^{(11)}$	$a_m = \left[\sum_i^n (x_i a_i^{0.5})\right]^2$ and $b_m = \sum_i^n x_i b_i$ $a_{ij} = \sqrt{a_i a_j}$	k_{12}=0
2- Modified van der Waal's mixing rules (MR2)$^{(11)}$	$a_m = \sum_i^n \sum_j^n x_i x_j a_{ij}$ and $b_m = \sum_i^n x_i b_i$ $a_{ij} = (1-k_{ij})(a_i a_j)^{0.5}$	k_{12}=value.
3- Quadratic mixing rules (MR3)$^{(12)}$	$a_m = \sum_i^n \sum_j^n x_i x_j a_{ij}$ and $b_m = \sum_i^n \sum_j^n x_i x_j b_{ij}$ with $a_{ij} = (1-k_{ij})(a_i a_j)^{0.5}$ and $b_{ij} = \frac{b_i + b_j}{2}(1-L_{ij})$	k_{12} =value , L_{12} = value.

Table (4):- Values of Adjustable Parameters Obtained from Fitting with PR,SRK-EOS

Ref.	MR3		MR2	MR 1	T (K)
	L_{12}	k_{12}	k_{12}	k_{12}	
CO_2-ethanol PR-EOS					
1	-0.015	0.1029395	0.1029395	0	288
1	-0.0225	0.1058132	0.1058132	0	298
1	-0.0435	0.1132868	0.1132868	0	308
1	-0.538	0.1306247	0.1306247	0	323
1					
CO_2-ethanol SRK-EOS					
1	-0.014	0.09770131	0.09770131	0	288
1	-0.0214	0.1007727	0.1007727	0	298
1	-0.0393	0.1086598	0.1086598	0	308
1	-0.523	0.1271771	0.1271771	0	323

Table (5):- %MAD Between the Experimental and Predicted Mole Fraction Solubility of CO_2 in Ethanol with Different Mixing Rules

Ref.	MR3	MR2	MR1	T (K)
CO_2-ethanol PR-EOS				
1	$3.306*10^{-5}$	$3.93*10^{-3}$	2.727	288
1	$5.282*10^{-6}$	$5.23*10^{-3}$	2.3946	298
1	$3.231*10^{-6}$	$6.9622*10^{-3}$	1.984	308
1	$4.698*10^{-6}$	$3.304*10^{-3}$	1.2363	323
CO_2-ethanol HYSYS PR-EOS				
1	-	$3.5*10^{-4}$	2.593	288
1	-	1.9710^{-2}	2.4018	298
1	-	4.110^{-2}	2.135	308
1	-	2.37110^{-2}	1.684	323
CO_2-ethanol SRK-EOS				
1	$8.451*10^{-5}$	$4.498*10^{-3}$	2.409	288
1	$6.219*10^{-6}$	$5.152*10^{-3}$	2.213	298
1	$6.034*10^{-6}$	$6.478*10^{-3}$	1.765	308
1	$4.027*10^{-6}$	$3.022*10^{-2}$	1.110	323
CO_2-ethanol HYSYS SRK-EOS				
1	-	$1.92*10^{-2}$	2.33	288
1	-	$3.72*10^{-2}$	2.16	298
1	-	$5.43*10^{-2}$	1.93	308
1	-	$1.36*10^{-2}$	1.37	323

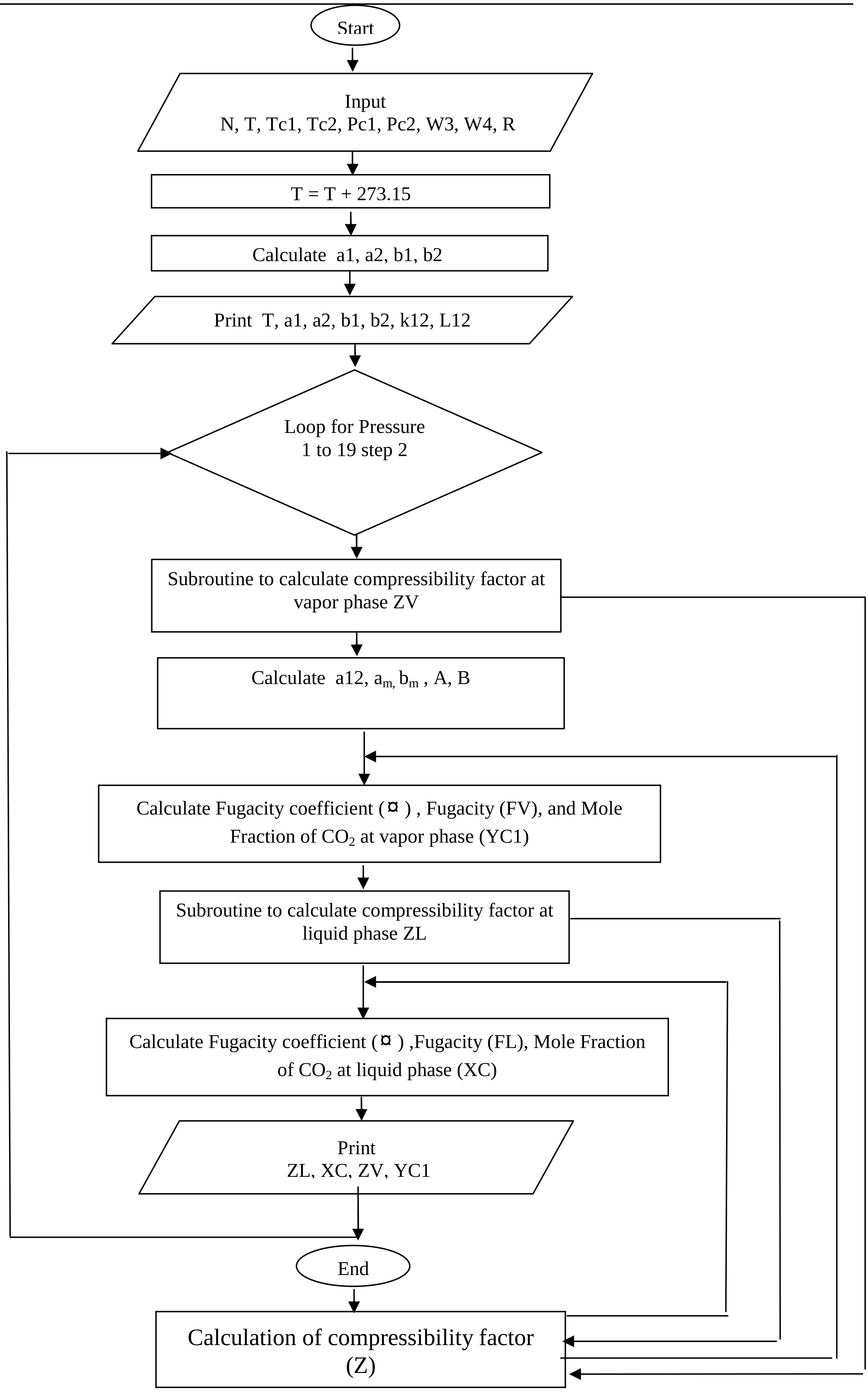

Fig. (1):- The steps of computer program in basic language

)

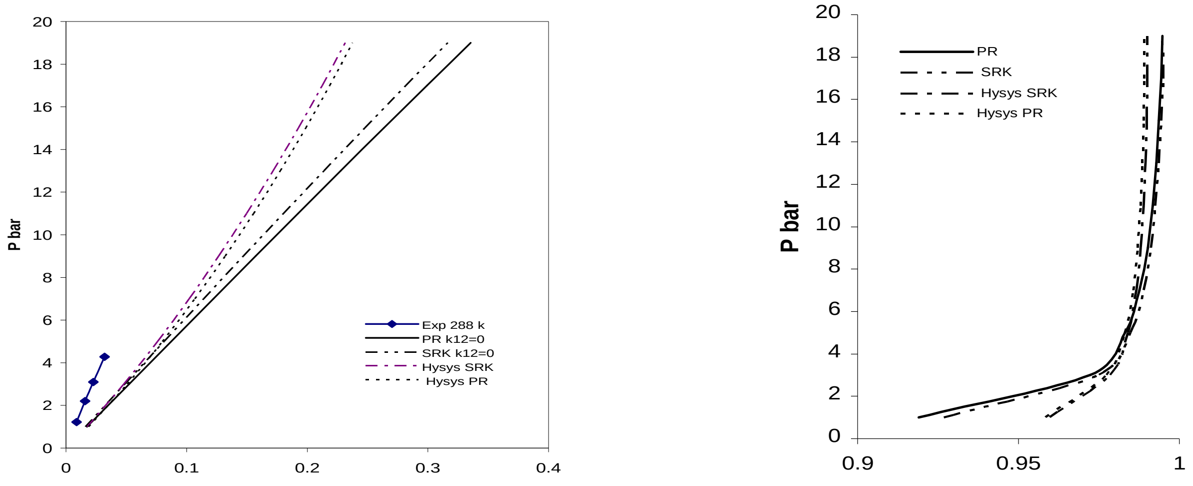

Fig. (2):- phase composition diagram of CO_2-ethanol system at 288K using MR1

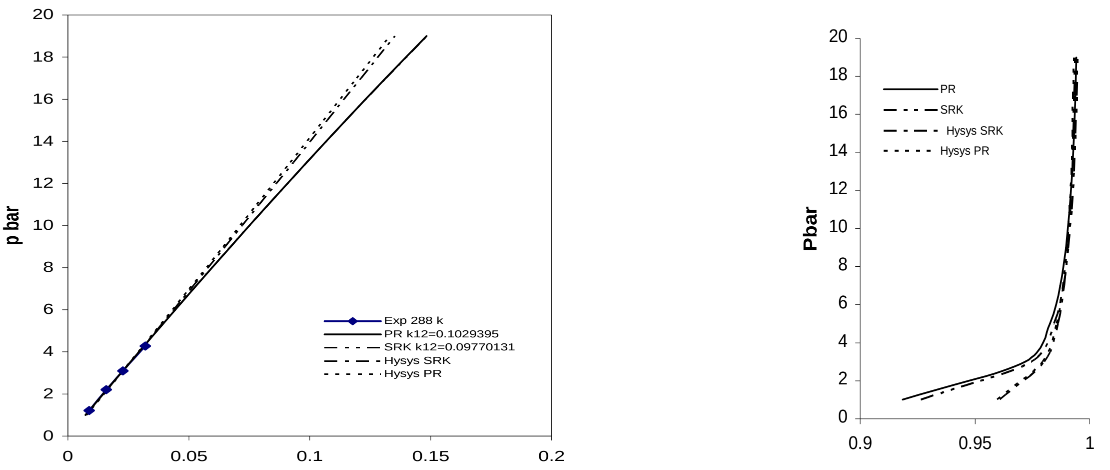

Fig. (3):- phase composition diagram of CO_2-ethanol system at 288K using MR2

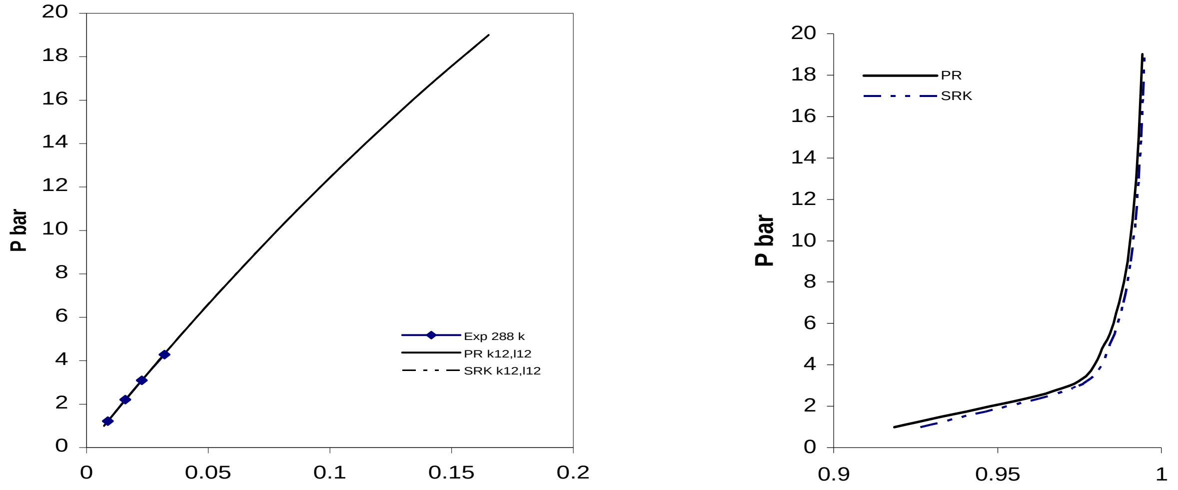

Fig.(4):- phase composition diagram of CO_2-ethanol system at 288K using MR3

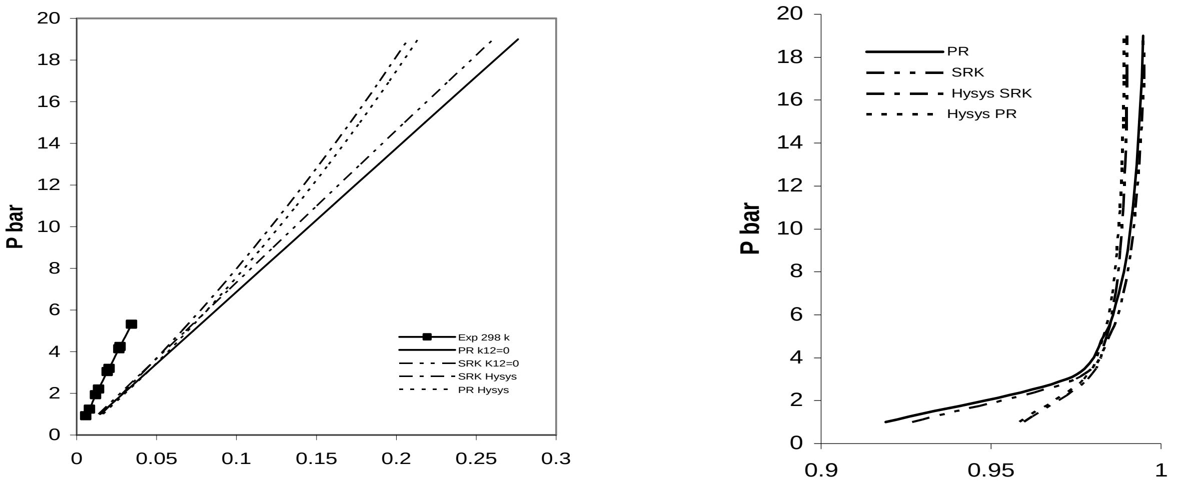

Fig. (5):- phase composition diagram of CO_2-ethanol system at 298K using MR1

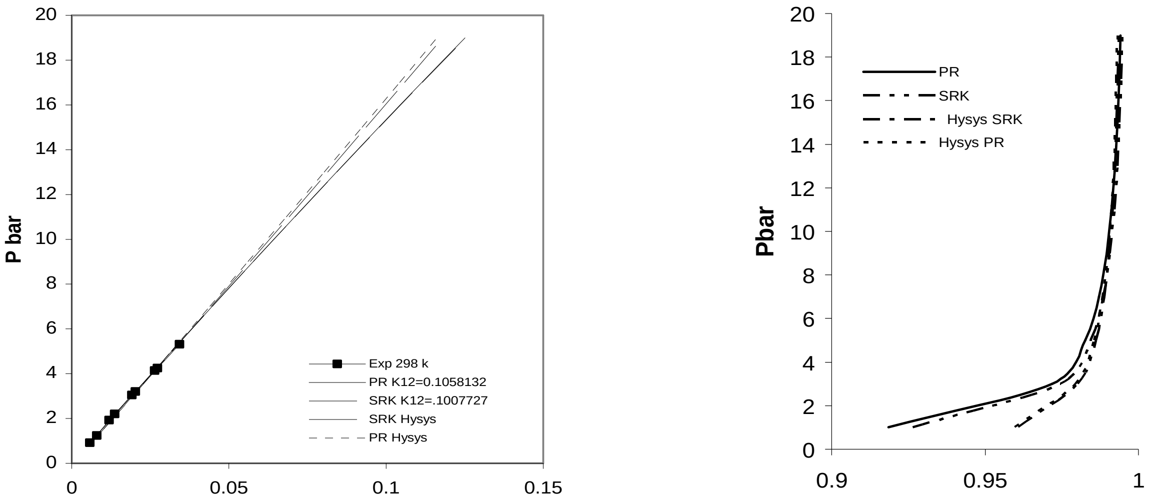

Fig. (6):- phase composition diagram of CO_2-ethanol system at 298K using MR2

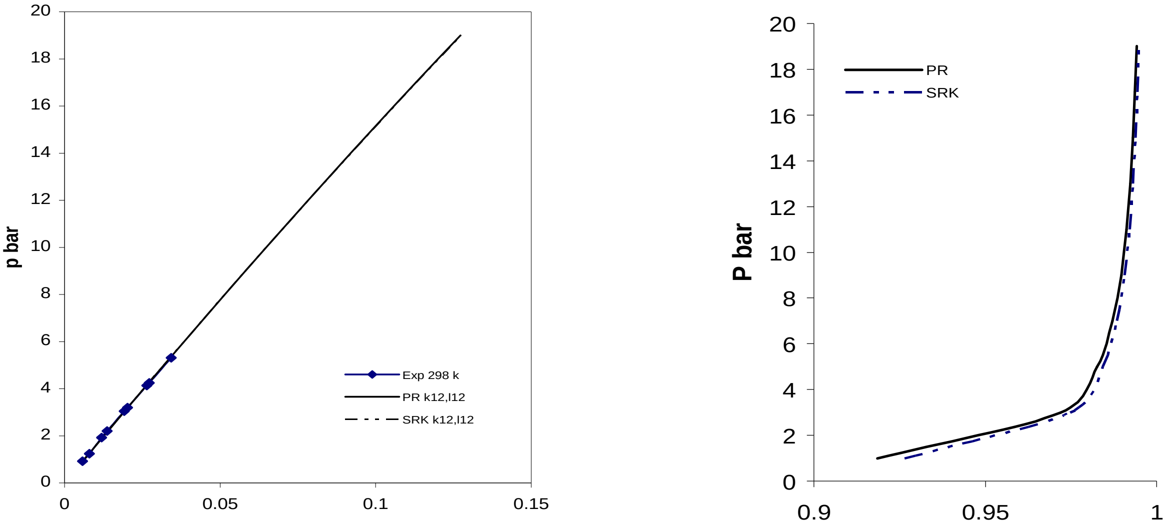

Fig. (7):- phase composition diagram of CO_2-ethanol system at 298K using MR3

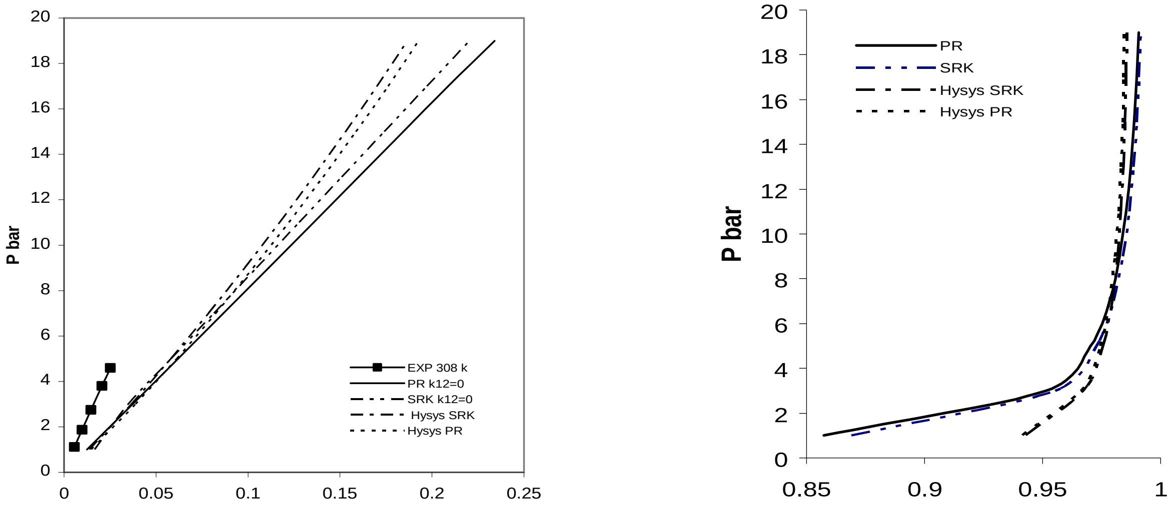

Fig.(8):- phase composition diagram of CO_2-ethanol system at 308K using MR1

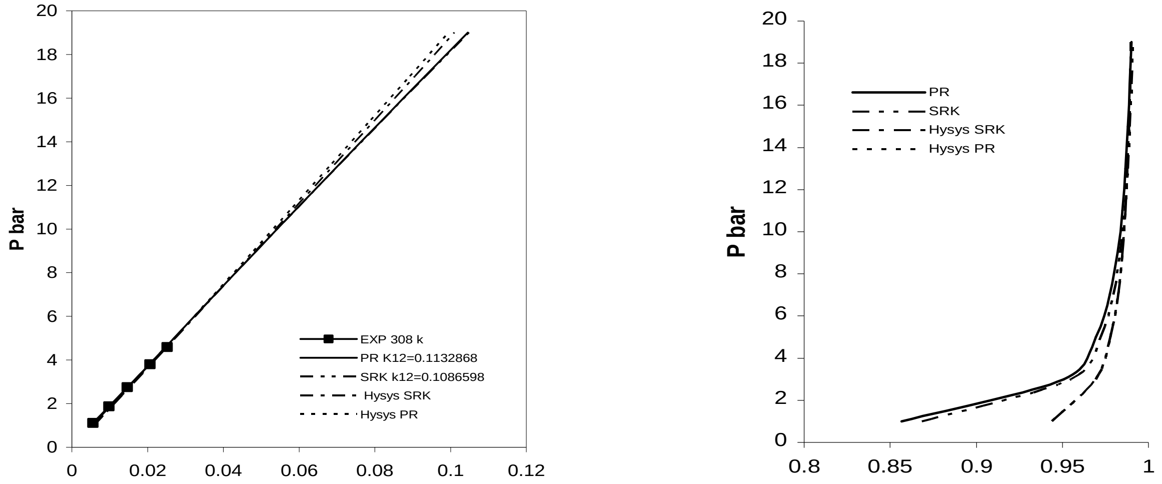

Fig.(9):- phase composition diagram of CO_2-ethanol system at 303K using MR2

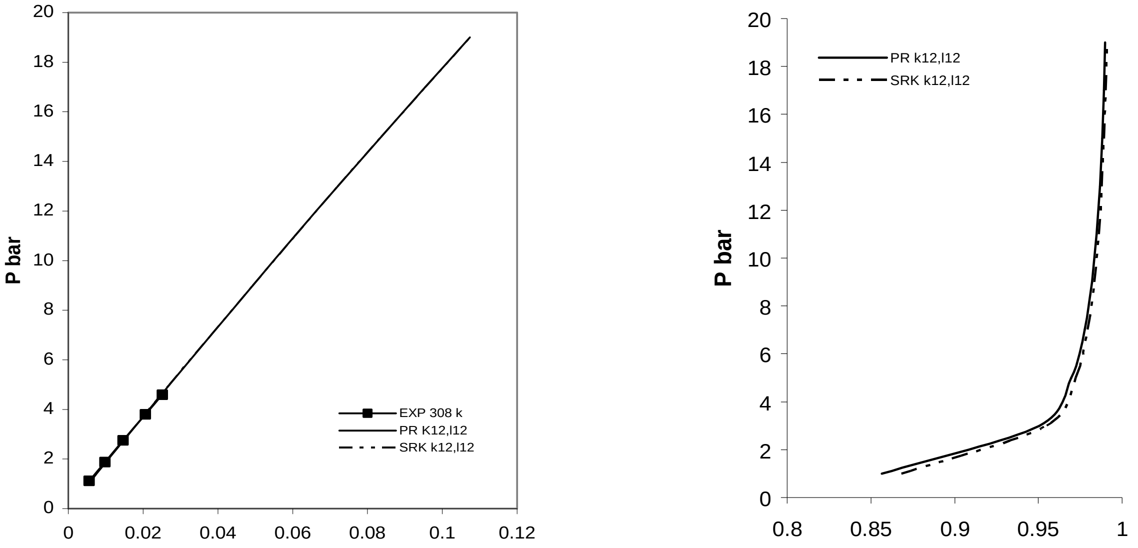

Fig.(10):- phase composition diagram of CO_2-ethanol system at 303K using MR3

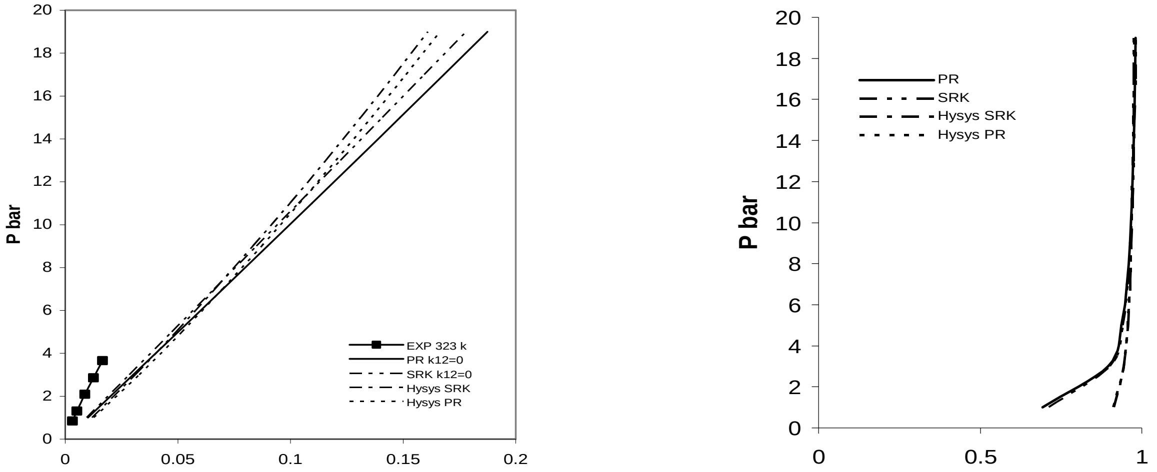

Fig.(11):- phase composition diagram of CO_2-ethanol system at 323K using MR1

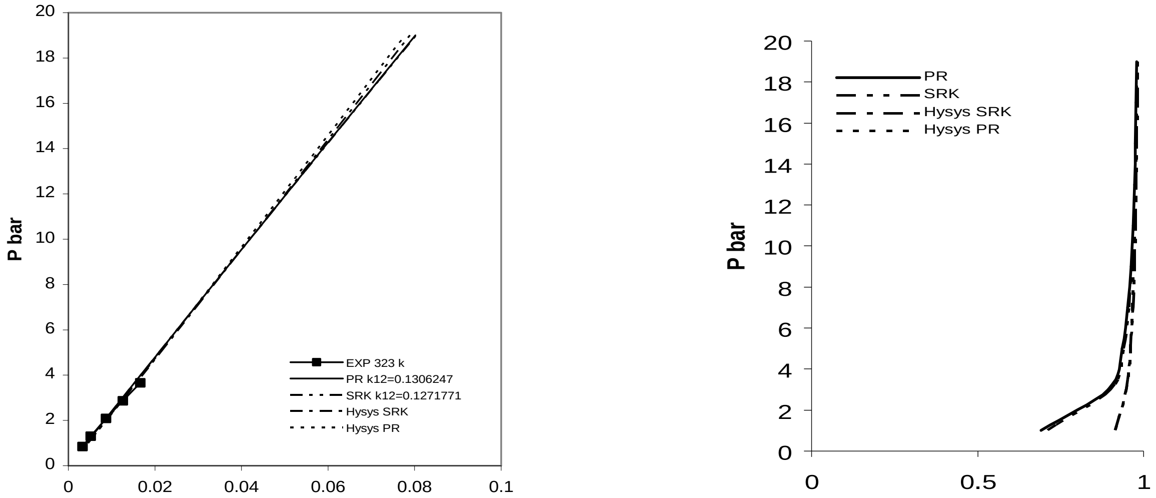

Fig.(12):- phase composition diagram of CO_2-ethanol system at 323K using MR2

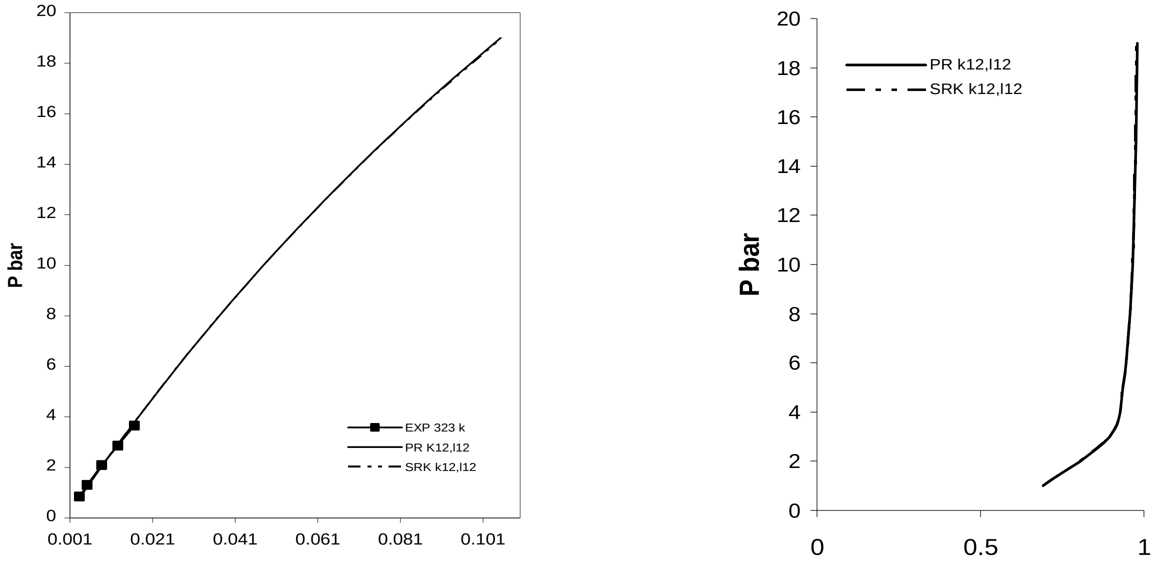

Fig.(13):- phase composition diagram of CO_2-ethanol system at 323K using MR3

تقدير اتزان غاز- سائل لنظام ثاني اوكسيد الكاربون- ايثانول عند ضغوط معتدلة ودرجات حرارة مختلفة

أركان جاسم هادي

مدرس مساعد

كلية الهندسة . جامعة تكريت

الخلاصة

تم إعداد نموذج لاتزان غاز-سائل للأنظمة الثنائية في الضغوط المعتدلة (الى حد ١٩ بار) وعند درجات حرارة مختلفة (٢٨٨-٣٢٣) كلفن لثاني أوكسيد الكاربون مع الايثانول بإستعمال معادلة Soave/Redlich/Kwong ومعادلة Peng-Robenson للحالة وقوانين خلط (mixing rules) مختلفة ومقارنة النتائج مع نتائج برنامج المحاكاة (Hysys) لنفس المعادلتين.

قورنت نتائج النموذج مع نتائج تجريبية تم الحصول عليها من الأدبيات المنشورة حديثا وقد تبين بان النموذج يعطي توافقا جيد جدا لأحد قوانين الخلط المستخدمة وجيد نوعا ما للأخرى، كذلك تم مقارنة النتائج مع نتائج برنامج (HYSYS) وظهر تطابق تام في النتائج وكان هناك انحراف بسيط عندما يكون الضغط أكثر من ١١ بار تتراوح نسبته من 4*10-4 إلى 2*10-4.

الكلمات الدالة: توازن غاز-سائل، قوانين خلط، ثاني اوكسيد الكاربون، ايثانول، ضغوط عالية، معادلة Soave/Redlich/Kwong ومعادلة Peng-Robenson للحالة.