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GAS-LIQUID EQUILIBRIUM PREDICTION OF SYSTEM CO₂-AQUEOUS ETHANOL AT MODERATE PRESSURE AND DIFFERENT TEMPERATURES USING PR-EOS

One of the most important design considerations that should not be ignored during industrial purpose equipment designing is vapour-liquid equilibrium (VLE). Thus, in chemical engineering, the first step is the computation of VLE properties of materials by employing equations of state (EOS). In this study, we have used a thermodynamic model established for a binary system of carbon dioxide (1)-aqueous ethanol (2), which was employed to estimate the gas-liquid equilibrium at moderate pressures (up to 6 bar) and varying temperatures (288-323 K). The Peng-Robinson EOS was employed to determine the VLE properties. Mixing rules such as van der Waals and quadratic mixing rules were also used for the determination of ethanol-water mixture critical parameters, which entails the pseudo-critical method as one component, and the results obtained from this study were similar to the ones reported in recent literature for empirical phase equilibrium studies.

Keywords: gas-liquid equilibrium, carbon dioxide, mixture, moderate pressure, PR-EOS.

Several attempts have been made during the last five decades to compute the VLE properties of different materials by employing a mathematical model, but unfortunately due to lack of theoretical basis, all attempts resulted in no significant outcome. The advent of computer technology and programs has made it possible to interpolate, extrapolate and predict thermodynamic information, which is crucial in designing of equipment sand modeling of process operations [1].

Intensive research has been conducted on gas solubility in liquids during the last three decades. This is significant from an industrial application point of view where gas solubility in pure and mixed liquids are of considerable importance, e.g. carbonation processes employed for wastewater treatment, stripping columns, gas absorption, soft drinks and alcoholic beverages, etc. [2].

However, gas solubility in diluted liquids is also of considerable importance from a theoretical point of view. Molecular theories are being tested by employing empirical solubility data and it is also utilized to illustrate the intermolecular interactions and microscopic structure of materials. Wilhem *et al.* [3] reported the dependence of benefits of low-pressure gas solubility over high-pressure equilibrium data and it was based on the observation that inaccuracies brought by semi-empirical relation is insignificant and it has no effect on the final observations, e.g. the impact of the solute's partial molar volume on indefinite diluted solvent and besides this some definite assumptions make possible the thermodynamic treatment of the system [2].

Other different thermodynamic information, such as volumetric characteristics and phase equilibrium of mixture and pure compounds (carbon dioxide either with alkane or alkanol), has great interest in the domains of chemical engineering, oil and biotechnology areas. It is also used for the establishment and validation of some models of thermodynamics. Identification of global phase behavior of different systems in a specified range of temperature and pressure is also crucial in this context [4].

Empirical observations for gas solubility in common systems that are employed for the establishment of models for studying different parameters, especially at high pressures, can be found in the existing literature. The carbon dioxide and water binary system was also studied by Alain *et al.* [5], who reported new empirical observations for VLE data at a wide range of temperature (278.2-318.2 K) and pressure around 80 bar. These observations were consistent with the ones already present in the literature. Gas solubility and Henry's data was also extensively researched by Dalmoelin *et al.* [2], who employed carbon dioxide gas to check its solubility in pure water and ethanol and a mixture of both and for this they chose temperature in range of (288-323K) whereas pressure was maintained up to 6 atm for pure solvents as well as their mixture with varying amounts of both solvents. The CO₂ and alkanol system was studied by Elizalde-Solis *et al.* [4], who measured their VLE values. The temperature range for carbon dioxide and 1-propanol system was around 344 to 426 K and its equilibrium values were determined. However, for CO₂ + 2-propanol, temperature in range of 334 to 443 K was used. 1-Butanol with CO₂ system was studied at temperature 354 to 430 K. Polyethylene glycol 200 as a solvent was also studied using carbon dioxide as gas model by Minqiang Hou *et al.* [6]. They used the following solvents and their mixtures in his study; PEG200, PEG with an average molecular weight of 200 g/mol), 1-pentanol and 1-octanol. PEG200 + 1-pentanol, and PEG200 + 1-octanol and the reported temperature range was 303.15, 313.15 and 323.15 K up to 8.0 MPa, respectively. With increase in the pressure, increase in the gas solubility was reported by [6]; also, increased alcohol concentration was found to also have significant impact on mixed solvents. However, at increasing temperature, the solubility decreases and it was found to be different for different solvents. Carbon dioxide had high solubility in PEG200 + 1-pentanol. Thiophene as a solvent for carbon dioxide was investigated by Elizalde and Galicia-Luna [7] and CO₂ + 1-propanol was also studied. The Peng-Robinson equation of state along with the classical mixing rule was employed for the computation of VLE data of binary mixtures. Comparative analysis of empirical and theoretical observations was made in the end. Secuianu *et al.* [8] studied the phase behavior of the carbon dioxide in methanol; they measured the VLE of this system and reported data at 293.15, 303.15, 313.15, 333.15 and 353.15 K and pressures between 5.2 and 110.8 bar. They modeled the measured VLE data and literature data by using a general cubic

equation of state combined with a classical van der Waals two parameter conventional mixing rule. They used one set of interaction parameters to predict the critical and subcritical VLE in binary mixture CO₂ and ethanol in a varied temperature. They also concluded from the comparison between the predicted results, experimental data and the literature data, the phase behavior was suitable reproduced.

Results obtained from this research for PR-EOS in CO₂ (1)-aqueous ethanol (2) at optimum pressure and temperature was analyzed and compared with empirical data obtained from [2].

THERMODYNAMIC MODEL

For the computation of phase equilibrium behaviour, the thermodynamic model employed for this purpose must meet the requirements mentioned in the expression mentioned below. This expression is for two-phase equilibrium in which one phase is represented by prime (') and the other by double prime (").

$$f_i' = f_i'', \quad i = 1,2,3,…,m \tag{1}$$

In the above expression f indicates the fugacity of component (i) in a multi-component mixture [9].

EOS

A component's fugacity in a phase is computed by employing a thermodynamic equilibrium model utilizing EOS. Interaction energies and size factors have been observed to have an impact on the results of the models used for fugacity computation. This creates the requirement of mixing rules development for the estimation of highest energy and size parameters as needed by EOS.

For modeling phase behaviour, cubic EOS are generally employed, which are quite simple and extensively employed for empirical data analysis [10,11].

The following modified equation was proposed by Peng and Robinson:

$$P = \frac{RT}{(v-b)} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{2}$$

At the critical point:

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \tag{3}$$

$$b(T_c) = 0.0778 \frac{RT_c}{P_c} \tag{4}$$

At other temperatures, the parameter T is changed as:

$$a(T) = a(T_c)\alpha(T_r, \omega) \qquad (5)$$

The efficiency of this term was improved by Graboski and Daubert [13] to explain the correlation terms of the vapour pressure curve up to the critical point as follows:

$$\alpha^{0.5} = 1 + (1 - T_r^{0.5})(0.37464 + 1.5422\omega - 0.26992\omega^2) \ (6)$$

Replacement of v in the general representation of Eq. (2) in terms of ZRT/P will give the expression for compressibility factor of PR-EOS as follows:

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - \\ -(AB - B^2 - B^3) = 0 \qquad (7)$$

A and *B* are defined as:

$$A = \frac{a\alpha P}{R^2 T^2} = 0.45724 \frac{\alpha P_r}{T_r^2} \qquad (8)$$

$$B = \frac{bP}{RT} = 0.0778 \frac{P_r}{T_r} \qquad (9)$$

Determination of compressibility factor can be made through the cubic EOS by simplifying it with an iterative procedure via the Newton-Raphson method.

As pressure-explicit EOS are the more general types of equations, the significant relation for determination of fugacity coefficients can be made by using the following equation:

$$\ln \hat{\varphi}_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,v,nj} - \frac{RT}{V} \right] dV - \ln Z \qquad (10)$$

where *V* indicates the total system volume whereas n_1 and n_2 represent the mole numbers of components 1 and 2, respectively. Substituting PR-EOS into Eq. (10) will yield the following closed-form expression for fugacity coefficient, which it acquires in the liquid phase:

$$\ln \hat{\varphi}_i = \frac{b_i}{b_m}(Z-1) - \ln \left[Z \left(1 - \frac{b_m}{v} \right) \right] + \frac{a_m}{2.828 RT b_m} \times$$

$$\times \left(\frac{b_i}{b_m} - \frac{2}{a_m} \sum_j x_i a_{ij} \right) \ln \left(\frac{1 + 2.414 \frac{b_m}{v}}{1 - 0.414 \frac{b_m}{v}} \right) \qquad (11)$$

Fugacity computation of components present in the gas phase was performed by employing equation 11 in which y_i and entire PR-EOS *a* and *b* values were substituted by their corresponding terms. EOS was first formulated for pure components and later it was modified for mixed components by using mixing rules which combine pure component parameters [16].

Mixing rules

Van der Waal's mixing rule has been used for the derivation of simple EOS expressions and later modifications may have been introduced in it. One-fluid mixing rules can be employed for the computation of the mixture parameters a_m and b_m for the EOS as shown in Eqs. (12) and (13). Combining rule is the exception between the two and it helps in the calculation of cross coefficients a_{ij} and b_{ij}.

$$a_m = \sum_i^n \sum_j^n x_i x_j a_{ij} \qquad (12)$$

and

$$b_m = \sum_i^n \sum_j^n x_i x_j b_{ij} \qquad (13)$$

The following mixing rule equations were employed in this study:

Modified van der Waal's mixing rules (MR1):

$$a_m = \sum_i^n \sum_j^n x_i x_j a_{ij} \ \text{ and } \ b_m = \sum_i^n x_i b_i$$

with

$$a_{ij} = (1 - k_{ij})(a_i a_j)$$

Quadratic mixing rules (MR2):

$$a_m = \sum_i^n \sum_j^n x_i x_j a_{ij} \ \text{ and } \ b_m = \sum_i^n \sum_j^n x_i x_j b_{ij}$$

with

$$a_{ij} = (1 - k_{ij})(a_i a_j) \ \text{ and } \ b_{ij} = (b_i + b_j /2)(1 - I_{ij}) .$$

RESULTS AND DISCUSSION

Prediction of VLE by employing cubic EOS expressions along with physical characteristics of pure components and adjustable parameters of binary system of CO₂ (1)-aqueous ethanol (2) was the major objective of this research. van der Waal's equation was altered by PR-EOS and mixing rule. The quadratic rule is generally employed for finding the correlations of empirical observations for VLE. Comparison of calculations with empirical observations was made after the computation of CO₂ mole fraction in the liquid phase (*x*). For comparative analysis, empirical data was obtained from [2].

Critical parameters of water-ethanol mixture at different compositions, such as critical temperature

(T_{cm}), critical pressure (P_{cm}) and acentric factor ω_m were approximated by the following expressions [18]:

$$T_{cm} = \sum T_{ci} x_i \tag{14}$$

$$P_{cm} = \sum p_{ci} x_i \tag{15}$$

$$\omega_m = \sum \omega_i x_i \tag{16}$$

In the above expression the symbols T_{cm}, P_{cm} and ω_m represent the critical temperature, pressure and acentric factor, respectively, for a given mixture, whereas T_{ci}, P_{ci} and ω_i are the critical parameters of ethanol and water. The expression x_i shows the mole fraction of components (water and ethanol). The critical properties of the carbon dioxide, ethanol and water are shown in Table 1.

Table 1. Critical properties (T_c and P_c) and acentric factor (ω) of CO₂, ethanol and water [8,14]

Component	T_c / K	P_c / bar	ω
CO₂	304.7	73.8	0.225
Ethanol	513.9	61.47	0.6447
Water	647.9	221	0.344

The mentioned Eqs. (14)-(16) were employed for the transformation of the multicomponent mixture (ethanol-water) to a single component and it was aimed to convert the ternary system (carbon dioxide--ethanol-water) system into a binary system (carbon dioxide and aqueous ethanol). Mixing rules entail some adjustable parameters such as k_{12} and L_{12} and the latter one can be calculated by using two different approaches and it need the empirical observations and later it is fitted into EOS expression. A trial and error method was adapted for the identification of MR2. Computation of mole fraction solubility was performed by using each isotherm pressure. The minimum mean absolute deviation (*MAD*) obtained by acceptable values of k_{12} and L_{12} was calculated as:

$$MAD = \frac{100}{N} \sum \left| x_{exp.} - x_{calc.} \right| \tag{17}$$

where N represents the number of considered data points.

Computational and programming details have been described previously [19]. For all the given compositions, acceptable values of k_{12} and L_{12} were used and the *MAD* values taken at different temperatures and varying compositions utilizing PR-EOS in CO₂--aqueous ethanol system are shown in Table 2. The comparative observations for computed and empirical data sets that took place at the temperature in the range of 288 to 323 K for all the given mixture compositions are shown in Table 2. *MAD* for MR2 was found to be lower than MR1 and this difference in the

Table 2. Values of adjustable parameters k_{12} and L_{12}, obtained from fitting with PR-EOS. Mean absolute deviation (MAD) percentage between the experimental and pedicted mole fraction solubility of CO₂ in aqueous ethanol with different mixing rules using PR-EOS

Composition of mixtures (ethanol + water)	T / K	MR1	MR2		*MAD* / %	
		k_{12}	k_{12}	L_{12}	MR1	MR2
0.1 Ethanol + 0.9 water	288	-0.1119	-0.1119	-0.117	2.285	2.069
	298	-0.1038	-0.1038	-0.181	2.198	1.828
	308	-0.0946	-0.0946	-0.004	0.926	0.918
	323	-0.0817	-0.0817	-0.087	0.691	0.625
0.25 Ethanol + 0.75 water	288	-0.0843	-0.0843	-0.025	2.337	2.272
	298	-0.0796	-0.0796	-0.046	3.397	3.306
	308	-0.0747	-0.0747	-0.228	3.023	2.733
	323	-0.06966	-0.06966	-0.003	1.281	1.279
0.5 Ethanol + 0.5 water	288	-0.0375	-0.0375	-0.088	2.358	2.160
	298	-0.03768	-0.03768	-0.091	2.063	1.872
	308	-0.03232	-0.03232	-0.048	3.113	2.990
	323	-0.02806	-0.02806	-0.017	0.957	0.930
0.75 Ethanol + 0.25 water	288	0.03148	0.03148	-0.134	3.971	3.740
	298	0.03541	0.03541	-0.074	5.334	5.177
	308	0.03722	0.03722	-0.163	2.535	2.530
	323	0.04064	0.04064	-0.321	3.086	2.706
0.9 Ethanol + 0.1 water	288	0.07616	0.07616	-0.035	0.747	2.661
	298	0.08107	0.08107	-0.116	2.093	1.948
	308	0.08797	0.08797	-0.154	1.827	1.610
	323	0.09538	0.09538	-0.158	2.055	1.928

values is negligible. We have found that thermodynamic model using PR-EOS along with MR1 and MR2 is best suited to run this system smoothly. Figures 1-8 show the comparative analysis of theoretical and empirical data values.
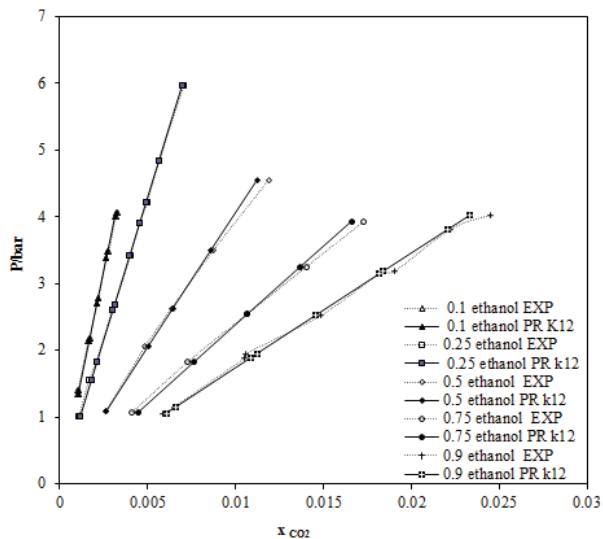

Figure 1. Phase composition diagram of CO$_2$-mixture system at 288 K using PR with MR1.
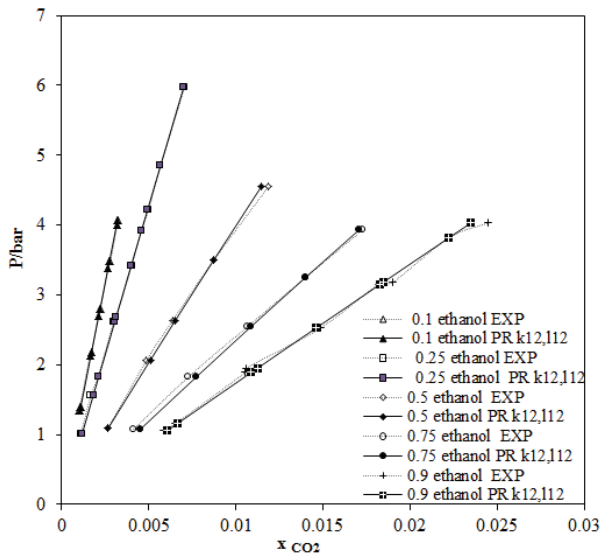

Figure 2. Phase composition diagram of CO$_2$-mixture system at 288 K using PR with MR2.

A decrease in k_{12} has been observed with increase in temperature. This data is valid for the mixtures of composition starting with 0.1 ethanol + 0.9 water and goes to 0.5 ethanol + 0.5 water. An increase in k_{12} values was noticed in mixtures with the following compositions; 0.75 ethanol + 0.25 water and 0.9 ethanol + 0.1 water. However, it should be noted that alteration in the values of k_{12} is insignificant when

compared to temperature values which are larger. L_{12} values are also referred as vacillation values. The binary interaction parameter k_{12} decreases with the increase in ethanol concentration in the mixture.
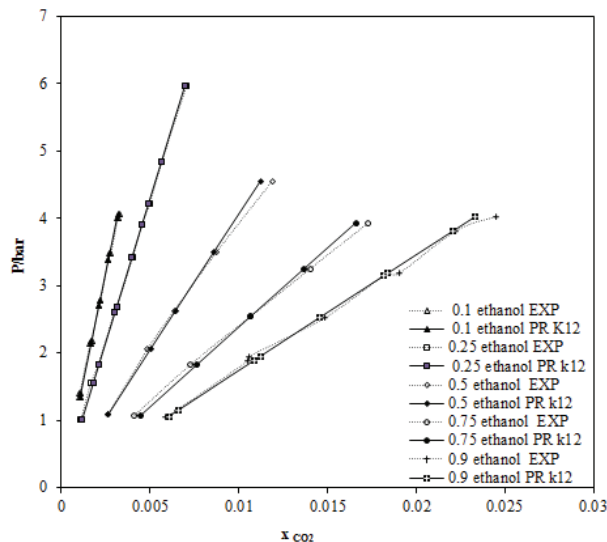

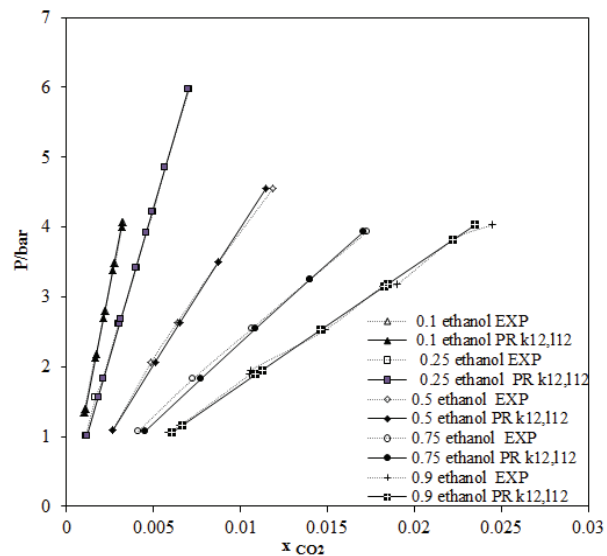Figure 3. Phase composition diagram of CO$_2$-mixture system at 298 K using PR with MR1.

Figure 4. Phase composition diagram of CO$_2$-mixture system at 298 K using PR with MR2.

It is obvious that there is good agreement between the calculated data using PR-EOS and the previous work Ghazi *et al*. [20] using the Soave-Redlich-Kwong equation of state (SRK) and experimental data. However, it is noticeable that there is small deviation between the results of the two equations where the MAD of the SRK that is less than the MAD for the PR-EOS for the two mixing rules.
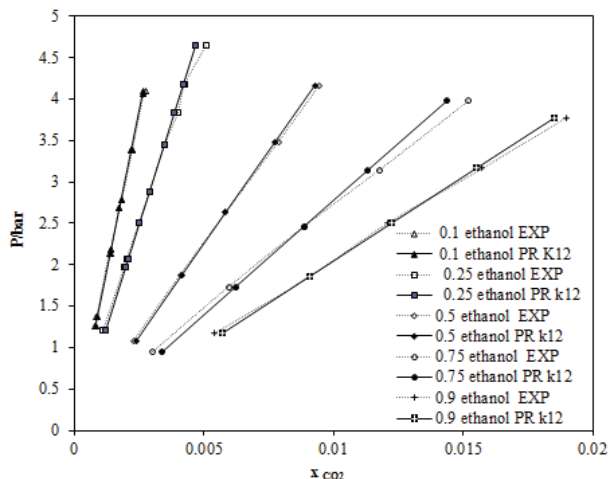
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Figure 5. Phase composition diagram of CO₂-mixture system at 308 K using PR with MR1.
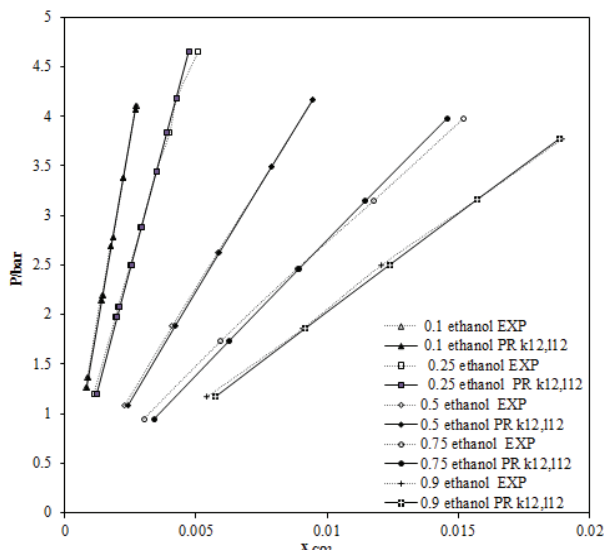

Figure 6. Phase composition diagram of CO₂-mixture system at 308 K using PR with MR2.

CONCLUSION

We used PR-EOS along with MR1 and MR2 for studying VLE and the obtained observations were consistent with empirical data provided in [2]. We used this model for the computation of VLE for CO_2 (1)-mixture (2) (ethanol and water) at varying temperatures and moderate pressures. In the mixing rule MR2, two adjustable parameters named k_{12} and L_{12} are used, which yielded reduced *MAD* compared to the one obtained by MR1. The latter one was used to determine the equilibrium data for CO_2 (1)-mixture (2). Besides this, *MAD* variation between MR1 and MR2 was insignificant. This results in the preferable use of MR1 with k_{12} parameter to study gas equilibrium

conditions in CO_2 mixtures. In the studied system, variation in the L_{12} values was observed.
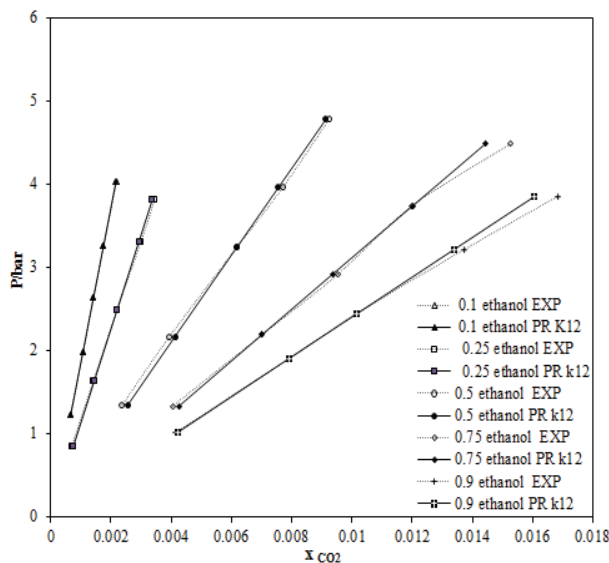

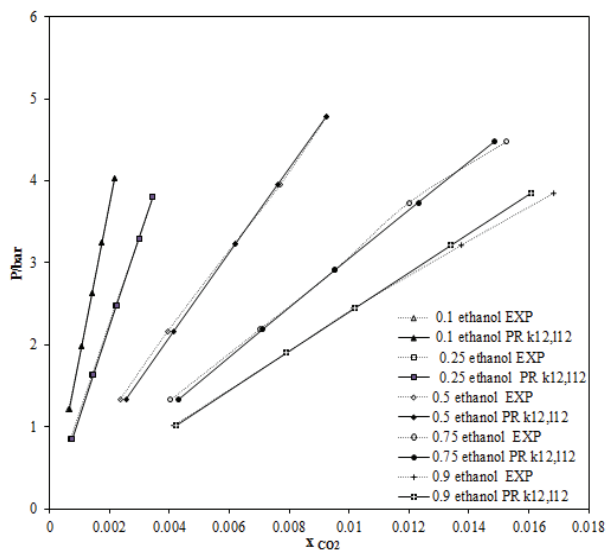*Figure 7. Phase composition diagram of CO₂-mixture system at 323 K using PR with MR1.*

Figure 8. Phase composition diagram of CO₂-mixture system at 323 K using PR with MR2.

Acknowledgment

Nomenclature

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, mol
N	number of data points
P	pressure, bar
R	universal gas constant, 0.08314 L bar/(mol K)
T	temperature , K
x, y	liquid and gas mole fractions, respectively
Z	compressibility factor
V	total system volume, L
v	total system molar volume , L/mol

Greek symbols

$\hat{\varphi}$	fugacity coefficient in mixture
ω	acentric factor

Subscripts and Superscripts

c	critical condition
exp.	experimental value
calc.	calculated value
g	gas phase
i,j	component
m	mixture
r	reduced property

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NAUČNI RAD

PREDVIĐANJE RAVNOTEŽE GAS-TEČNOST SISTEMA CO$_2$-VODENI RASTVOR ETANOLA NA UMERENOM PRITISKU I RAZLIČITIM TEMPERATURAMA PRIMENOM PENG-ROBINSON-OVE JEDNAČINE STANJA

Jedan od navažnijih aspekata projektovanja, koji ne sme biti zanemaren pri projektovanju opreme za industrijsku primenu, jeste ravnoteža para-tečnost (VLE). Zbog toga je u hemijskom inženjerstvu prvi korak izračunavanje ravotežnih podataka primenom jednačine stanja. U ovom radu je korišćen termidinamički model koji je utvrđen za binarni system CO$_2$-vodeni rastvor etanola. Ovaj model je korišćen za izračunavanje ravnoteže gas-tečnost na umerenim pritiscima (do 6 bar) i različitim temperaturama (280-323 K). Peng-Robinson-ova jednačina stanja je korišćena za određivanje ravnotežnih svojstava. Pravila mešanja, kao što su van der Waals-ovo i kvadratno pravilo, su takođe korišćeni za određivanje kritičnih parametara smeše etanol-voda koji zahteva pseudo-kritičnu metodu kao jednu komponentu. Dobijeni rezultati su slični sa nedavno objavljenim empirijskim istraživanjima fazne ravnoteže.

Ključne reči: ravnoteža gas-tečnost, CO$_2$, smeša, umereni pritisak, Peng-Robinson-ova jednačina stanja.