

## Introduction of a Novel Two-Dimensional Equation of State to Predict Gas Equilibrium Adsorption in Highly-Nonideal Systems

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### Abstract

The accurate calculations of adsorption equilibrium for multicomponent gas systems are of great importance in many applications. In this paper, five two-dimensional equations of state 2D-EOS, i.e. Van der Waals, Eyring, Zhou-Ghasem-Robinson, Soave-Redlich-Kwong and Peng-Robinson, were examined to find out their abilities to predict adsorption equilibrium for pure and multi-component gas adsorption systems. Also, a new 2D-EOS named Rahimi-Talaie (RT) was developed for accurately predicting adsorption equilibrium of the gas mixtures having highly non-ideal behavior. The pure parameters of all these equations were obtained by fitting 2D-EOS into pure gas-adsorption equilibrium data, and then the mixture parameters were calculated by recommended mixing rules. It was concluded that all equations were capable of accurately predicting pure adsorption equilibrium. However, among the six above-mentioned 2D-EOSs, RT was more successful to provide more accurate prediction of gas-mixture adsorption equilibrium, especially for the mixture showing azeotropic behavior.

### Keywords

*Equilibrium calculation, gas adsorption, two-dimensional equation of state, non-ideal mixture.*

### Introduction

The prediction of adsorption equilibrium plays a crucial part in an adsorption bed design. One of the most important approaches to calculate gas adsorption equilibrium is using two-dimensional equations of state. Many attempts have been made to develop two-dimensional equations of state and apply them to perform gas adsorption equilibrium calculations. Hill (1946) described a systematic thermodynamic treatment for mobile and monolayer adsorption of gas mixtures on homogeneous surfaces. They defined a surface fugacity for each component and they have utilized Van der Waals (VDW) EOS to predict adsorption equilibrium for binary gas mixtures [1]. Payne et al. (1968) derived a two-dimensional equation of state from the Hirschfelder-Eyring

modification of VDW and applied it to predict high pressure adsorption equilibrium of pure and mixed hydrocarbons on charcoal [2]. Friederich and Mullins (1972) have used VDW to predict adsorption equilibrium of a mixture of hydrocarbons on carbon black [3]. Patrekiejew et al. (1977) have developed the two-dimensional forms of Eyring, Redlich-Kwong (RK) and Peng-Robinson (PR) EOSs using statistical mechanics [4]. Konno et al. (1985) have obtained an isotherm equation by modifying PR EOS [5]. Zhou (1994) introduced a general two-dimensional equation of state (ZGR) and derived the fugacity equations to describe the adsorbed phase for adsorption from gas mixtures [6]. The results of ZGR has been compared with those of multicomponent Langmuir model and ideal solution theory and

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found out that ZGR produced better results in multicomponent gas adsorption systems. Zheng et al. (1998) proposed a modified two-dimensional VDW EOS model for the prediction of multicomponent gas adsorption isotherms from corresponding single-component adsorption equilibrium data. Then, they employed this equation to predict adsorption isotherms of CO–CO<sub>2</sub> mixtures and CO<sub>2</sub>–N<sub>2</sub> mixtures on Cu(I)–NaY zeolite [7]. Pan (2004) applied 2D EOS of ZGR and PR using new mixing rules to predict the adsorption of pure gas and several binary mixtures of gases on a carbon bed utilizing. A new computational algorithm has been developed for this purpose [8]. Fitzgerald et al. (2005) employed 2D-EOS of ZGR to predict the adsorption of a mixture of gases on wet Tiffany coal [9]. In that work, a modified form of Van der Waals equation was developed by adding a new term. The four key parameters of this equation were obtained based on fitting to adsorption equilibrium data of pure gases using nonlinear regression method. In addition, the results of this equation are compared with those of VDW, Eyring, ZGR, SRK and PR for adsorption equilibrium of several pure and binary systems. The main objective of the present study is to compare the results obtained by two-dimensional EOS of VDW, Eyring, ZGR, SRK and PR in predicting equilibrium adsorption of pure gases and the mixtures of gases. The sets of experimental data on pure and mixture gas adsorption found in literature were introduced in tables 2 and 3. Also, it was intended to develop a powerful 2D-EOS which is capable of producing more accurate results for predicting equilibrium adsorption of highly non-ideal gas mixtures.

### Development of RT 2D EOS

The following general 2D EOS can be developed from three-dimensional equations of state (3D EOS) [10]:

$$\left[ A\pi + \frac{\alpha w^2}{1 + U(\beta w) + W(\beta w)^2} \right] [1 - (\beta w)^m] = wRT \quad (1)$$

Where  $\pi$ ,  $A$ ,  $T$ ,  $R$  and  $w$  are spreading pressure, surface area of the adsorbent, absolute temperature, universal gas constant and the material amount adsorbed per mass of adsorbent.  $\alpha$  and  $\beta$  are two parameters of this equations. Applying different values of  $U$ ,  $W$  and  $m$ , which are mentioned in table 1, one can generate different types of 2D-EOSs.

**Table 1.** The values of  $W$ ,  $U$  and  $m$  for generating different types of EOSs.

2D-EOS	$m$	$U$	$w$
VDW	0	0	0
Eyring	1/2	0	0
ZGR	1/3	0	0
SRK	1	1	0
P-R	1	1	-2

VW equation can be obtained by using the following equation for  $A\pi$ :

$$A\pi = \frac{wRT}{1 - (\beta w)} - \alpha w^2 \quad (2)$$

In the right-hand side of the above equation, the first and second terms show repulsive and attractive energy of adsorption. By investigating equilibrium adsorption of different systems employing VDW, It was revealed that repulsive term is under-predicted and the attractive term is over-predicted overall. Thus, in order to modify these terms, the following corrections were added to the right-hand side of equation 32:

$$RT \ln(1 + \lambda w) \text{ Repulsive correction term} \quad (3)$$

$$\frac{RT}{1 + \lambda w} \text{ Attractive correction term} \quad (4)$$

Where  $\lambda$  is an additional parameter of the new 2D EOS. Using these two terms, the best results were obtained amongst the numerous different terms tested. As a result, the following equation was obtained for the term  $A\pi$ :

$$A\pi = \frac{wRT}{1 - \beta w} - \alpha w^2 + \frac{RT}{1 + \lambda w} + RT \ln(1 + \lambda w) \quad (5)$$

The main difference between RT and VDW is the addition of the third parameter of  $\lambda$ .

### Mixing rule

For RT equation the following common mixing rule were applied [11]:

$$\alpha = \sum_i \sum_j x_i x_j \alpha_{ij} \quad (6)$$

$$\beta = \sum_i \sum_j x_i x_j \beta_{ij} \quad (7)$$

$$\alpha_{ij} = (1 - C_{ij}) \frac{(\alpha_i + \alpha_j)}{2} \quad (8)$$

$$\beta_{ij} = (1 + D_{ij}) \sqrt{\beta_i \beta_j} \quad (9)$$

$$\lambda = \sum x_i \lambda_i \quad (10)$$

Where  $x_i$  and  $x_j$  are mole fractions of the components  $i$  and  $j$ , and  $C_{ij}$  and  $D_{ij}$  are the binary correction factors which can be determined by fitting the results into mixture experimental data. However, in this study these parameters were set equal to zero. Also  $\alpha$ ,  $\beta$  and  $\lambda$  are the mixture parameters and  $\alpha_i$ ,  $\beta_i$ , and  $\lambda_i$  are the pure parameters of the 2D EOS.

### Fugacity coefficients in adsorbed phase

The fugacity coefficient relation can be derived using the following thermodynamic equation [11]:

$$\ln \hat{\phi}_i = \int_0^w \left\{ \frac{1}{RTw} \left[ \frac{\partial(A\pi)}{\partial w_i} \right]_{T, M_s, n_j} - \frac{1}{w} \right\} dw - \ln Z_a \quad (11)$$

Where  $Z_a$  is the compressibility factor for two-dimensional adsorbate phase which is defined as follows:

$$Z_a = \frac{\pi a}{RT} \quad (12)$$

Where  $a$  is defined as:

$$a = \frac{A}{w} \quad (13)$$

Using the above equations the following general relations for mixture fugacity coefficient of the new EOS were found:

$$\left\{ \begin{array}{l} \ln \hat{\phi}_i = \frac{2 \sum_j \beta_{ij} w_j - \beta w}{(\beta w)^{1-m} - (\beta w)} - \frac{1}{m} \ln[1 - (\beta w)^m] - \\ \quad \ln Z_a + Q_1 + Q_2 + \delta \\ \quad \quad \quad U^2 - 4W > 0 \\ \ln \hat{\phi}_i = \frac{2 \sum_j \beta_{ij} w_j - \beta w}{(\beta w)^{1-m} - (\beta w)} - \frac{1}{m} \ln[1 - (\beta w)^m] - \\ \quad \ln Z_a - \frac{2}{RT} \sum_j \alpha_{ij} w_j + \delta \\ \quad \quad \quad U = W = 0 \end{array} \right. \quad (14)$$

Where  $Q_1$ ,  $Q_2$  and  $\delta$  are:

$$Q_1 = -\frac{2\alpha \sum_j \beta_{ij} w_j - \alpha \beta w}{RT\beta[1 + U(\beta w) + W(\beta w)^2]} \quad (15)$$

$$Q_2 = -\frac{\alpha \beta w + 2\beta \sum_j \alpha_{ij} w_j - 2\alpha \sum_j \beta_{ij} w_j}{RT\beta^2 w \sqrt{U^2 - 4W}}$$

$$\ln \left| \frac{2 + (U + \sqrt{U^2 - 4W})(\beta w)}{2 + (U - \sqrt{U^2 - 4W})(\beta w)} \right| \quad (16)$$

$$\delta = \frac{-\lambda}{1 + \lambda w} + \lambda \quad (17)$$

The term  $w_j$  in the above equations denotes the mass of component  $j$  in the adsorbate-phase mixture. It should be differentiated from  $w_{ij}$  which is the mass of component  $j$  in the pure adsorbate phase. The fugacity coefficient relations for pure components were obtained by taking  $i=j=1$  in the equations, as follows:

$$\ln \phi_i = \frac{\beta_i w_{ii}}{(\beta_i w_{ii})^{1-m} - (\beta_i w_{ii})} - \frac{1}{m} \ln[1 - (\beta_i w_{ii})^m] - \ln Z_a + Q_{01} + Q_{02} + \delta_i \quad (18)$$

Where  $\phi_i$  and  $w_{ii}$  are Fugacity coefficient and the mass of component  $i$  in the pure adsorbed phase.

For  $U^2 - 4W > 0$ :

$$Q_{01} = -\frac{\alpha_i w_{ii}}{RT[1 + U(\beta_i w_{ii}) + W(\beta_i w_{ii})^2]} \quad (19)$$

$$Q_{02} = -\frac{\alpha_i}{RT\beta_i \sqrt{U^2 - 4W}} \ln \left| \frac{2 + (U + \sqrt{U^2 - 4W})(\beta_i w_{ii})}{2 + (U - \sqrt{U^2 - 4W})(\beta_i w_{ii})} \right| \quad (20)$$

$$\delta_i = \frac{-\lambda_i}{1 + \lambda_i w_{ii}} + \lambda_i \quad (21)$$

For  $U = W = 0$ :

$$Q_{01} + Q_{02} = -\frac{2}{RT} \alpha_i w_{ii} \quad (22)$$

$$\delta_i = 0 \quad (23)$$

### Equilibrium calculation for pure-component system

The equilibrium relation for pure component is in the following form:

$$Z_a \phi_i^a w_{ii} = k_i f_i^g \quad (24)$$

Where  $f_i^g$  is fugacity of component  $i$  in the pure gas phase. Also,  $k_i$  is the Henry's constant for single-component adsorption which is the ratio of  $\frac{w_{ii}}{P}$  at very low pressures ( $P \rightarrow 0$ ).

Taking logarithm from both sides of equation 24 yields:

$$f(w_{ii}) = \ln Z_a + \ln \phi_i + \ln w_{ii} - \ln(k_i f_i^g) = 0 \quad (25)$$

Substituting the relation for pure component fugacity coefficient in adsorbed phase gives:

$$f(w_{ii}) = \ln w_{ii} + \frac{(\beta_i w_{ii})^m}{1 - (\beta_i w_{ii})^m} - \frac{1}{m} \ln[1 - (\beta_i w_{ii})^m] + Q_{01} + Q_{02} + \delta_0 - \ln(k_i f_i^g) = 0 \quad (26)$$

Knowing the values of temperature, pressure and also the parameters of  $a_i$ ,  $\beta_i$ ,  $k_i$  and  $\lambda_i$ , one can determine the total amount of the adsorbed phase ( $w_{ii}$ ). The fugacity of pure component  $i$  in gas phase,  $f_i^g$ , was calculated using 3D PR equation of state.

#### Determination of optimum parameters

In order to determine single-component parameters,  $a_i$ ,  $\beta_i$ ,  $k_i$  and  $\lambda_i$ , the adsorption equilibrium several sets of experimental data found in literature for pure component adsorption on a particular adsorbents were used as shown in tables 2 and 3. These parameters were calculated by fitting  $w_{ii}$  determined by the 2D EOS to the experimental data for the pure systems. Then, using the mixing rules one can find the EOS parameters for a multicomponent system with a given composition.

#### Equilibrium calculation for a multi-component system

The equilibrium relations used in equilibrium adsorption calculations of a multi-component system are:

$$Z_a \widehat{\phi}_i^a w_i = k_i \widehat{f}_i^g \quad i = 1, 2, \dots, N_c \quad (27)$$

Where  $N_c$  is the number of components. Knowing temperature, pressure and composition one can determine gas-phase composition  $\{y_i\}$  and adsorbed phase composition  $\{w_i\}$ . Determining the multi-component parameters of  $\alpha$ ,  $\beta$  and  $\lambda$  using the mixing rules one can calculate  $\widehat{\phi}_i^a$  (using equation 14) and  $\widehat{f}_i^g$ , which is the fugacity of component  $i$  in the gas-phase mixture (using 3-

D PR). Substituting these values into the set of equilibrium relations (equation 27), the following system of  $N_c$  equations for  $N_c$  variables which are the amount of each component in adsorbed mixture ( $w_i$ ) was obtained:

$$F_i(w_1, w_2, \dots, w_{N_c}) = \ln w_i + \frac{2 \sum_j \beta_{ij} w_j - \beta w}{(\beta w)^{1-m} - (\beta w)} - \frac{1}{m} \ln[1 - (\beta w)^m] + Q_1 + Q_2 + \delta - \ln(k_i \widehat{f}_i^g) = 0 \quad i = 1, 2, \dots, N_c \quad (28)$$

Solving the above using the iterative Newton numerical method equations one can determine the mass of each component in the adsorbed mixture ( $w_i$ ).

## Result and Discussion

The adsorption equilibrium data predicted by new 2-D EOS (RT) were compared to the ones collected from literature. In order to conduct equilibrium calculations for a multi-component system, the parameters of single component adsorption of all respective constituents are required. It means that a set of adsorption equilibrium data for a multi-component system on a specific adsorbent cannot be employed until the single-component equilibrium data of all components on that particular adsorbent are available. These data are necessary to find the single-component parameters. This fact created a huge restriction on the adsorption equilibrium data released in literature. In this regard, the appropriate sets of data were collected by an extensive literature survey. In this study, 24 sets of pure-component data containing 441 equilibrium points and 15 sets of binary data comprising 175 equilibrium points were used to compare the performances of different 2-D EOSs. Table 4 compares the predictions of various 2-D EOSs with each other and reported their respective relative average deviations (%RAD) which are defined as:

$$\%RAD = \frac{100}{N_c} \sum_{i=1}^{N_c} \left| \frac{w_{ii}^c - w_{ii}^e}{w_{ii}^e} \right| \quad (29)$$

Where  $w_{ii}^c$  and  $w_{ii}^e$  are the calculated and experimental amount of adsorbed phase of pure component  $i$  respectively.

**Table 2.** The comparison of relative average deviations in predicting single-component adsorption equilibrium data using various 2-D EOSs.

System	NP	%RAD						Adsorbent	Adsorbate	T(K)	Ref
		VDW	EYRING	ZGR	SRK	P-R	R-T				
1	16	2.90	2.86	2.84	2.94	2.92	2.88	13X	i-C <sub>4</sub> H <sub>10</sub>	298.15	[12]
2	30	5.04	4.55	4.08	4.75	4.69	3.61	13X	C <sub>2</sub> H <sub>4</sub>	298.15	[12]
3	16	1.48	1.59	1.67	1.48	1.47	1.48	13X	i-C <sub>4</sub> H <sub>10</sub>	323.15	[12]
4	25	2.70	2.77	2.99	2.66	2.67	2.77	13X	C <sub>2</sub> H <sub>4</sub>	323.15	[12]
5	31	2.92	2.32	4.61	3.32	3.46	1.97	13X	C <sub>2</sub> H <sub>6</sub>	298.15	[12]
6	20	2.47	1.75	3.00	2.67	2.77	2.63	13X	C <sub>2</sub> H <sub>6</sub>	323.15	[12]
7	20	5.44	4.87	4.11	5.06	4.84	2.69	13X	CO <sub>2</sub>	298.15	[12]
8	17	2.65	2.77	3.00	2.56	2.56	2.69	13X	CO <sub>2</sub>	323.15	[12]
9	18	0.54	1.95	4.07	0.53	0.52	0.54	13X	CH <sub>4</sub>	300	[13]
10	15	2.57	1.74	2.36	1.74	1.86	1.83	13X	C <sub>3</sub> H <sub>8</sub>	300	[13]
11	18	3.95	3.94	4.63	3.95	3.94	4.00	5A	CH <sub>4</sub>	300	[13]
12	15	0.91	1.21	2.26	1.18	1.23	0.82	5A	C <sub>2</sub> H <sub>6</sub>	300	[13]
13	12	6.13	5.34	5.23	5.65	5.74	5.58	5A	C <sub>3</sub> H <sub>8</sub>	300	[13]
14	38	3.81	2.59	2.20	2.44	1.98	2.11	13X	CO <sub>2</sub>	293	[14]
15	30	0.76	1.28	2.90	1.43	1.64	0.55	13X	C <sub>2</sub> H <sub>6</sub>	293	[14]
16	5	2.44	4.35	6.67	2.15	1.99	2.37	4A	C <sub>3</sub> H <sub>8</sub>	423	[15]
17	20	2.99	3.06	3.21	3	3.01	2.99	4A	C <sub>3</sub> H <sub>6</sub>	423	[15]
18	5	2.25	2.12	2.50	2.24	2.24	2.25	4A	C <sub>3</sub> H <sub>8</sub>	473	[15]
19	18	2.71	3.06	3.68	2.76	2.78	2.70	4A	C <sub>3</sub> H <sub>6</sub>	473	[15]
20	19	0.50	0.53	0.59	0.50	0.50	0.51	10X	O <sub>2</sub>	298	[16]
21	19	0.35	0.30	0.25	0.34	0.33	0.26	10X	N <sub>2</sub>	298	[16]
22	12	2.04	0.60	3.12	1.82	1.64	.49	Norit R1	CH <sub>4</sub>	298	[17]
23	10	.84	2.03	5.18	0.79	0.76	.69	Norit R1	N <sub>2</sub>	298	[17]
24	12	3.36	1.58	3.28	3.07	2.87	1.63	Norit R1	CO <sub>2</sub>	298	[17]
TOTALL	441	2.67	2.47	3.14	2.54	2.51	2.09	----	----	----	----

**Table 3.** The comparison of relative average deviations in predicting multi-component adsorption equilibrium data using various 2-D EOSs.

NAME	Adsorbate	Adsorbent	T (K)	P (KPa)	Quantities
A	i-C <sub>4</sub> H <sub>10</sub> (1)-C <sub>2</sub> H <sub>4</sub> (2)	13X Zeolite	298.15	137.8	wi w
B	i-C <sub>4</sub> H <sub>10</sub> (1)-C <sub>2</sub> H <sub>4</sub> (2)	13X Zeolite	323.15	137.8	wi w
C	i-C <sub>4</sub> H <sub>10</sub> (1)-C <sub>2</sub> H <sub>6</sub> (2)	13X Zeolite	298.15	137.8	wi w
D	i-C <sub>4</sub> H <sub>10</sub> (1)-C <sub>2</sub> H <sub>6</sub> (2)	13X Zeolite	323.15	137.8	wi w
E	C <sub>2</sub> H <sub>4</sub> (1)-CO <sub>2</sub> (2)	13X Zeolite	298.15	137.8	wi w
F	C <sub>2</sub> H <sub>4</sub> (1)-CO <sub>2</sub> (2)	13X Zeolite	323.15	137.8	wi w
G	CH <sub>4</sub> (1)-C <sub>3</sub> H <sub>8</sub> (2)	13X Zeolite	300	345	wi w
H	CH <sub>4</sub> (1)-C <sub>2</sub> H <sub>6</sub> (2)	5A Zeolite	300	345	wi w
I	C <sub>2</sub> H <sub>6</sub> (1)-C <sub>3</sub> H <sub>8</sub> (2)	5A Zeolite	300	345	wi w
J	CO <sub>2</sub> (1)-C <sub>2</sub> H <sub>6</sub> (2)	13X Zeolite	293	101.3	wi w
K	C <sub>3</sub> H <sub>6</sub> (1)-C <sub>3</sub> H <sub>8</sub> (2)	4A Zeolite	423	84.61-98.41	wi w

L	C <sub>3</sub> H <sub>6</sub> (1)-C <sub>3</sub> H <sub>8</sub> (2)	4A Zeolite	473	102.93-118.99	w <sub>i</sub> w
M	O <sub>2</sub> (1)-N <sub>2</sub> (2)	10X Zeolite	298	6.38-28.65	w <sub>i</sub> w
N	CH <sub>4</sub> (1)-N <sub>2</sub> (2)	Activated carbon	298	151-5975	w <sub>i</sub> w
O	CH <sub>4</sub> (1)-CO <sub>2</sub> (2)	Activated carbon	298	98-5916	w <sub>i</sub> w
OVERALL					w <sub>i</sub> w

VDW	Eyring	ZGR	SRK	PR	R-T	NP	ref
%RAD							
24.65	23.35	22.70	22.25	19.77	5.69	10	[12]
3.86	3.70	3.50	3.54	3.21	2.20		
8.28	9.25	10.30	16.99	9.80	5.24	8	[12]
3.97	4.62	4.29	3.71	4.32	2.52		
37.43	36.54	38.16	44.03	49.51	32.21	10	[12]
6.38	6.38	6.77	6.79	6.69	6.07		
31.57	29.81	30.04	33.24	34.24	22.51	7	[12]
4.25	4.03	4.86	3.97	4.03	5.39		
11.51	10.24	9.67	15.36	20.57	12.70	6	[12]
5.72	4.00	3.18	5.82	8.03	1.06		
9.04	8.87	18.84	14.06	17.13	8.64	5	[12]
3.00	1.55	1.24	4.20	5.75	1.25		
43.94	26.67	18.45	50.91	50.97	26.95	8	[13]
1.68	2.99	3.88	1.71	1.90	3.41		
13.90	13.71	13.45	14.18	14.77	14	27	[13]
6.62	6.24	6.06	7.64	8.35	6.04		
20.21	21.33	21.40	20.72	19.88	22.32	16	[13]
6.90	6.99	6.94	6.99	7.22	6.72		
9.90	10.09	7.23	40.4	49.31	10.25	6	[14]
5.09	5.030	4.19	9.31	14.21	1.81		
11.37	12.20	14.13	9.25	11.52	11.18	7	[15]
2.88	2.64	2.77	3.15	4.06	2.32		
10.89	12.50	14.82	9.46	8.98	10.85	6	[15]
3.26	3.44	3.99	3.45	3.80	2.97		
11.19	33.64	6.92	11.27	10.79	10.08	11	[16]
1.74	18.85	9.43	3.49	4.01	2.34		
16.64	10.46	8.37	10.56	10.60	9.51	24	[17]
3.72	4.12	5.78	4.54	6.16	3.69		
22.66	18.13	18.72	20.11	20.44	18.33	24	[17]
3.50	2.64	3.55	4.66	6.14	2.82		
19.10	18.22	16.36	20.22	20.79	15.04	175	
4.44	5.37	5.13	5.17	6.11	3.87		

As expected, the results obtained by all EOSs are in good agreement with the experimental data for pure-component systems. Adsorption of propane on zeolite 5A using VDW having %RAD of 6.13 is the worst case. This table shows that RT EOS having the total relative average error of 2.09 demonstrates the best performance, while the highest total average error is associated with ZRG having the error of 3.14. Using the optimum values of the single-component parameters ( $\alpha_i$ ,  $\beta_i$ ,  $k_i$  and  $\lambda_i$ )

obtained through the calculations related to table 4, the multicomponent parameters ( $\alpha$ ,  $\beta$  and  $\lambda$ ) were determined. Table 5 shows the relative average deviations, %RAD ( $w_i$ ) and %RAD( $w$ ), of different 2-D EOSs for binary systems. These relative errors were calculated using the following equations:

$$\%AAD(w_i) = \frac{100}{N_c N_p} \sum_{i=1}^{N_c} \sum_{j=1}^{N_p} \left| \frac{w_i^c(j) - w_i^e(j)}{w_i^e(j)} \right|$$

(30)

$$\%AAD(w) = \frac{100}{N_p} \sum_{j=1}^{N_p} \left| \frac{w^c(j) - w^e(j)}{w^e(j)} \right| \quad (31)$$

Where  $N_C$  is the total number of components and  $N_p$  is the total number of equilibrium points in a set of data. The superscript  $c$  and  $e$  stand for calculated and experimental respectively.  $w$  and  $w_i$  are total amount of adsorbed phase and the amount of component  $i$  in adsorbed phase respectively.

As it is apparent from Table 3, RT equation of state having  $\%RAD(w_i)=15.04$  and  $\%RAD(w)=3.87$  reveals the best prediction among the others. PR is ranked as the worst

having  $\%RAD(w_i)=20.79$  and  $\%RAD(w)=6.11$ . The good prediction of highly-nonideal systems where shows azeotropic behavior is the primary advantage of the new EOS. In order to demonstrate this capability, three sets of experimental data showing highly-nonideal behavior were selected to be compared with the predictions of different EOSs. For each case the single-component parameters and  $\%RAD$  for various EOSs are shown through the tables. Also, the variation of one component ( $w_i$ ) and total ( $w$ ) adsorbed amounts were plotted versus mole fraction of one component. Because of the limitation of the data released in literature on gas adsorption, the following three cases were considered.

### Case 1: Adsorption of isobutene-ethylene on zeolite 13X

**Table 4.** The single-component parameters and  $\%RAD$  for various EOSs

Adsorbate	2-D-EOS	NP	$10^{-4} \alpha_i$	$\beta_i$	$\ln k_i$	$\lambda_i$	$\%AAD$	P (KPa)	T (K)	Ref
Iso-butane	VDW	16	-2.286	0.4074	8.554	---	2.90	24-137.84	298.15	[12]
	Eyring	16	-0.0452	0.3680	8.953	---	2.86	24-137.84	298.15	
	ZGR	16	1.829	0.3439	9.993	----	2.84	24-137.84	298.15	
	SRK	16	-3.782	0.4135	9.069	----	2.94	24-137.84	298.15	
	P-R	16	-4.416	0.4104	9.126	----	2.92	24-137.84	298.15	
	R-T	16	-1.872	0.3912	8.405	-0.3912	2.88	24-137.84	298.15	
Ethylene	VDW	30	-0.4643	0.2362	5.065	----	5.04	24-137.84	298.15	[12]
	Eyring	30	0.6790	0.2093	5.612	----	4.55	24-137.84	298.15	
	ZGR	30	1.802	0.1973	6.627	----	4.08	24-137.84	298.15	
	SRK	30	-0.6323	0.2405	5.129	----	4.75	24-137.84	298.15	
	P-R	30	-0.7564	0.2396	5.157	----	4.69	24-137.84	298.15	
	R-T	30	0.3001	0.2559	6.131	2.406	3.61	24-137.84	298.15	

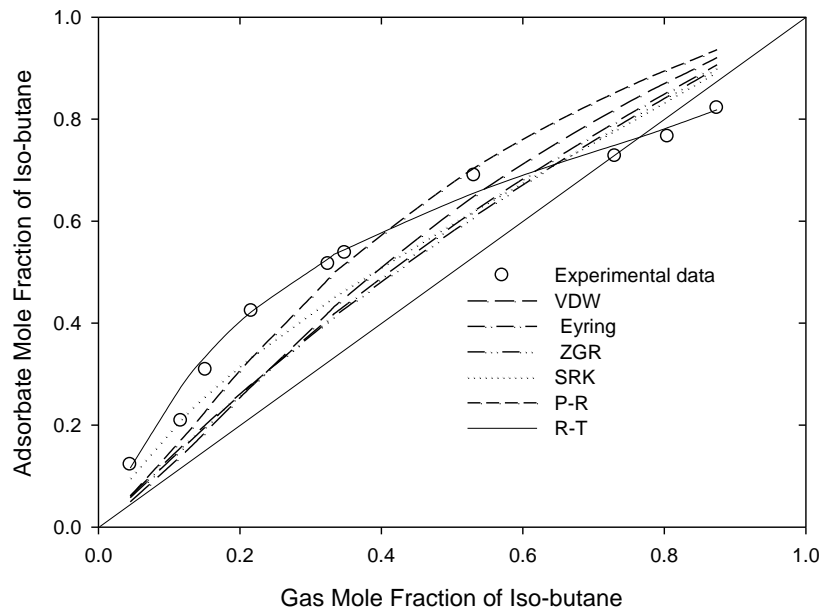


Figure 1. The variation of adsorbate mole fraction of isobutene versus gas mole fraction of isobutene.

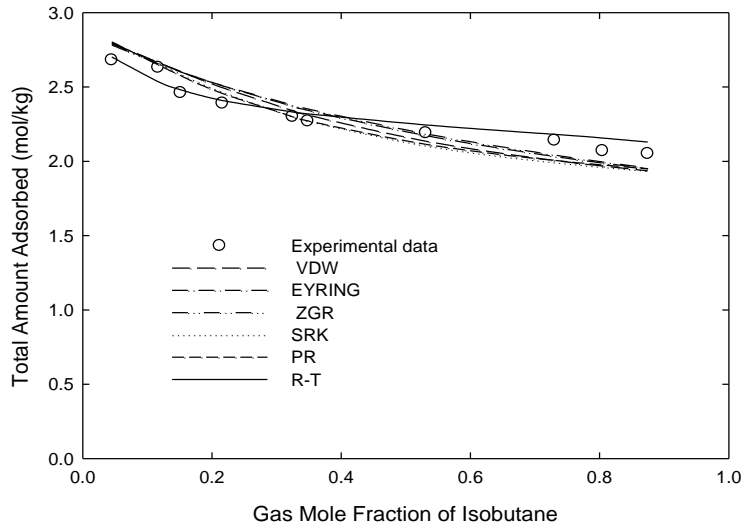
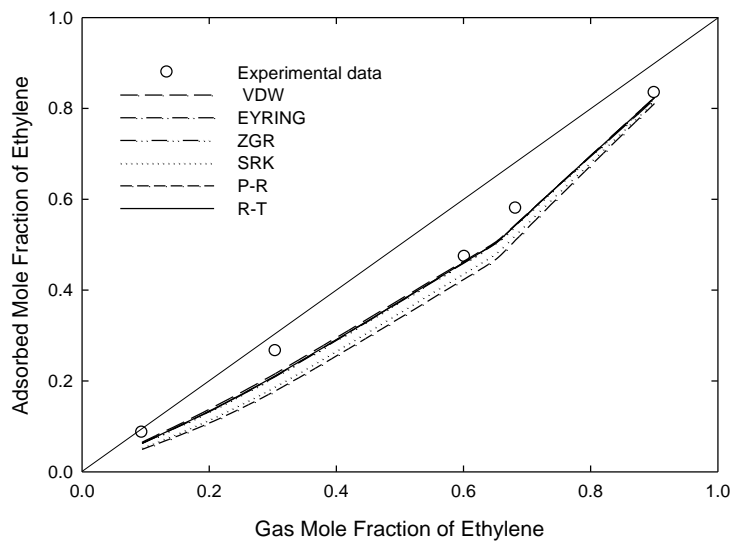


Figure 2. the variation of total amount of adsorbate versus gas mole fraction of isobutene.

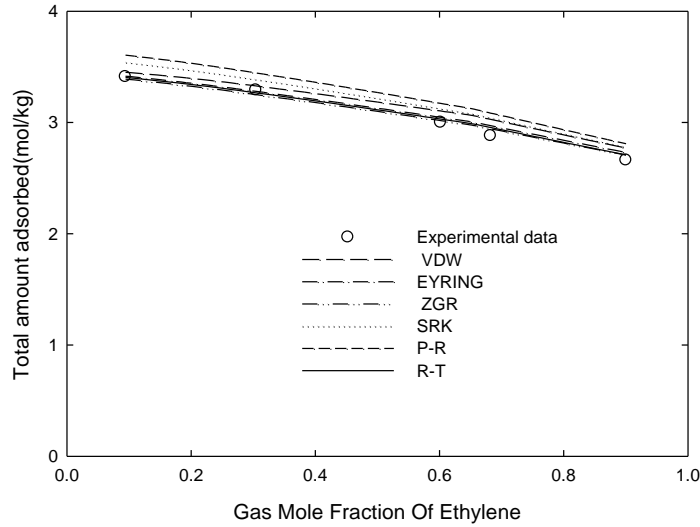
## Case 2: Adsorption of carbon dioxide-ethylene on zeolite 13X

Table 5. The single-component parameters and %RAD for various EOSs

Adsorbate	2-D-EOS	NP	$10^{-4} \alpha_i$	$\beta_i$	$\ln k_i$	$\lambda_i$	%AAD	P (KPa)	T (K)	Ref
Ethylene	VDW	25	-6.322	0.2108	3.887	---	2.70	67-137.87	323.15	[12]
	Eyring	25	6.527	0.1968	4.375	---	2.77	67-137.87	323.15	
	ZGR	25	20.170	0.1942	5.335	---	2.99	67-137.87	323.15	
	SRK	25	-7.511	0.2236	3.926	---	2.66	67-137.87	323.15	
	P-R	25	-8.822	0.2233	3.951	---	2.67	67-137.87	323.15	
	R-T	25	1.497	0.2479	4.210	1.419	2.77	67-137.87	323.15	
Carbon dioxide	VDW	17	-8.398	0.0966	4.0477	---	2.65	0.44-137.84	323.15	[12]
	Eyring	17	1.120	0.1180	4.4618	---	2.77	0.44-137.84	323.15	
	ZGR	17	11.470	0.1265	5.3763	---	3	0.44-137.84	323.15	
	SRK	17	-8.481	0.1333	4.0770	---	2.56	0.44-137.84	323.15	
	P-R	17	-9.670	0.1356	4.1082	---	2.56	0.44-137.84	323.15	
	R-T	17	-2.571	0.1505	4.2643	1.080	2.69	0.44-137.84	323.15	





**Figure 3.** The variation of adsorbate mole fraction of ethylene versus gas mole fraction of ethylene.**Figure 4.** The variation of total amount of adsorbate versus gas mole fraction of ethylene.**Case 3: Adsorption of Nitrogen-oxygen on zeolite 10X****Table 6.** The single-component parameters and %RAD for various EOSs

Adsorbate	2-D-EOS	NP	$10^{-4} \alpha_i$	$\beta_i$	$\ln k_i$	$\lambda_i$	%AAD	P (KPa)	T (K)	Ref
Oxygen	VDW	25	12.6552	0.5593	-1.852	---	0.505	92.9-212.39	273.15	[16]
	Eyring	25	67.6354	0.8062	-1.368	---	0.537	92.9-212.39	273.15	
	ZGR	25	128.2308	0.9011	-0.3409	----	0.592	92.9-212.39	273.15	
	SRK	25	11.0082	0.4634	-1.855	----	0.504	92.9-212.39	273.15	
	P-R	25	10.7484	0.4289	-1.858	----	0.503	92.9-212.39	273.15	
	R-T	25	32.0132	0.7882	-1.831	1.244	0.510	92.9-212.39	273.15	
Nitrogen	VDW	17	-10.8017	5.00E-05	-0.3447	----	0.351	99.5-212.4	273.15	[16]
	Eyring	17	0.9828	0.1212	0.0285	----	0.307	99.5-212.4	273.15	
	ZGR	17	12.3812	0.1370	0.9070	----	0.253	99.5-212.4	273.15	
	SRK	17	-9.2520	0.0917	-0.3313	----	0.342	99.5-212.4	273.15	
	P-R	17	-9.7411	0.1022	-0.3143	----	0.333	99.5-212.4	273.15	
	R-T	17	18.4780	0.4298	0.8526	3.199	0.262	99.5-212.4	273.15	

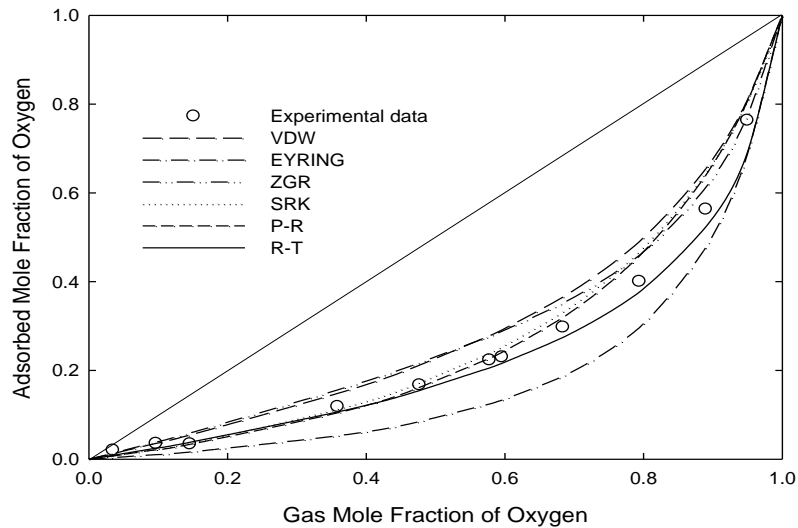


Figure 5. the variation of adsorbate mole fraction of oxygen versus gas mole fraction of oxygen.

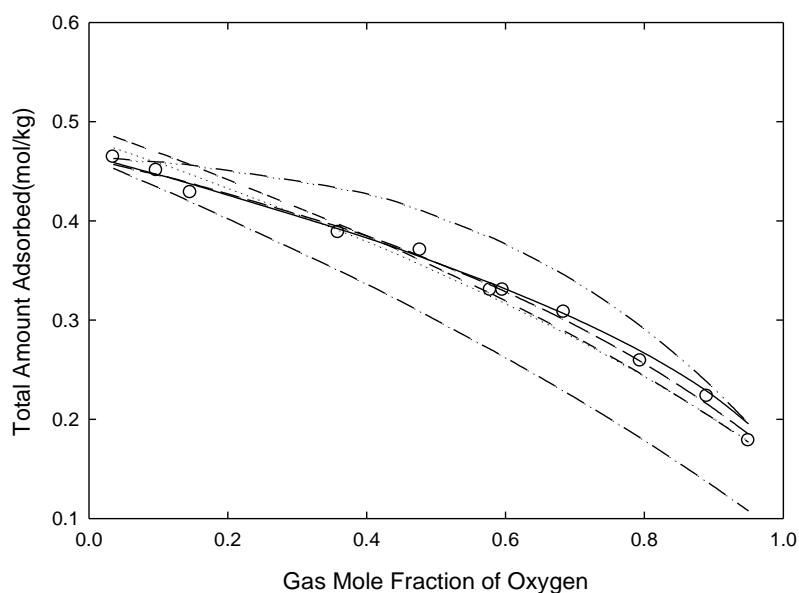


Figure 6. The variation of total amount of adsorbate versus gas mole fraction of oxygen.

As it can be seen from figures 1 through 6 for all cases, especially for case 1, the performance of the RT EOS outreaches the rest significantly.

## Conclusion

In the present study a new 2D-EOS was developed based on VDW EOS. The repulsive and attraction terms of VDW were modified to have more agreement with the experimental data of gas-mixture adsorption equilibrium. The performance of the new equation, RT, is better than five other EOSs. RT EOS needs 3 parameters compared to the other EOSs which require two parameters. However, it is not a disadvantage for this EOS as all parameters must be determined by tuning the pure parameters with the experimental data, and all types of EOS are subject to this restriction. The primary advantage of RT EOS is its high capability of predicting azeotrope gas mixtures which make it distinguished among the others. Both negative and positive values of  $\alpha$  were obtained for 2D-EOSs, while the equivalent parameter for 3D-EOSs is always positive. It can be attributed to the fact that adsorption equilibrium is not only a function of involved gases but also it depends on the adsorbent characteristics.

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