

Thermodynamical VLE modeling of water and methanol mixture using PRSV2 equation of state

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Abstract

Nowadays, researchers are trying to synthesis a hundreds of new material that acquiring their thermodynamical properties using experimental procedure is impossible. So by using modeling softwares and accessibility of thermodynamical equations, thermodynamic and equilibrium properties can be predicted accurately. PRSV2 equation of state is a modified form of Peng-Robinson EOS that is recently considered by researchers for prediction of multicomponent mixtures thermodynamic equilibrium behavior. In this study is tried to emphasize on advantages of VLE thermodynamic modeling using EOS for liquid and vapor phases rather than using EOS for vapor phase and activity coefficient method for liquid phase. Equilibrium calculations were performed using experimental data in two condition of isothermal and isobar. In two condition advantages of using EOS for vapor and EOS for liquid rather than using EOS for vapor and activity model for liquid has been demonstrated. A first order equation was obtained to show the dependence of k_{ij} to temperature that has shown good relation in the temperature range $TR < 0.7$.

KEYWORDS

Thermodynamic properties, prsv2 equation of state, VLE(vapor-liquid equilibrium), binary coefficient

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1. introduction

Thermodynamic liquid-vapor equilibrium is determined primarily by two general methods. These two methods are the fugacity coefficient for both liquid and vapor phase in which the equation of state is used for both phases equilibrium calculation and the second method is that the fugacity coefficient is used for vapor phase equilibrium calculation and the activity coefficient is used for liquid phase equilibrium calculation.

There are a lots of equation of state and activity models that has been used to vapor liquid equilibrium calculation which can be mentioned to Peng-Robinson, PRSV2, SRK and van der waals equations of state and Wilson, NRTL and UNIQUAC activity models.

Simple equations of state at high pressures don't offer an accurate prediction of the vapor phase behavior. For such non ideal systems using a good mixing rules can increase the equations of state prediction ability significantly, so the fugacity coefficient of the vapor and liquid fugacity coefficient can be used instead of the fugacity coefficient of the vapor and liquid activity coefficient.

PRSV2 equation of state is a modified form of peng-robinson equation that its calculation Accuracy for pure and multi-component mixtures is improved by using three adjustable parameters named k_1 , k_2 and k_3 . In this study, VLE behavior of the water and methanol mixture is modeled in two main methods consisting of using PRSV2 equation of state for both phases and using of the peng-robinson equation of the state for vapor phase and NRTL activity model for liquid phase and then the isothermal vapor pressure of the mixture in different mole fractions of the methanol is calculated using the obtained values of the k_1 , k_2 and k_3 and the superiority of the PRSV2 EOS was proved clearly.

1.1. PRSV2 equation of state

The PRSV2 Equation of the state is in the form of the peng-robinson EOS

$$P = \frac{RT}{v-b} - \frac{a}{v^2+2bv-b^2} \quad (1)$$

That

$$a = \left(0.457235 \frac{R^2 T_c^2}{P_c}\right) \alpha \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha = [1 + k(1 - T_R^{0.5})]^2 \quad (4)$$

The parameter k in peng-robinson EOS is just a function of the acentric factor ω while in PRSV2 EOS the parameter k is a function of the acentric factor ω and reduced temperature T_R

$$m_i = k_0 + [k_1 + k_2(k_3 - T_R)(1 - T_R^{0.5}) * (1 + T_R^{0.5})(0.7 - T_R)] \quad (5)$$

That k_0 parameter is

$$k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (6)$$

In the above relations the parameters k_1 , k_2 and k_3 are the adjustable parameters for pure components. In this study primary values of the parameters k_1 , k_2 and k_3 for calculation procedure are obtained from Previous studies[1].

As mentioned in Previous studies peng-robinson EOS is available for hydrocarbons and less polar mixtures in reduced temperatures equal to 0.7 or greater but PRSV2 EOS is useful for all components regardless of the size, form and their polarities[2].

1.2. Mixing rules used in vapor liquid equilibrium

The mixing rule was used in this study is

$$b = \sum x_i b_i \quad (7)$$

$$a = \sum x_i x_j a_{ij} \quad (8)$$

The fugacity coefficient of the component i in multicomponent mixtures is defined as

$$\ln(\varphi_i) = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \left(\frac{\bar{a}_i}{a} + 1 - \frac{b_i}{b} \right) \ln \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \quad (9)$$

$$\bar{a}_i = \left(\frac{\partial n_a}{\partial n_i} \right)_{n_j \neq i} \quad (10)$$

Below relations have good result for calculating parameter a_{ij}

a) Relation without the binary interaction coefficient

$$a_{ij} = (a_{ii} \cdot a_{jj})^{0.5} \quad (11)$$

b) Relation with one of the van der waals binary interaction coefficient

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \quad (12)$$

c) Relation with two margules binary interaction coefficient

$$a_{ij} = (a_{ii} \cdot a_{jj})^{0.5} (1 - x_i k_{ij} - x_j k_{ji}) \quad (13)$$

d) Relation with two van laar binary interaction coefficient

$$a_{ij} = (a_{ii} \cdot a_{jj})^{0.5} \left(1 - \frac{k_{ij} k_{ji}}{x_i k_{ij} + x_j k_{ji}} \right) \quad (14)$$

In this study because of the better flexibility for water and methanol mixture the Relation with one of the van der waals binary interaction coefficient was used for calculations of a_{ij} . Also the NRTL activity model was used for liquid phase and for isothermal VLE calculation the value of the binary interaction coefficient k_{ij} was fitted using experimental data and the P-xy figure was plotted [3,4].

In isobar calculations the VLE modeling was done in different temperatures and the primarily linear equation obtained for binary interaction coefficient k_{ij} .

2. Results and discussion

2.1. Isothermal VLE calculation for water and methanol mixture

For isothermal modeling, the experimental data of the water and methanol mixtures vapor pressure in different mole fractions and in temperature $T=312.91\text{k}$ and pure component data were supplied from Dortmund data bank and given in table 1 [5].

Table 1. Experimental vapor pressure data of the water and methanol mixture[5].

Methanol mole fraction in liquid phase(x_1)	Methanol mole fraction in vapor phase(y_1)	Experimental pressure(kp)	Methanol mole fraction in liquid phase(x_1)	Methanol mole fraction in vapor phase(y_1)	Experimental pressure(kp)
0.0478	0.259	9.079	0.2866	0.7383	18.425
0.0925	0.4562	11.412	0.3065	0.7612	19.025
0.0925	0.4668	11.506	0.3716	0.8053	20.705
0.1335	0.6214	13.012	0.4172	0.8048	21.532
0.1523	0.6164	13.786	0.4362	0.8238	22.318
0.1809	0.6486	14.639	0.5033	0.8457	23.385
0.2032	0.6734	15.785	0.5933	0.8619	25.091
0.2027	0.6796	15.879	0.6917	0.8835	26.998
0.2228	0.6954	16.319	0.6949	0.8974	27.518
0.2557	0.7263	17.599	0.8002	0.9536	29.744
0.2866	0.7383	18.425	0.927	0.9761	32.571

The procedure of the this modeling is beginning by carrying out the flash calculation for mixture and obtaining the values of the k_1 , k_2 and k_3 for PRSV2 EOS. These values are the point that the vapor liquid equilibrium is done and the fugacity of the phases becoming equal.

The result of the k_1 , k_2 and k_3 calculations are given in table 2 and the values of the k_0 for water and methanol that gained using related equation and the acentric factor are 0.8716 and 1.1699 respectively.

This study has done in 21 points of the mole fraction for isothermal modeling in two case, one time by using PRSV2 EOS for both vapor and liquid phases and again by using peng-robinson EOS for vapor phase and the NRTL activity model for liquid phase. For the first case, the calculated vapor pressures had an error $\%10^{-4}$ rather than experimental data and for the second case the error was higher near $\%10$. These results are showing the advantages of the PRSV2 EOS and EOS using for both phases. P-xy diagram and the numerical result of the mixture properties and the errors are given in table 3 and figure 1.

Table 2. Results obtained for k_1 , k_2 and k_3 for water and methanol in different mol fractions.

methanol			$K_0 = 1.1699$	water			$K_0 = 0.8716$
k_1	k_2	k_3	k	k_1	k_2	k_3	k
-0.0032	0.0055	-0.0026	1.1713	0.0145	0.0075	-0.0079	0.8004
-0.0071	0.0084	-0.0016	1.1768	0.0236	0.0149	-0.0124	0.7476
-0.0072	0.0085	-0.0016	1.1769	0.0239	0.0151	-0.0127	0.7458
-0.0089	0.0104	-0.0018	1.1786	0.0302	0.0191	-0.0157	0.7127
0.0111	-0.0174	-0.0374	1.1636	0.033	0.0207	-0.0142	0.6984
0.0144	-0.0205	-0.0398	1.1596	0.0386	0.0203	-0.0192	0.6808
0.0248	-0.0281	-0.0396	1.145	0.049	0.0151	-0.0267	0.6618
0.0251	-0.0283	-0.04	1.1447	0.0493	0.0152	-0.0269	0.6603
0.0181	-0.021	-0.0469	1.1523	0.0431	0.0258	-0.0118	0.6492
0.026	0.0312	0.0071	1.0837	0.051	0.017	-0.0924	0.6477
0.0643	0.0386	0.0091	0.9945	0.021	0.0326	-0.1163	0.6973
0.0477	-0.0086	-0.0664	1.0766	0.0197	0.056	-0.0533	0.632
0.0797	-0.0091	-0.1049	1.0089	0.0446	0.0072	-0.0134	0.7006
0.0723	0.0037	-0.0087	1.0113	0.0159	0.0223	-0.0366	0.7499
0.06	0.0428	-0.0346	0.9985	-0.0014	0.0105	-0.0257	0.8441
0.0472	0.0337	-0.0271	1.0352	-0.0009	0.0084	-0.0205	0.8491
0.0411	0.0103	0.0007	1.0718	0.0181	-0.0213	-0.0343	0.8768
0.0276	0.0069	0.0002	1.104	0.0122	-0.0143	-0.0231	0.8747
0.0296	0.0074	0.0003	1.0991	0.0132	-0.0154	-0.0248	0.8748
0.0194	0.0056	-0.0132	1.1227	0.0053	-0.0199	0.0004	0.914
0.0114	0.0034	-0.0074	1.1422	0.0032	-0.0118	0	0.8968

Table 3. Calculated errors for both modeling methods rather than experimental data.

mixture	method	Absolute average errors/ AAD	Root mean square errors (RMS)
Water - methanol	PRSV2(Φ - Φ)	0.000624	0.000113
	Nrtl+Pr (γ - Φ)	10.2819	1.7665

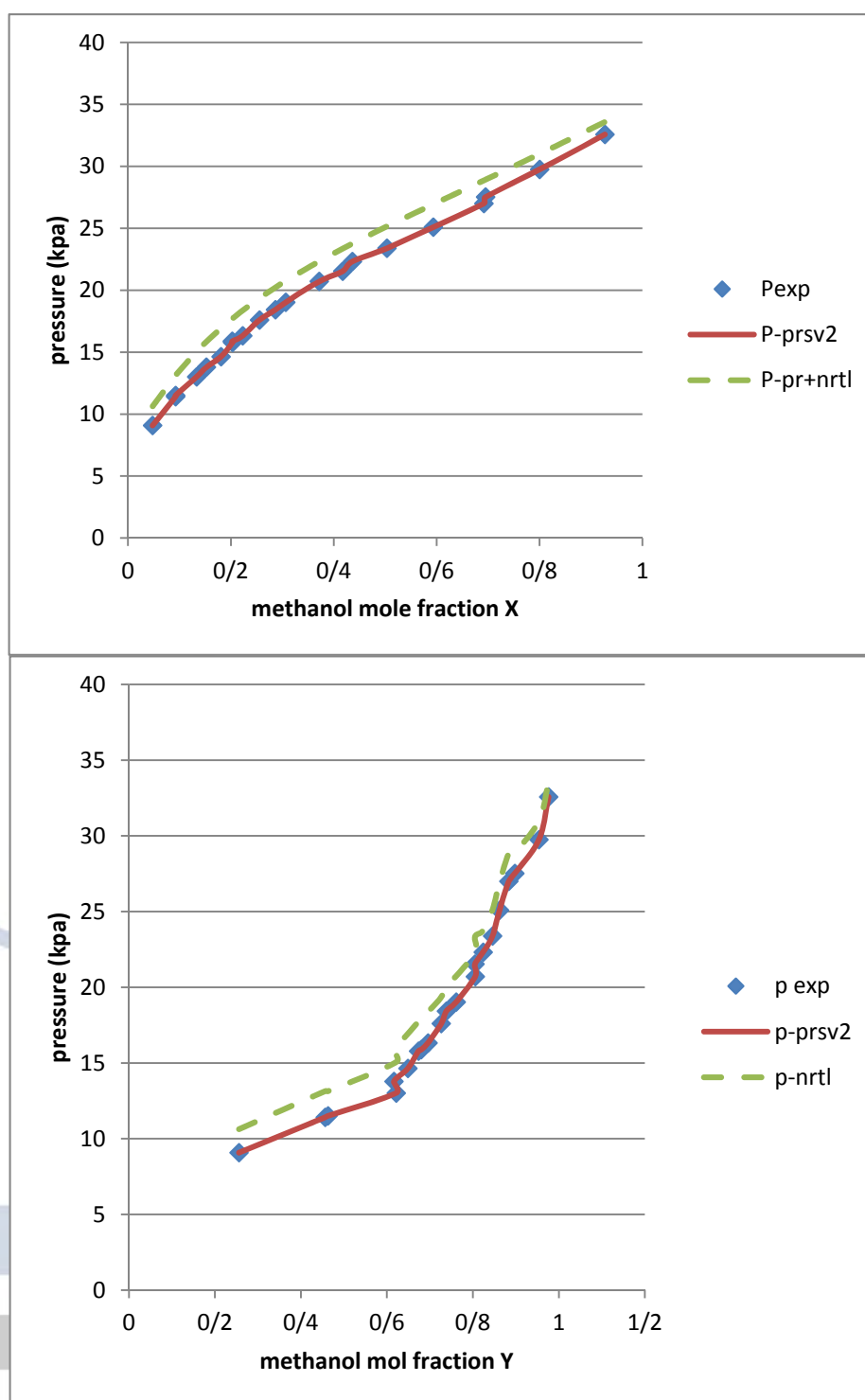


Figure 1. Φ - Φ and Φ - γ methods results given in vapor pressure P-xy diagrams

2.2. Isobar VLE calculation for water and methanol mixture

For water and methanol isobar VLE modeling experimental data of the mole fractions and equilibrium temperature at constant pressure $P=98$ kpa was obtained from Dortmund data bank and given in table 4.

Table 4. Experimental equilibrium temperature for water and methanol mixture in P = 98kp [5].

Temperature [K]	Methanol mole fraction in liquid phase(x_1) [mol/mol]	Methanol mole fraction in vapor phase(y_1) [mol/mol]
369.65	0.0084	0.103
365.45	0.0258	0.227
360.65	0.068	0.391
353.25	0.137	0.568
349.05	0.24	0.68
343.75	0.48	0.79
341.85	0.572	0.82
339.55	0.741	0.906

In isobar calculation, the values of the k_1 , k_2 and k_3 are constant because of the constant pressure but the value of the K that is a function of the k_1 , k_2 and k_3 and reduced temperature, is variable.

Calculated vapor pressures in isobar modeling of the water and methanol mixture using PRSV2 for both vapor and liquid phases are given in table 5.

Table 5. Calculated and experimental vapor pressures and the calculated errors.

x_1 exp	P_{exp} (Kpa)	P_{cal} (Kpa)	ΔP^2	%AD	RMS	%AAD
0.0084	98	97.9893	0.00000049	0.000714	0.00029	0.00022
0.0258	98	97.9902	0.00000004	0.000204		
0.068	98	97.9901	0.00000001	0.000102		
0.137	98	97.9899	0.00000001	0.000102		
0.24	98	97.9902	0.00000004	0.000204		
0.48	98	97.9901	0.00000001	0.000102		
0.572	98	97.9898	0.00000004	0.000204		
0.741	98	97.9901	0.00000001	0.000102		

The main purpose of the isobar modeling is to achieve a primary linear equation for binary interaction coefficient k_{ij} to show its dependence to temperature, so the values of the k_{ij} were given in figures 2,3 and the equation obtained using first order linearization for k_{ij} is

$$k_{ij} = -0.0017 T + 0.5597 \quad (16)$$

$$R^2 = 0.8093 \quad (17)$$

As shown in results, the calculations are almost accurate except in two points of temperatures 365.45k and 369.65k that the values of the k_{ij} were deviated from normal procedure at these points. This deviation can be explained by the restriction of $T_R < 0.7$ that is in equation 5. The points of the temperatures 365.45k and 369.65k are in the range of the $T_R > 0.7$ for methanol and this make the deviation in calculations and if these points eliminate

from the calculations, the primary linear equation for binary interaction coefficient k_{ij} will achieve in form of

$$k_{ij} = -0.0027 T + 0.8836 \quad (18)$$

$$R^2 = 0.9197 \quad (19)$$

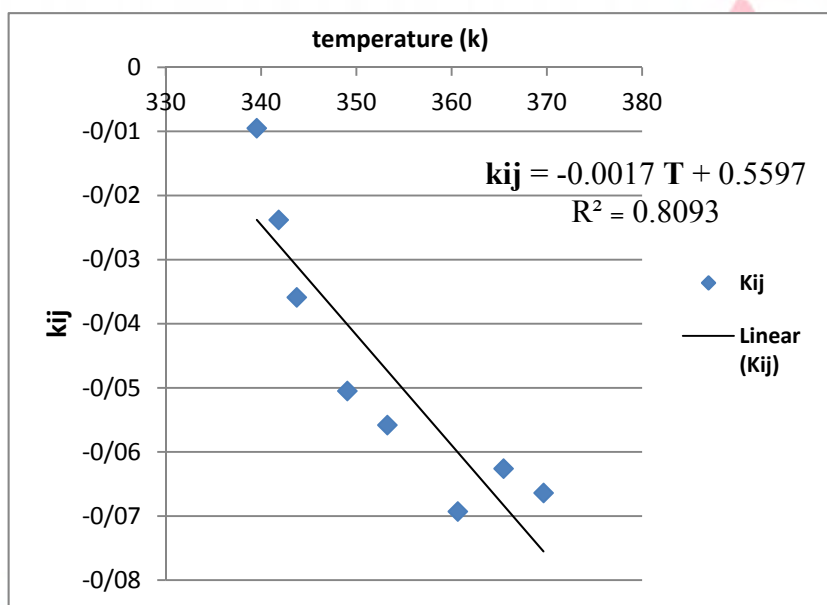


Figure 2. Calculated binary interaction coefficient k_{ij} in different temperature

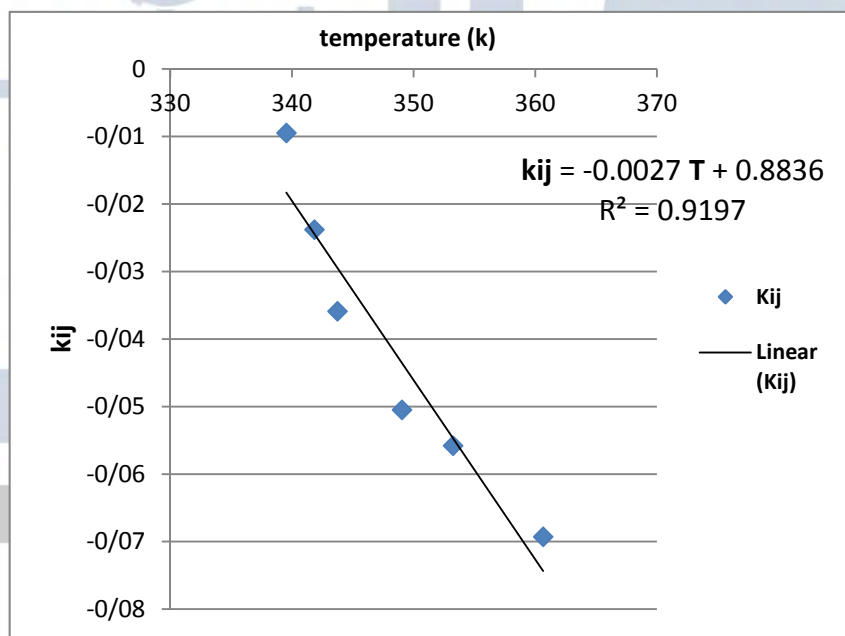


Figure 3. Calculated binary interaction coefficient k_{ij} with the elimination of the temperatures 369.65 k, 365.45 k

3. Results

In isothermal VLE of the water and methanol mixture the superiority of the fugacity coefficient method for both vapor and liquid phases ($\Phi - \Phi$ Approach) rather than fugacity coefficient for vapor phase and activity coefficient for liquid ($\gamma - \Phi$ Approach) was proved. The calculated errors for both methods have shown the accuracy and well performance of the equation of the state for both phases.

In isobar VLE of the water and methanol mixture the calculated values for the binary interaction coefficient obtained as a function of the temperature and the linear equation was achieved that the restriction of the mixing rule was shown in the temperatures out of the restriction of $T_R < 0.7$.

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