Estimation of Activity Coefficients for binary mixture VLE Data using MATLAB

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Abstract: Vapor- liquid equilibrium data for three strongly associated binary systems was taken for estimation of parameters of four different thermodynamic models by developing a general code using optimization techniques in MATLAB software. Isobaric vapor-liquid equilibrium measurements are considered in this work for three binary systems methanol-ethanoic acid, methanol-water and water-ethanoic acid at 101.325 kpa. None of the systems form an azeotrope. The activity coefficient has been calculated taking into consideration the non-ideality of the mixture. The experimental T, x, y data are used to estimate nonrandom two-liquid (NRTL), Wilson, Margules and VanLaar model parameters, and these parameters in turn are used to calculate vapor phase compositions. The activity coefficients of the solution were correlated with NRTL, Wilson, Margules, and VanLaar models through fitting by least-squares method. The VLE data of binary system were well predicted from these binary interaction parameters of NRTL, Wilson, Margules, and VanLaar model parameters without any additional adjustment to build the thermodynamic model of VLE for binary system and obtain the vapor-pressure compositions and the calculated bubble points.

Keywords: Binary mixture, Vapor liquid equilibrium, Wilson, Margules, VanLaar, NRTL.

1. INTRODUCTION

Mass transfer operations such as distillation are extensively used for separation or extraction of large number of liquid mixtures. Due to this, the knowledge of Vapor liquid equilibrium data is of great importance when it comes to accurate designing of required equipment. Nonideality plays a very important role in industrial processes and equipment design calculations.

When VLE data is generated and phases are analyzed using samples. While sampling the compositions of both liquid and gaseous phase change and accordingly behavior of system also changes. This decreases the possibility of highly accurate VLE data.

This fact points towards the necessity for much analytical work which leads to enhance an interest in exploring new methods for determination of equilibrium data that do not involve sampling and analysis of vapor phase components. Several methods have been suggested for determination of accurate data. Van Ness and coworkers classified these methods in two categories, direct and indirect methods [1]. Direct method contains calculation of vapor compositions by integration of coexistence equation which was derived from Gibbs-Duhem equation [2]. Indirect methods involve ascertaining which of the selected solution equations to the Gibbs-Duhem equation which lead to best fit to the experimental data, and determination of parametric values producing the best fit. This paper reports novel correlation and prediction of VLE data for these isobaric binary systems at 101.25 kpa. Non ideality of mixture was corrected by the calculation of its activity coefficient, which was obtained based on NRTL, Wilson, Margules and VanLaar models as function of T,x,y through non-linear fit of least squares method.

2. RESULTS AND DISCUSSION

2.1 Calculation of vapor-phase Mole Fraction y for Binary Systems from Model

There are several methods concerning the correlation and predicting VLE data. VLE data can also be predicted and correlated using model-free approach. It was suggested by Wisniak's group that novel model-free computation techniques and limiting conditions have been applied for azeotropic systems [3]. But Segura and coworkers stated that model-free approach dealt with VLE data in application of ternary systems [4, 5]. In this paper, for all three binary systems, activity coefficients were correlated with Wilson [6], Margules [7], NRTL [8] and Van-Laar [9] equations. The Interaction parameters were computed by minimizing the objective function using fitting by least-squares method.

2.2 Equations and models used for calculations are-

1. Wilson Model

One limitation of Wilson's equation is that it is unable to model liquid-liquid equilibria, but it is reasonably accurate for modeling the liquid phase when correlating the vapor-liquid equilibria of many mixtures. Wilson equation should be used only for liquid systems that are completely miscible or else for those limited regions of partially limited systems where only one liquid phase is present.

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$

$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right)$$

2. Van-Laar Model

The Van-Laar equation was derived from Van der Waals equation. The original van der Waals parameters didn't

give good description of vapor-liquid phase equilibria, which forced the user to fit the parameters to experimental results. Because of this, the model lost the connection to molecular properties, and therefore it has to be regarded as an empirical model to correlate experimental results.

$$\ln\gamma_1 = A_{12}\left(\frac{A_{21}x_2}{A_{12}x_1+A_{21}x_2}\right)^2$$
$$\ln\gamma_1 = A_{21}\left(\frac{A_{21}x_1}{A_{12}x_1+A_{21}x_2}\right)^2$$

3. Margules Model

The Margules activity model is a simple thermodynamic model for the excess Gibbs free energy of a liquid mixture introduced in 1895 by Max Margules. In chemical engineering the Margules Gibbs free energy model for liquid mixtures is better known as the Margules activity or activity coefficient model. Although the model is old it has the characteristic feature to describe extrema in the activity coefficient which other models cannot.

$$\ln\gamma_1 = [A_{12}+2(A_{21}-A_{12})x_1]x_2^2$$
$$\ln\gamma_2 = [A_{21}+2(A_{12}-A_{21})x_2]x_1^2$$

4. NRTL (Non-Random Two-Liquid) Model

The Non-random two-liquid model is an activity coefficient model that correlates the activity coefficients of a compound i with its mole fractions in the liquid phase concerned. It is frequently applied in the field of chemical engineering to calculate phase equilibria. The concept of NRTL is based on the hypothesis of Wilson that the local concentration around a molecule is different from the bulk concentration.

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G21}{x1+x2G21}\right)^2 + \tau_{12}\frac{G12}{(x2+x1G12)2}\right]$$
$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G12}{x2+x1G12}\right)^2 + \tau_{21}\frac{G21}{(x1+x2G21)2}\right]$$
$$\ln G_{12} = -\alpha_{12}\tau_{12}$$
$$\ln G_{21} = -\alpha_{21}\tau_{21}$$

Objective function in our work was taken as –

$$\text{Objective function} = \sum_{i=1}^{N}\left(\frac{\gamma_{i,cal}-\gamma_{i,exp}}{2}\right)^2$$

Where N is the number of experimental points, $\gamma_{i,calc}$, $\gamma_{i,exp}$ are activity coefficients of component i calculated and experimental values from measured data, respectively. The method of least squares is a standard approach in regression analysis to the approximate solution of overdetermined systems, i.e., sets of equations in which there are more equations than unknowns. "Least squares" means that the overall solution minimizes the sum of the squares of the errors made in the results of every single equation. The most important application is in data fitting. The best fit in the least-squares sense minimizes the sum of squared residuals, a residual being the difference between an observed value and the fitted value provided by a model.

Table 1: Antoine coefficients of the compounds

Compound	Ai	Bi	Ci
Methanol	7.19736	1574.99	-34.29
Water	7.07404	1657.46	-46.13
Ethanoic acid	6.42452	1479.02	-56.34

Table 2: Correlation parameters of activity coefficient

Equation	Parameters	Methanol(1)+water(2)	Methanol(1)+ Ethanoic acid (2)	Water(1)+Ethanoic acid (2)
Van-Laar	A_{12}	0.8407	-	0.2777
	A_{21}	0.5386	-	0.4607
	Fmin	0.0075	-	0.0421
Margules	Λ_{12}	0.8256	-0.335	0.2416
	Λ_{21}	0.4791	0.0219	0.4632
	Fmin	0.0080	0.0599	0.0360
Wilson	A_{12}	0.4139	0.5307	1.2795
	A_{21}	1.0354	1.8843	0.4759
	Fmin	0.0074	0.0784	0.0423
NRTL	G_{12}	-0.2831	2.7759	1.0233
	G_{21}	1.1457	-1.5237	-0.4846
	Fmin	0.0075	0.0390	0.0405

Table 3: Experimental data for Methanol (1) + Water (2) System at 101.25 kpa

x_1	y_1	T_{exp}	γ_{1exp}	γ_{2exp}
0.0484	0.2704	365.54	2.1436	1.0034
0.0539	0.3009	364.88	2.1147	1.0042

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0.0607	0.3213	364.12	2.0799	1.0053
0.0696	0.3492	363.19	2.0358	1.0069
0.0806	0.3866	362.13	1.9835	1.0092
0.0911	0.4126	361.21	1.9360	1.0117
0.1056	0.4492	360.05	1.8739	1.0155
0.1197	0.4762	359.04	1.8172	1.0197
0.1354	0.4885	358.02	1.7584	1.0248
0.1436	0.5047	357.53	1.7293	1.0277
0.1586	0.5323	356.70	1.6788	1.0334
0.1815	0.5677	355.56	1.6083	1.0428
0.2092	0.5969	354.35	1.5325	1.0555
0.2202	0.6031	353.91	1.5049	1.0609
0.2380	0.6237	353.24	1.4633	1.0701
0.2648	0.6519	352.32	1.4066	1.0847
0.2918	0.6681	351.48	1.3561	1.1005
0.3166	0.6923	350.76	1.3148	1.1157
0.3442	0.7197	350.02	1.2740	1.1336
0.4015	0.7431	348.61	1.2038	1.1730
0.4282	0.7443	348.00	1.1767	1.1924
0.4644	0.7613	347.21	1.1449	1.2194
0.5240	0.7860	345.98	1.1026	1.2656
0.6091	0.8231	344.33	1.0595	1.3338
0.6899	0.8633	342.85	1.0325	1.3995
0.8213	0.9221	340.56	1.0086	1.5038

Table 4: Experimental data for Methanol (1) + Ethanoic acid (2) System at 101.25 kpa

x_1	y_1	T_{exp}	γ_{1exp}	γ_{2exp}
0.0359	0.1574	386.23	0.9388	0.9999
0.0410	0.1664	385.56	0.9393	0.9999
0.0648	0.2719	382.68	0.9419	0.9997
0.0741	0.3133	381.90	0.9428	0.9996
0.0859	0.3333	380.60	0.9441	0.9995
0.1040	0.3830	379.06	0.9460	0.9992
0.1280	0.4602	377.35	0.9485	0.9988
0.1629	0.5213	374.70	0.9521	0.9981
0.1919	0.5873	372.43	0.9551	0.9973
0.2510	0.6495	368.44	0.9609	0.9954
0.3391	0.7538	363.56	0.9692	0.9916
0.4401	0.8232	357.71	0.9776	0.9857
0.5829	0.8999	350.75	0.9874	0.9748
0.7050	0.9389	346.39	0.9936	0.9633
0.7509	0.9533	344.06	0.9955	0.9583
0.8109	0.9693	342.35	0.9974	0.9515
0.8711	0.9766	340.75	0.9988	0.9442
0.9161	0.9850	340.00	0.9995	0.9384

Table 5: Experimental data for Water (1) + Ethanoic acid (2) System at 101.25 kpa

x_1	y_1	T_{exp}	γ_{1exp}	γ_{2exp}
0.0665	0.1140	387.22	1.4161	1.0025
0.0749	0.1288	387.00	1.4046	1.0031
0.0855	0.1603	386.48	1.3903	1.0040
0.0995	0.1938	385.86	1.3117	1.0054
0.1507	0.2802	384.16	1.2888	1.0121
0.1722	0.3155	383.44	1.2684	1.0156
0.2168	0.3676	382.39	1.2171	1.0242

0.2502	0.4101	381.53	1.1838	1.0316
0.2936	0.4407	380.94	1.1589	1.0425
0.3303	0.4815	380.20	1.1318	1.0528
0.3756	0.5253	379.40	1.0965	1.0666
0.4465	0.5890	378.27	1.0768	1.0908
0.4946	0.6274	377.61	1.0543	1.1087
0.5615	0.6777	376.80	1.0427	1.1355
0.6036	0.7137	376.24	1.0315	1.1533
0.6517	0.7546	375.59	1.0213	1.1746
0.7067	0.7849	375.11	1.0217	1.1998
0.7045	0.7848	375.11	1.0148	1.1988
0.7507	0.8173	374.71	1.0091	1.2207
0.8008	0.8501	374.31	1.0035	1.2451
0.8723	0.9011	373.80	1.0016	1.2809
0.9116	0.9315	373.54	1.0004	1.3009
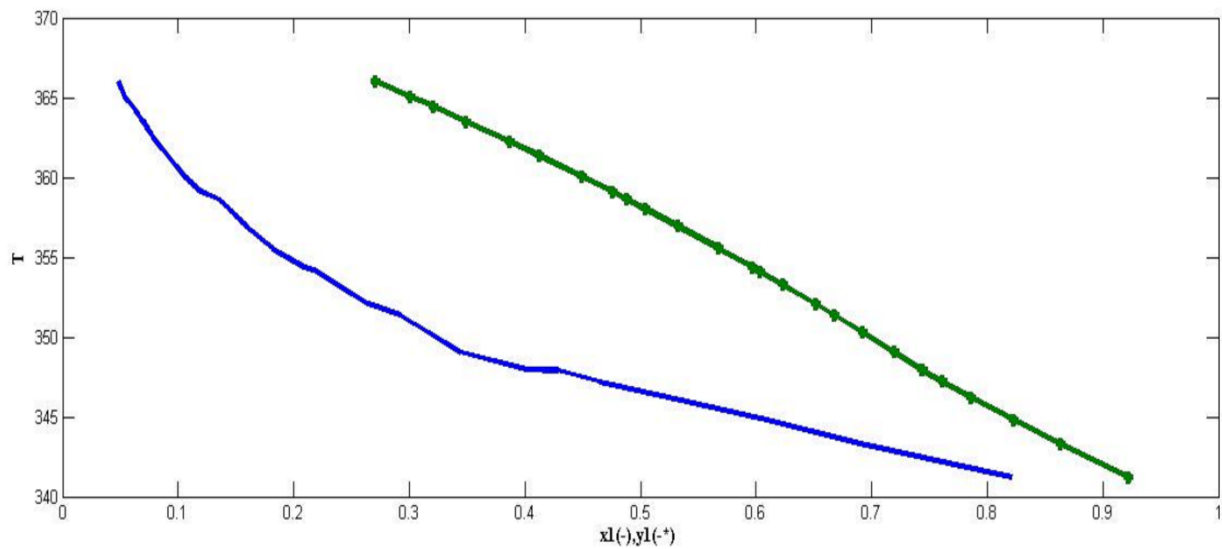
Figure 1- T-xy diagram of Methanol (1) +Water(2) System at 101.25 kpa
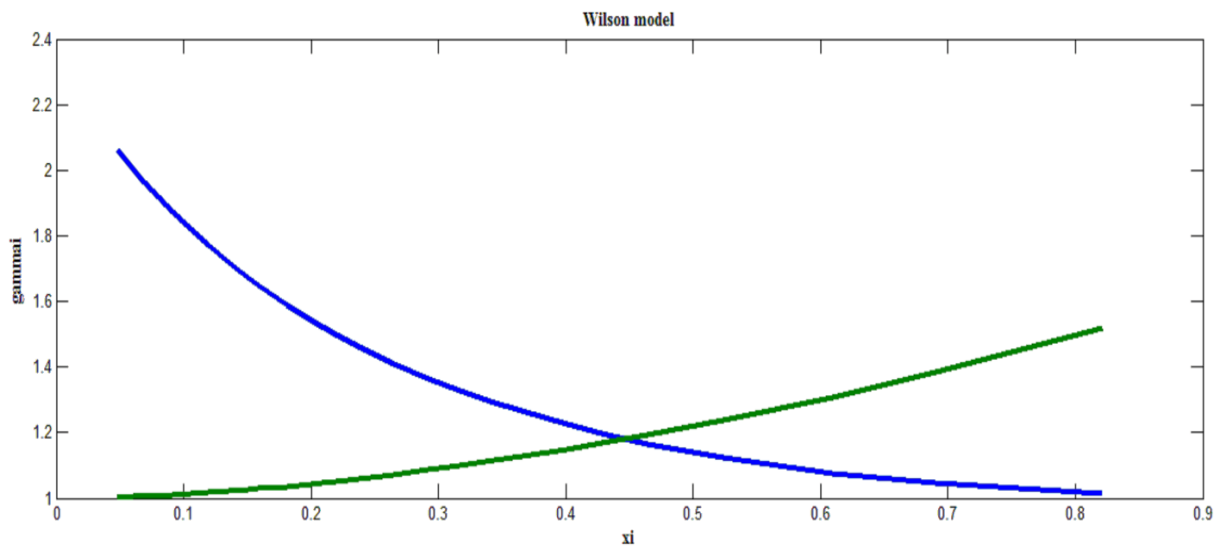
Figure 2- Plot of γ_1 and γ_2 vs x_1 of Methanol(1)+Water(2) System at 101.25 kpa
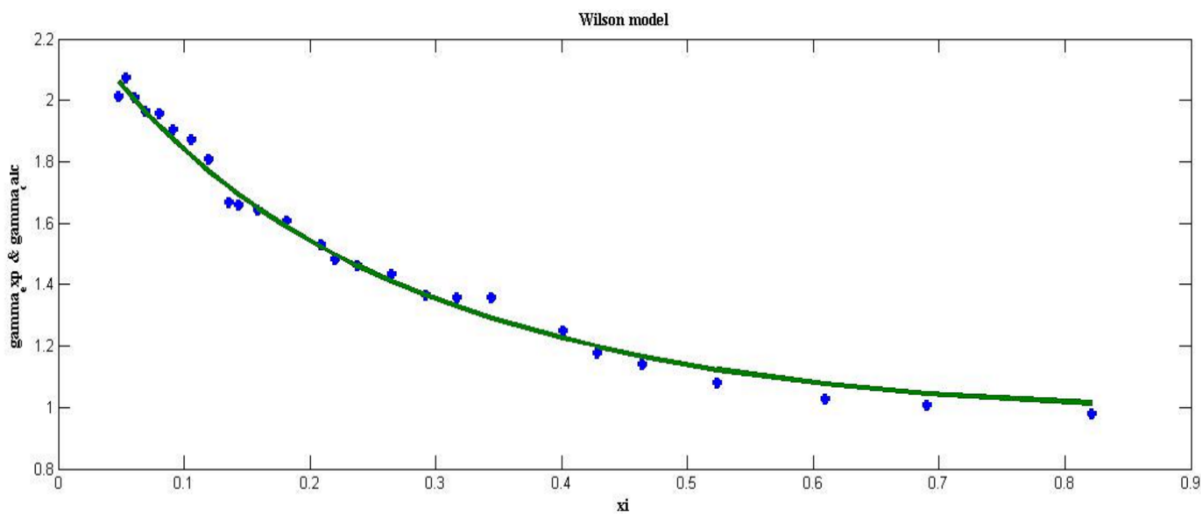
Figure 3- γ_{calc} and γ_{exp} vs x_1 of Methanol(1)+Water(2) System at 101.25 kpa
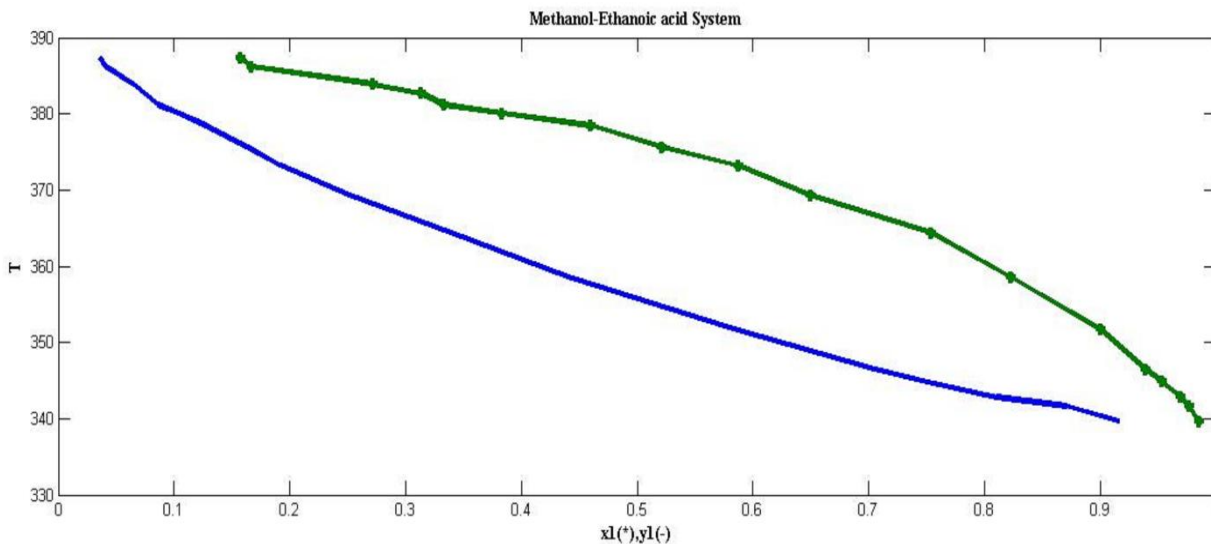

Figure 4- T-xy diagram of Methanol(1)+Ethanoic acid(2) System at 101.25 kpa

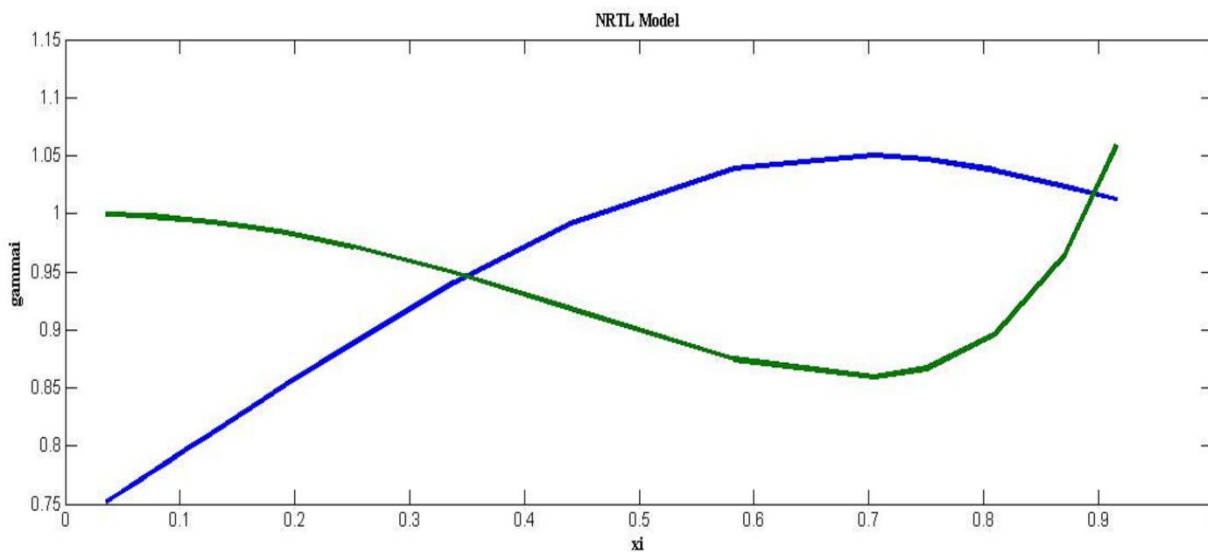Figure 5- Plot of γ_1 and γ_2 vs x_1 of Methanol(1)+Ethanoic acid(2) System at 101.25 kpa

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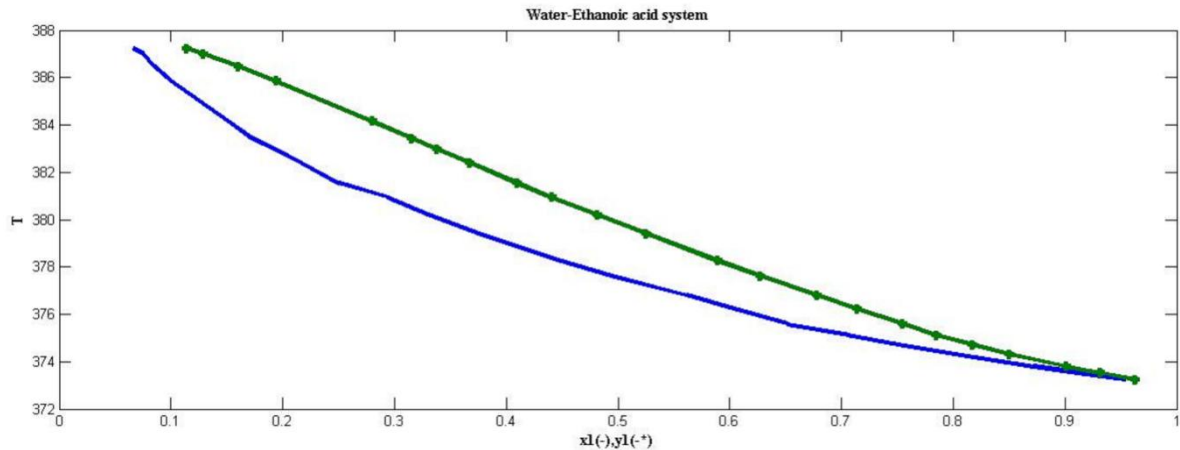
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Figure 6- T-xy diagram of Water(1)+Ethanoic acid(2) System at 101.25 kpa
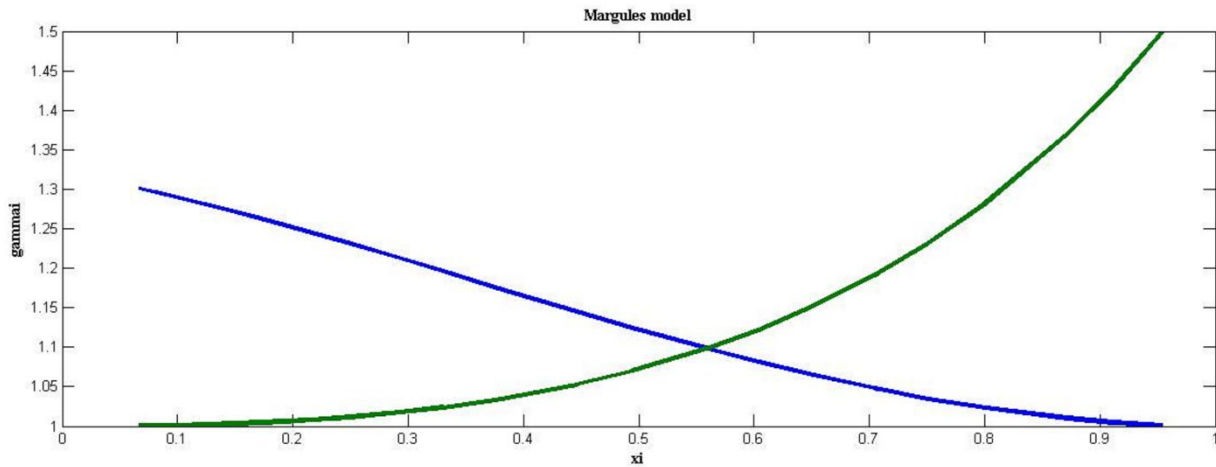

Figure 7- Plot of γ_1 and γ_2 vs x_1 of Water(1)+Ethanoic acid(2) System at 101.25 kpa

3. MATLAB CODE

3.1 Code for determining activity coefficients of binary Methanol(1)+Water(2) System using various models.

```
%----------------------Methanol(1)+Water(2) SYSTEM----------%

P=101.325;
a1=7.19736;b1=1574.99;c1=-34.29;
a2=7.07404;b2=1657.46;c2=-46.13;
 %-------------------VAN LAAR-------------------%
 x1=[0.0484 0.0539 0.0607 0.0696 0.0806 0.0911 0.1056
0.1197 0.1354 0.1436 0.1586 0.1815 0.2092 0.2202
0.2380 0.2648 0.2918 0.3166 0.3442 0.4015 0.4282
0.4644 0.5240 0.6091 0.6899 0.8213 ];
y1=[0.2704 0.3009 0.3213 0.3492 0.3866 0.4126 0.4492
0.4762 0.4885 0.5047 0.5323 0.5677 0.5969 0.6031
0.6237 0.6519 0.6681 0.6923 0.7197 0.7431 0.7443
0.7613 0.7860 0.8231 0.8633 0.9221 ];
T=[366.00 365.05 364.40 363.50 362.25 361.35 360.05
359.09 358.60 358.00 356.95 355.55 354.35 354.10
353.25 352.05 351.35 350.30 349.05 347.95 347.90
347.20 346.20 344.80 343.31 341.20 ];
Tsat1 = 338.1; Tsat2 = 373.16;
x2=1-x1;
```

```
y2=1-y1;
p1= 10.^(a1 - b1./(T+c1));
p2= 10.^(a2 - b2./(T+c2));
gamma1_exp=(y1.*P)./(p1.*x1);
gamma2_exp=(y2.*P)./(p2.*x2);
gamma1_calc=
@(c)exp(c(1).*(((c(2).*x2)./(c(1).*x1+c(2).*x2)).^2));
gamma2_calc=
@(c)exp(c(2).*(((c(1).*x1)./(c(1).*x1+c(2).*x2)).^2));
ini_guess = [1,1];
U=@(c)(0.5*(sum(((gamma1_calc(c)-
gamma1_exp)+(gamma2_calc(c)-gamma2_exp)).^2)));
display 'Vanlaar model activity coeffcients'
[c,fmin] = fminsearch(U,ini_guess)
gamma1_calcvalue=exp(c(1).*(((c(2).*x2)./(c(1).*x1+c(2)
.*x2)).^2));
gamma2_calcvalue=exp(c(2).*(((c(1).*x1)./(c(1).*x1+c(2)
.*x2)).^2));
%--------Graphs----------%
subplot(3,3,1),plot(x1,T,'*',y1,T,'-*'),xlabel('x1(*),y1(-
)'),ylabel('T'),title('Methanol-Water
system'),subplot(3,3,2),plot(x1,gamma1_calcvalue,x2,gam
ma2_calcvalue),xlabel('xi'),ylabel('gammai'),title('Van
```

Laar model'),
,subplot(3,3,6),plot(x1,gamma1_exp,x1,gamma1_calcvalu
e),xlabel('xi'),ylabel('gamma_exp &
gamma_calc'),title('Van Laar model');

4. CONCLUSION

The experimental data of three binary mixture i.e. methanol + water, methanol + ethanoic acid and water + ethanoic acid at 101.325 kpa was correlated using the NRTL, Wilson, Margules, and van Laar equations. The vapor liquid equilibrium data of these binary mixture was available in literature. So activity coefficients of these systems were determined using MATLAB. It was shown that the deviations of NRTL, Wilson, Margules, and van Laar equations are reasonably small. The calculated bubble points accorded well with the experimental data. The results show that the calculated bubble point is well fitted by the models, which satisfy the need for the design and operation of separation process in chemical industry. Moreover, the method will provide theoretical guidance for the research of VLE data of strongly associating system of vapor and liquid phase in non-ideal behavior.

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