ETHANOL AND WATER

MARGULES MODEL

Aim:

Use modified Raoult's law with activity coefficients given by Margules Model to study the "attached" system and then plot :

a) isobaric T vs x, y diagram

b) y vs x diagram.

Theory:

The modified Raoult's law has been used to study the liquid mixtures which includes the interactions between particles of liquid mixture by introducing another quantity – "Activity Coefficient". Margules Model is one of the most famous model which is used to compute activity coefficient.This model is based on the principle that $g^E/(RTx1x2)$ (g^E is excess Gibbs Energy) follows a linear relation with x1 and x2 .(x1 and x2 are the respective mole fractions in liquid phase.)

Equations Used:

1.

2. Antoine Vapor Pressure Equation

The Antoine vapor pressure equation is used in the following form:

$$\log[p_i^0] = A - \frac{B}{t + C} \qquad (70)$$

with $[p_i^0]$ vapor pressure of pure component i in mm Hg

t temperature in degrees Celsius (° C)

The Antoine constants A, B, and C are given with respective temperature regions (in ° C).

Note- Here it is log (Base 10).

2.

Activity Coefficient Model –

Margules

Type of Equation	Parameters	$\ln \gamma_1 =$ $\ln \gamma_2 =$		Notation of Parameters in Data Sheet
Margules [6]	A_{12}	$[A_{12} + 2(A_{21} - A_{12})\, x_1]\, x_2^2$	(28a)	A 12
	A_{21}	$[A_{21} + 2(A_{12} - A_{21})\, x_2]\, x_1^2$	(28b)	A 21

3. Modified Rault's Law:

$$y_i P = x_i \gamma_i P_i^{sat}$$

$$P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}$$

Constants used:

(1) ETHANOL C2H6O

(2) WATER H2O

+++++ ANTOINE CONSTANTS			REGION +++++		CONSISTENCY
(1)	8.11220	1592.864	226.184	20- 93 C	METHOD 1 +
(2)	8.07131	1730.630	233.426	1- 100 C	METHOD 2 +

PRESSURE= 760.00 MM HG (1.013 BAR)

CHEM.ENG.PROG. 48,192(1952).

CONSTANTS:	A12	A21	α_{12}	γ_1^∞	γ_2^∞	OBJECTIVE FUNCTION
MARGULES	1.6721	.7462		5.32	2.11	.0743 G
				5.69	2.52	.0312 G

Procedure:

1. Start looping x1 (mole fraction of ethanol in liquid phase) from 0.0001 to 1.0000 ,considering upto 4 decimal places.
2. To accurately guess T value, use Antonie equation and use P as P1_sat to find T1_sat and similarly find T2_sat and then to finally evaluate T_guess ,use the formula :

   T1_sat * x1 + T2_sat * x2

3. Evaluate activity coefficients (Y1 and Y2) From Margules Model using x1,x2.
4. Evaluate P1_sat and P2_sat using T_guess from Antoine Equation.
5. Then to find P1_sat ,use the relation :

   P1_sat = (P * P1_sat)/(x1 * Y1 * P1_sat + x2 * Y2 * P2_sat)

for simplifying calculations , let say “alpha” = P1_sat/P2_sat

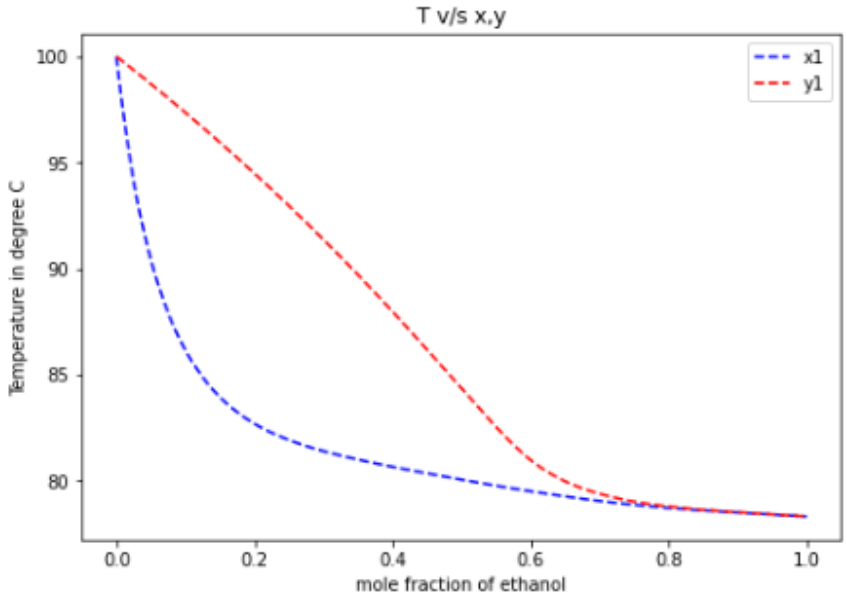
So final relation becomes:

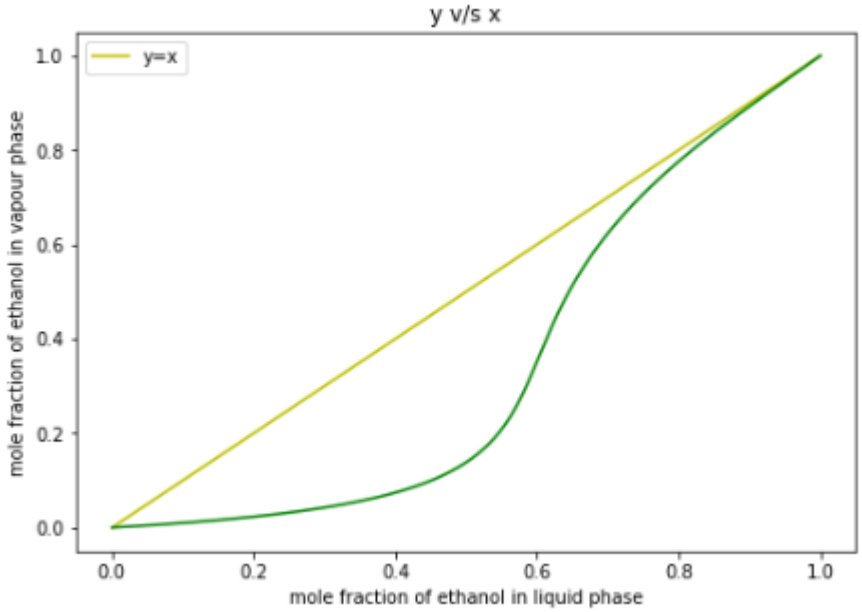
$$P1\_sat = P/(x1*Y1+ (x2*Y2)/alpha)$$

6. From P1_sat calculated in step 5 , evaluate Temperature.
7. Check error and repeat the above steps until error is less than 0.01%.This will indicate that Temperature converges.

Observation:

Following are the graphs that we get using the above procedure :



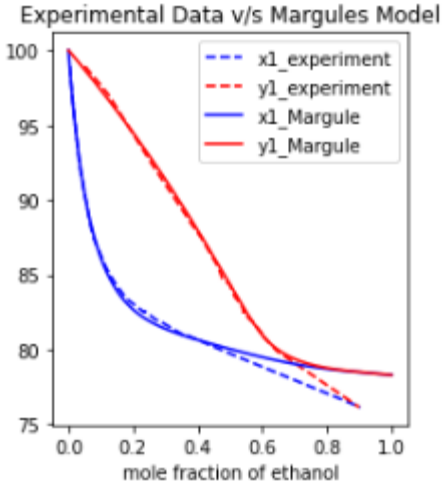


From the above T vs x1,y1 graph and x1 vs y1 graph ,we can easily observed that as soon as x1 reaches 0.95 , x1 and y1 both graph start to coincide at nearly at T ~ 78 degree C.This indicates the formation of *Azeotrope* .As the boiling point of both water(100 degree C) and ethanol (78.4 degree c) is more than this Temperature , so it would be ***minimum Boiling Point Azeotrope***

Results obtained from above method has been compared with the given experimental data and we get the following plot:

EXPERIMENTAL DATA

T DEG C	X1	Y1
98.93	.0044	.0510
97.05	.0110	.1230
92.30	.0340	.2610
88.32	.0680	.3830
87.47	.0770	.4110
85.49	.1160	.4640
84.75	.1350	.4760
84.34	.1470	.4990
83.47	.1770	.5160
83.42	.1780	.5190
82.94	.2070	.5360
82.50	.2330	.5440
82.56	.2360	.5410
81.99	.2700	.5620
81.84	.2870	.5720
80.90	.3610	.6050
80.92	.3700	.6010
79.91	.4800	.6450
76.15	.9040	.9000



Conclusion:

With the help of Margules Model and Iterative algorithm, we study system of Ethanol and Water and compare it with the experiment data.