

Executive Summary

For the first question, a set of experimental VLE data has been obtained to compete with the Isobaric VLE Binary Data. Calculation of percentage error has been done at different value of temperature, liquid mole fraction and vapour mole fraction, and it was found out that the highest value out of all percentage error is only 0.33%. If the value of percentage error is more than 5%, then the obtained experimental VLE data is not able to be used.

In question 1(b), Peng Robinson mixing rules are applied in the calculation because it is a binary mixture system. All the calculations were done in Excel. The average fugacity coefficient of methanol is more than 1 and it is quite higher than the benzene in liquid phase. Average fugacity coefficient of benzene in liquid phase is less than 1. Besides, fugacity coefficient of methanol is slightly higher than benzene in vapor phase. Both compounds are less than 1 but near to ideal condition. It can conclude methanol and benzene in vapor phase are close to ideal condition. We also can conclude that fugacity coefficient decreases when temperature decreases.

For question 1(c), the estimated value of vapour mole fraction for methanol and benzene is calculated. The suitability of the Peng-Robinson Equation of State is determined. The estimated value of the vapour mole fraction is calculated in Excel. However, the result of the estimated value for the vapour mole fraction of methanol has a big difference from the experimental value. So, we can conclude that Peng-Robinson EOS is not suitable for this system.

In question 1(d), the data was calculated with three-suffix Margules model, Van Laar model and Wilson model by using Excel. From the data we can observe that in Van Laar model γ_a and γ_b fluctuates around 1 where else three-suffix Margules model and Wilson model generally decrease with the temperature.

For question 1(e), equilibrium vapour fraction is predicted using the activity models consequently to the experimental data from 1(d). After that, y-x plot of vapour mole fraction (y_a) against liquid mole fraction (x_a) is plotted and we can observe that three-suffix model suits the methanol-benzene system.

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1.0 Introduction

Alkylation of benzene with methanol has recently emerged as a viable option for producing toluene from coal and natural gas. The method produces a combination of methanol and benzene in the effluent. Due to the presence of minimum-boiling homogenous azeotrope at atmospheric pressure, properly separating them is difficult. Separation by distillation relies on differences in the volatility of the components to be separated, however for combinations including azeotropes, traditional distillation has failed to achieve the needed separation. As a result, advanced distillation techniques including pressure swing distillation and extractive distillation have received a lot of attention.

Pressure swing distillation can be used to separate azeotropes having pressure sensitive properties. This separation technique does not require any extra components, which eliminates the possibility of product contamination. Extractive distillation, on the other hand, need a third higher boiling solvent injected at the top of the column to selectively absorb one of the essential components in the binary new feed.

Background

The VLE data for the isobaric methanol-benzene system is needed in order to compare it with the experimental VLE data obtained from the literature as well as generate VLE data for the methanol-benzene system based on the UNIQUAC activity model by using Aspen Plus process simulator[#]. The specific volumes and the fugacity coefficients of vapour and liquid are necessitated for the purpose of parameters summarisation in table form and comparison with the experimental data by using Microsoft Excel. The activity coefficients obtained from the three activity models are required to compare its equilibrium vapour mole fraction with the experimental data by using Microsoft Excel.

1.1 Objectives

The objectives of this assignment are to:

- Determine the fugacity coefficients using equation of state by fitting them against a representative sample of experimental data,
- Determine the adjustable parameters of activity models by fitting them against a representative sample of experimental data,

- Select suitable thermodynamic model(s) to simulate the system,
- Obtain and generate VLE curve using process simulator,
- Visualise how pressure-swing distillation shift the VLE of the methanol-benzene system.

2.0 Part 1: VLE Data for Methanol -Benzene System

(a)

2.1 Experiment VLE Data from Literature and NIST

Table 2.1.1: Experimental VLE data obtained from the literature. (Source: <http://www.ddbst.com/en/EED/VLE/VLE%20Benzene%3BMethanol.php>, Vapor-Liquid Equilibrium Data Set 39)

Pressure: 101.33 kPa

Temperature, T (K)	Liquid Mole Fraction of Methanol, x_A (mol A/mol)	Vapour Mole Fraction of Methanol, y_A (mol A/mol)
351.76	0.0020	0.0410
350.80	0.0028	0.0660
350.67	0.0030	0.0684
350.43	0.0030	0.0812
350.37	0.0041	0.0820
349.20	0.0055	0.1172
348.45	0.0058	0.1386
346.92	0.0134	0.1924
346.21	0.0190	0.2060
344.11	0.0276	0.2658

Table 2.1.2 : Isobaric VLE Binary Data 040 from NIST database.

Pressure: 101.00 kPa

Temperature, T (K)	Liquid Mole Fraction of Methanol, x_A (mol A/mol)	Vapour Mole Fraction of Methanol, y_A (mol A/mol)
350.98	0.0020	0.0410
350.77	0.0028	0.0660
350.64	0.0030	0.0684
350.40	0.0030	0.0812
350.34	0.0041	0.0820
349.17	0.0055	0.1172
348.42	0.0058	0.1386
346.90	0.0134	0.1924
346.18	0.0190	0.2060
344.08	0.0276	0.2658

Percentage Error: Pressure and Temperature

$$\text{Pressure: } \frac{(101.33 \times 10^3) - (101.00 \times 10^3)}{(101.33 \times 10^3)} \times 100\% = 0.33\%$$

$$\text{Temperature 1: } \frac{(351.76) - (350.98)}{(351.76)} \times 100\% = 0.22\%$$

$$\text{Temperature 2: } \frac{(350.80) - (350.77)}{(350.80)} \times 100\% = 0.01\%$$

$$\text{Temperature 3: } \frac{(350.67) - (350.64)}{(350.67)} \times 100\% = 0.01\%$$

$$\text{Temperature 4: } \frac{(350.43) - (350.40)}{(350.43)} \times 100\% = 0.01\%$$

$$\text{Temperature 5: } \frac{(350.37) - (350.34)}{(350.37)} \times 100\% = 0.01\%$$

$$\text{Temperature 6: } \frac{(349.20) - (349.17)}{(349.20)} \times 100\% = 0.01\%$$

$$\text{Temperature 7: } \frac{(348.45) - (348.42)}{(348.45)} \times 100\% = 0.01\%$$

$$\text{Temperature 8: } \frac{(346.92) - (346.90)}{(346.92)} \times 100\% = 0.01\%$$

$$\text{Temperature 9: } \frac{(346.21) - (346.18)}{(346.21)} \times 100\% = 0.01\%$$

$$\text{Temperature 10: } \frac{(344.11) - (344.08)}{(344.11)} \times 100\% = 0.01\%$$

Percentage Error: Pressure and Temperature

$$\text{Liquid Mole Fraction 1: } \frac{(0.0020) - (0.0020)}{(0.0020)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 2: } \frac{(0.0028) - (0.0028)}{(0.0028)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 3: } \frac{(0.0030) - (0.0030)}{(0.0030)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 4: } \frac{(0.0030) - (0.0030)}{(0.0030)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 5: } \frac{(0.0041) - (0.0041)}{(0.0041)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 6: } \frac{(0.0055)-(0.0055)}{(0.0055)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 7: } \frac{(0.0058)-(0.0058)}{(0.0058)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 8: } \frac{(0.0134)-(0.0134)}{(0.0134)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 9: } \frac{(0.0190)-(0.0190)}{(0.0190)} \times 100\% = 0\%$$

$$\text{Liquid Mole Fraction 10: } \frac{(0.0276)-(0.0276)}{(0.0276)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 1: } \frac{(0.0410)-(0.0410)}{(0.0410)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 2: } \frac{(0.0660)-(0.0660)}{(0.0660)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 3: } \frac{(0.0684)-(0.0684)}{(0.0684)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 4: } \frac{(0.0812)-(0.0812)}{(0.0812)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 5: } \frac{(0.0820)-(0.0820)}{(0.0820)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 6: } \frac{(0.1172)-(0.1172)}{(0.1172)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 7: } \frac{(0.1386)-(0.1386)}{(0.1386)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 8: } \frac{(0.1924)-(0.1924)}{(0.1924)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 9: } \frac{(0.2060)-(0.2060)}{(0.2060)} \times 100\% = 0\%$$

$$\text{Vapour Mole Fraction 10: } \frac{(0.2658)-(0.2658)}{(0.2658)} \times 100\% = 0\%$$

(b)

2.2 Specific Volume and Fugacity Coefficient of Methanol and Benzene

Table 2.2.1 Molecular Weight, Critical Temperature, Critical Pressure and Pitzer acentric factor for Methanol and Benzene

Component	Methanol, CH ₄ O	Benzene, C ₆ H ₆
Molecular Weight, MW (kg/mol)	0.032042	0.078112
Critical Temperature, T _c (K)	512.6	562.1
Critical Pressure, P _c (bar)	80.96	48.94
Pitzer acentric factor, ω	0.559	0.212

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (\text{Equation 1})$$

$$b = 0.07780 \frac{R T_c}{P_c} \quad (\text{Equation 2})$$

$$k = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \quad (\text{Equation 3})$$

Table 2.2.2 Value of a, b and k for Methanol and Benzene

Component	Methanol, CH ₄ O (1)	Benzene, C ₆ H ₆ (2)
$a \left(\frac{m^2}{mol^2} \right)$	1.0258	2.0405
$b \left(\frac{m^3}{mol} \right)$	4.0954E-05	7.4292E-05
k	1.1524	0.6895

a, b and k value for methanol and benzene are calculated by using equation 1 for a, equation 2 for b and equation 3 for k. Calculation for $\alpha(T)$ in methanol and benzene will be calculated by using Equation 4. Values of $\alpha(T)$, reduced temperature and $a\alpha$ will be provided in Table 2.2.3 at below.

$$\alpha(T) = [1 + k(1 - \sqrt{Tr})]^2 \text{ (Equation 4)}$$

$$\text{Reduced Temperature, } Tr = \frac{T}{T_c} \text{ (Equation 5)}$$

Table 2.2.3 Reduced Temperature, $\alpha(T)$, $a\alpha(T)$ values for Methanol (1)

Temperature, T (K)	Reduced temperature, Tr (K)	$\alpha(T)$	$a\alpha(T)$
351.76	0.6862	1.4346	1.4716
350.80	0.6844	1.4378	1.4748
350.67	0.6841	1.4382	1.4753
350.43	0.6836	1.4390	1.4761
350.37	0.6835	1.4392	1.4763
349.20	0.6812	1.4430	1.4802
348.45	0.6798	1.4455	1.4827
346.92	0.6768	1.4505	1.4879
346.21	0.6754	1.4528	1.4903
344.11	0.6713	1.4598	1.4974

Table 2.2.4 Reduced Temperature, $\alpha(T)$, $a\alpha(T)$ Values for Benzene (2)

Temperature, T (K)	Reduced temperature, Tr (K)	$\alpha(T)$	$a\alpha(T)$
351.76	0.6258	1.3088	2.6706
350.80	0.6241	1.3106	2.6741
350.67	0.6239	1.3108	2.6746
350.43	0.6234	1.3112	2.6755
350.37	0.6233	1.3113	2.6757
349.20	0.6212	1.3134	2.6799
348.45	0.6199	1.3147	2.6827
346.92	0.6172	1.3175	2.6883
346.21	0.6159	1.3188	2.6909
344.11	0.6122	1.3225	2.6986

Methanol- Benzene is binary mixture. Mixing rule will be applied to solve the question. For Equation 8, mole fraction x_1 and x_2 (liquid phase) will be replaced to y_1 and y_2 when it is at vapor phase. Table 2.2.5 and 2.2.6 shows the values for $a\alpha(T)_{12}$, $a\alpha(T)_{\text{mix}}$ and b_{mix} .

$$a\alpha_{12} = (\sqrt{a\alpha(T)_1 a\alpha(T)_2} (1 - k_{12})) ; \text{ assume } k_{12} = 0; \text{ so}$$

$$a\alpha_{12} = (\sqrt{a\alpha(T)_1 a\alpha(T)_2}) \text{ (Equation 6)}$$

$$a\alpha_{\text{mix}} = x_1^2 a\alpha_1 + 2x_1 x_2 a\alpha_{12} + x_2^2 a\alpha_2 \text{ (Equation 7)}$$

$$b_{\text{mix}} = x_1 b_1 + x_2 b_2 \text{ (Equation 8)}$$

Table 2.2.5: Mixing Properties Value for Liquid Phase

Temperature, T (K)	$a\alpha(T)_{12}$	$a\alpha(T)_{\text{mix}}$	b_{mix}
351.76	1.9825	2.6679	7.4225E-05
350.80	1.9859	2.6703	7.4198E-05
350.67	1.9864	2.6705	7.4192E-05
350.43	1.9873	2.6713	7.4192E-05
350.37	1.9875	2.6700	7.4155E-05
349.20	1.9917	2.6724	7.4108E-05
348.45	1.9944	2.6747	7.4098E-05
346.92	1.9999	2.6698	7.3845E-05
346.21	2.0025	2.6648	7.3658E-05
344.11	2.0102	2.6607	7.3371E-05

Table 2.2.6: Mixing Properties Value for Vapor Phase

Temperature, T (K)	$a\alpha(T)_{12}$	$a\alpha(T)_{mix}$	b_{mix}
351.76	1.9825	2.6145	7.2925E-05
350.80	1.9859	2.5841	7.2091E-05
350.67	1.9864	2.5813	7.2011E-05
350.43	1.9873	2.5649	7.1585E-05
350.37	1.9875	2.5640	7.1558E-05
349.20	1.9917	2.5210	7.0384E-05
348.45	1.9944	2.4953	6.9671E-05
346.92	1.9999	2.4299	6.7877E-05
346.21	2.0025	2.4147	6.7424E-05
344.11	2.0102	2.3450	6.5430E-05

To calculate the molar volume, v for both liquid and vapor phase, Peng-Robinson equation is used to calculate it. Table 2.2.7 and 2.2.8 shows the possible roots for molar volume in both liquid and vapor phase.

$$P(P\alpha) = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)+b(v-b)} \quad \text{Equation 9}$$

Equation 6 is then simplified to:

$$v^3 + \left(b_{mix} - \frac{RT}{P}\right)v^2 + \left(\frac{a\alpha(T)_{mix}}{P} - 3b_{mix}^2 - \frac{2RTb_{mix}}{P}\right)v + \left(b_{mix}^3 + \frac{RTb_{mix}^2}{P} - \frac{b_{mix}a\alpha(T)_{mix}}{P}\right) = 0 \quad \text{(Equation 10)}$$

Substitute the value of b_{mix} , gas constant, temperature, pressure, $a\alpha(T)_{mix}$ (at above) into Equation 10 to find the molar volume.

Table 2.2.7: Value of Possible Root for Molar Volume from Peng-Robinson Equation of State for Liquid Phase

Temperature, T (K)	$v_1 \left(\frac{m^3}{mol} \right)$	$v_2 \left(\frac{m^3}{mol} \right)$	$v_3 \left(\frac{m^3}{mol} \right)$
351.76	0.0280	9.2670E-05	6.9134E-04
350.80	0.0279	9.2510E-05	6.9575E-04
350.67	0.0279	9.2499E-05	6.9587E-04
350.43	0.0279	9.2475E-05	6.9633E-04
350.37	0.0279	9.2429E-05	6.9601E-04
349.20	0.0278	9.2230E-05	7.0060E-04
348.45	0.0277	9.2106E-05	7.0489E-04
346.92	0.0276	9.1636E-05	7.0777E-04
346.21	0.0275	9.1311E-05	7.0993E-04
344.11	0.0274	9.0763E-05	7.1357E-04

Table 2.2.8: Value of Possible Root for Molar Volume from Peng-Robinson Equation of State for Vapor Phase

Temperature, T (K)	$v_1 \left(\frac{m^3}{mol} \right)$	$v_2 \left(\frac{m^3}{mol} \right)$	$v_3 \left(\frac{m^3}{mol} \right)$
351.76	0.0280	9.1114E-05	6.7672E-04
350.80	0.0280	9.0000E-05	6.7122E-04
350.67	0.0279	8.9890E-05	6.7087E-04
350.43	0.0279	8.9353E-05	6.6699E-04
350.37	0.0279	8.9315E-05	6.6695E-04
349.20	0.0278	8.7769E-05	6.5855E-04
348.45	0.0278	8.6821E-05	6.5364E-04
346.92	0.0277	8.4484E-05	6.4000E-04
346.21	0.0276	8.3860E-05	6.3789E-04
344.11	0.0275	8.1207E-05	6.2463E-04

There are three possible roots for molar volume. To choose the right molar volume to certain temperature, we assume that smallest value of v is for liquid phase while the largest value of v

is chosen in vapor phase. So, v_2 is the smallest molar volume so it will be selected as molar volume in liquid phase in Table 2.2.7. v_1 has the largest molar volume so it will be the molar volume in vapor phase in Table 2.2.8.

Table 2.2.9 Molar Volume in Liquid Phase and Vapor Phase

Temperature, T (K)	v (liquid) ($\frac{m^3}{mol}$)	v (vapor) ($\frac{m^3}{mol}$)
351.76	9.2670E-05	0.0280
350.80	9.2510E-05	0.0280
350.67	9.2499E-05	0.0279
350.43	9.2475E-05	0.0279
350.37	9.2429E-05	0.0279
349.20	9.2230E-05	0.0278
348.45	9.2106E-05	0.0278
346.92	9.1636E-05	0.0277
346.21	9.1311E-05	0.0276
344.11	9.0763E-05	0.0275

To calculate specific volume, \hat{v} in both liquid and vapor phase:

$$\hat{v} = \frac{v}{m} \quad \text{Equation 11}$$

Where \hat{v} = specific volume

v = molar volume

m = mass [$n(mol) \times MW(kg/mol)$]

$$\hat{v} = \frac{v}{n_1 MW_1 + n_2 MW_2} \quad \text{Equation 12}$$

Table 2.2.10: Specific Volume for Methanol -Benzene in Liquid and Vapor Phase

Temperature, T (K)	\hat{v} (liquid) ($\frac{m^3}{kg}$)	\hat{v} (vapor) ($\frac{m^3}{kg}$)
351.76	1.1878E-03	0.3673
350.80	1.1863E-03	0.3730
350.67	1.1863E-03	0.3722
350.43	1.1860E-03	0.3751
350.37	1.1862E-03	0.3753
349.20	1.1846E-03	0.3823
348.45	1.1832E-03	0.3876
346.92	1.1825E-03	0.4000
346.21	1.1822E-03	0.4022
344.11	1.1812E-03	0.4175

To calculate fugacity coefficient of binary mixture, Equation 13 will be applied for the Peng-Robinson EOS.

$$\ln \hat{\phi}_1 v = \frac{b_1}{b_{mix}} (z - 1) - \ln \left(\frac{(v - b_{mix})P}{RT} \right) + \frac{a\alpha_{mix}}{2\sqrt{2}b_{mix}RT} \left[\frac{b_1}{b_{mix}} - \frac{2}{a\alpha_{mix}} (y_1(a\alpha)_1 + y_2(a\alpha)_2) \right] \ln \left[\frac{v + (1 + \sqrt{2})b_{mix}}{v + (1 - \sqrt{2})b_{mix}} \right] \quad \text{Equation 13}$$

Whereas Compressibility factor, z is calculated as below:

$$z = \frac{Pv}{RT}; v = \text{molar volume} \quad \text{Equation 14}$$

Table 2.2.11: Compressibility factor for Methanol- Benzene in Liquid and Vapor Phase

Temperature, T (K)	z (liquid)	z (vapor)
351.76	3.2107E-03	0.9701
350.80	3.2139E-03	0.9728
350.67	3.2147E-03	0.9696
350.43	3.2161E-03	0.9703
350.37	3.2151E-03	0.9705
349.20	3.2189E-03	0.9702
348.45	3.2215E-03	0.9723
346.92	3.2192E-03	0.9731
346.21	3.2143E-03	0.9716
344.11	3.2145E-03	0.9740

Equation 13 will be applied to calculate fugacity coefficient for methanol and benzene in liquid and vapor phase.

$$\ln \hat{\phi}_1 v = \frac{b_1}{b_{mix}} (z - 1) - \ln \left(\frac{(v - b_{mix})P}{RT} \right) + \frac{a\alpha_{mix}}{2\sqrt{2}b_{mix}RT} \left[\frac{b_1}{b_{mix}} - \frac{2}{a\alpha_{mix}} (y_1(a\alpha)_1 + y_2(a\alpha)_{12}) \right] \ln \left[\frac{v + (1 + \sqrt{2})b_{mix}}{v + (1 - \sqrt{2})b_{mix}} \right] \text{ Equation 13}$$

Table 2.2.12: Fugacity Coefficient of Methanol (1) and Benzene (2) in Liquid Phase

Temperature (K)	$\ln \hat{\phi}_1$	$\hat{\phi}_1$	$\ln \hat{\phi}_2$	$\hat{\phi}_2$
351.76	0.8038	2.2339	-0.0713	0.9311
350.80	0.7728	2.1658	-0.1001	0.9048
350.67	0.7685	2.1566	-0.1040	0.9012
350.43	0.7608	2.1399	-0.1112	0.8948
350.37	0.7585	2.1351	-0.1130	0.8931
349.20	0.7202	2.0548	-0.1484	0.8621
348.45	0.6957	2.0050	-0.1712	0.8426
346.92	0.6429	1.9021	-0.2181	0.8040
346.21	0.6177	1.8547	-0.2401	0.7866
344.11	0.5442	1.7233	-0.3056	0.7367

Table 2.2.13: Fugacity Coefficient of Methanol (1) and Benzene (2) in Vapor Phase

Temperature (K)	$\ln \hat{\phi}_1$	$\hat{\phi}_1$	$\ln \hat{\phi}_2$	$\hat{\phi}_2$
351.76	-1.3729E-02	0.9864	-2.9425E-02	0.9710
350.80	-1.5036E-02	0.9851	-2.9565E-02	0.9709
350.67	-1.3710E-02	0.9864	-2.9691E-02	0.9707
350.43	-1.4022E-02	0.9861	-2.9730E-02	0.9707
350.37	-1.4105E-02	0.9860	-2.9737E-02	0.9707
349.20	-1.4186E-02	0.9859	-3.0026E-02	0.9704
348.45	-1.5173E-02	0.9849	-3.0071E-02	0.9704
346.92	-1.5684E-02	0.9844	-3.0337E-02	0.9701
346.21	-1.5206E-02	0.9849	-3.0644E-02	0.9698
344.11	-1.6443E-02	0.9837	-3.0833E-02	0.9696

We can conclude that the fugacity coefficient for methanol (1) in liquid phase is more than 1. The fugacity coefficient for methanol (1) in liquid phase have more than ideal gas. It exhibits repulsive force because the molecules are close to each other. For fugacity coefficient in benzene (2) in liquid phase, fugacity coefficients are less than one but some of them near to 1.

This indicates that benzene at higher temperature, its attractive and repulsive force are nearly to balance and reach ideal while at low temperature, attractive forces dominate the system behavior. On the other hand, fugacity coefficient of methanol (1) and benzene (2) in vapor phase, both of their value were less than 1 but quite near to ideal gas. This indicate that these systems are nearly to ideal and it deviate little from ideal gas behavior.

(c)

2.3 Estimation of Vapour Mole Fraction and Suitability of Using Peng- Robinson

We can get the estimation of equilibrium vapour mole fraction by substitute value of $\hat{\phi}_1^v$ and $\hat{\phi}_1^l$ from Table 2.3.1 and Table 2.3.2 into the equation below:

$$y_i \hat{\phi}_1^v = x_i \hat{\phi}_1^l$$

Table 2.3.1: Fugacity Coefficient of Methanol (1) and Benzene (2) in Liquid and Vapour Phase

Temperature (K)	$\hat{\phi}_1^l$	$\hat{\phi}_2^l$	$\hat{\phi}_1^v$	$\hat{\phi}_2^v$
351.76	2.2339	0.9311	0.9864	0.9710
350.80	2.1658	0.9048	0.9851	0.9709
350.67	2.1566	0.9012	0.9864	0.9707
350.43	2.1399	0.8948	0.9861	0.9707
350.37	2.1351	0.8931	0.9860	0.9707
349.20	2.0548	0.8621	0.9859	0.9704
348.45	2.0050	0.8426	0.9849	0.9704
346.92	1.9021	0.8040	0.9844	0.9701
346.21	1.8547	0.7866	0.9849	0.9698
344.11	1.7233	0.7367	0.9837	0.9696

Table 2.3.2: Liquid and Vapour mole fraction of Methanol (1) and Benzene (2)

Temperature (K)	Liquid mole fraction		Vapour mole fraction	
	x1	x2	y1	y2
351.76	0.0020	0.9980	0.0410	0.9590
350.80	0.0028	0.9972	0.0660	0.9340
350.67	0.0030	0.9970	0.0684	0.9316
350.43	0.0030	0.9970	0.0812	0.9188
350.37	0.0041	0.9959	0.0820	0.9180
349.20	0.0055	0.9945	0.1172	0.8828
348.45	0.0058	0.9942	0.1386	0.8614
346.92	0.0134	0.9866	0.1924	0.8076
346.21	0.0190	0.9810	0.2060	0.7940
344.11	0.0276	0.9724	0.2658	0.7342

Table 2.3.3: Estimated Vapour mole fraction of methanol (1) and Benzene (2)

Temperature (K)	Experimental		Estimated	
	y1	y2	y1	y2
351.76	0.0410	0.9590	0.0045	0.9570
350.80	0.0660	0.9340	0.0062	0.9293
350.67	0.0684	0.9316	0.0066	0.9256
350.43	0.0812	0.9188	0.0065	0.9190
350.37	0.0820	0.9180	0.0089	0.9163
349.20	0.1172	0.8828	0.0115	0.8835
348.45	0.1386	0.8614	0.0118	0.8633
346.92	0.1924	0.8076	0.0259	0.8177
346.21	0.2060	0.7940	0.0358	0.7957
344.11	0.2658	0.7342	0.0484	0.7388

The Peng-Robinson Equation of State is not suitable for this system. This is because the value of the estimated vapour mole fraction of methanol has a big difference from the experimental value. The estimated vapour mole fraction of benzene also has a slight difference from the experimental value.

(d)

2.4 Adjustable Parameters and Activity Coefficients from Different Models

Table 3: Experimental VLE data obtained from the literature. (Source: <http://www.ddbst.com/en/EED/VLE/VLE%20Benzene%3BMethanol.php>, Vapor-Liquid Equilibrium Data Set 39)

Pressure: 101330 Pa

Temperature, T (K)	Liquid Mole Fraction of Methanol, x_A (mol A/mol)	Vapour Mole Fraction of Methanol, y_A (mol A/mol)
351.76	0.0020	0.0410
350.80	0.0028	0.0660
350.67	0.0030	0.0684
350.43	0.0030	0.0812
350.37	0.0041	0.0820
349.20	0.0055	0.1172
348.45	0.0058	0.1386
346.92	0.0134	0.1924
346.21	0.0190	0.2060
344.11	0.0276	0.2658

Table 2.4.1: Three-suffix Margules equation activity model for methanol-benzene system.

	8.314 J/molK			A=	7718.5460 J/mol						
P	101330 Pa			B=	0.0000 J/mol		Objective Function			$y_a=x_aP_{a,sat}/P_{calc}$	
Temperature (K)	x_a	x_b		y_a	y_b	Pcalc	(P-Pcalc)^2		$P_{a,sat}$	$P_{b,sat}$	y_a
351.76	0.0020	0.9980		13.8557	1.0000	101329.93	0.004817		172291.20	96747.99	3.40E-03
350.80	0.0028	0.9972		13.8969	1.0000	100107.26	1495089.340465		166423.94	93892.45	4.65E-03
350.67	0.0030	0.9970		13.8958	1.0000	100137.78	1421389.636669		165642.25	93510.92	4.96E-03
350.43	0.0030	0.9970		13.9208	1.0000	99391.21	3758892.013039		164207.09	92809.74	4.96E-03
350.37	0.0041	0.9959		13.8464	1.0000	101561.23	53466.205530		163849.91	92635.10	6.61E-03
349.20	0.0055	0.9945		13.8658	1.0001	100770.97	312512.305154		157012.08	89280.84	8.57E-03
348.45	0.0058	0.9942		13.9223	1.0001	99018.43	5343371.619647		152754.19	87181.47	8.95E-03
346.92	0.0134	0.9866		13.5288	1.0005	108117.48	46069848.654957		144363.70	83019.38	1.79E-02
346.21	0.0190	0.9810		13.2053	1.0010	114954.49	185626774.079646		140601.74	81142.00	2.32E-02
344.11	0.0276	0.9724		12.8205	1.0021	134591.17	1106305639.597350		129946.80	75784.61	2.66E-02
						Total	1350386983.457280				
Species	A	B	C								
methanol	11.9673	3626.55	-34.29								
benzene	9.2806	2788.51	-52.36								

Table 2.4.2: Van Laar activity model for methanol-benzene system.

R	8.314 J/molK		A	31 J/mol					
P	101330 Pa		B	50 J/mol		Objective Function			$y_a = x_a P_{a,sat} / P_{calc}$
Temperature	x_a	x_b	y_a	y_b	P_{calc}	$(P - P_{calc})^2$	$P_{a,sat}$	$P_{b,sat}$	y_a
351.76	0.002	0.998	1.0106298	1	101332.1569	4.652200612	51204648	101535.23	1.01063
350.8	0.0028	0.9972	1.0106484	1	101333.0264	9.159287661	36575735	101617.56	1.010648
350.67	0.003	0.997	1.0106497	1	101333.2434	10.51966573	34137470	101638.16	1.01065
350.43	0.003	0.997	1.010657	1	101333.2456	10.53415635	34137718	101638.17	1.010657
350.37	0.0041	0.9959	1.0106442	1	101334.4334	19.65485057	24978794	101751.63	1.010644
349.2	0.0055	0.9945	1.0106613	1	101335.962	35.54488817	18621151	101896.41	1.010661
348.45	0.0058	0.9942	1.0106803	1	101336.2996	39.68439619	17658380	101927.5	1.01068
346.92	0.0134	0.9866	1.0106252	1.000001	101344.5479	211.6423735	7643384	102721.13	1.010625
346.21	0.019	0.981	1.0105713	1.000002	101350.5958	424.1859544	5390632	103313.81	1.010571
344.11	0.0276	0.9724	1.010519	1.000005	101359.9337	896.0264472	3711092	104237.42	1.010519
					Total	1661.60422			
Species	A	B	C						
Methanol	11.9673	3626.55	-34.29						
Benzene	9.2806	2788.51	-52.36						

Table 2.4.3: Wilson equation activity model for methanol-benzene system.

	8.314 J/molK		A	0.0403 J/mol					
P	101330 Pa		B	1.2958 J/mol		Objective Function			$y_a = x_a P_{a,sat} / P_{calc}$
Temperature (K)	x_a	x_b	y_a	y_b	P_{calc}	$(P - P_{calc})^2$	$P_{a,sat}$	$P_{b,sat}$	y_a
351.76	0.0020	0.9980	16.8466	0.9987	102236.76	822212.65	172291.20	96747.99	3.37E-03
350.80	0.0028	0.9972	16.2767	0.9982	101043.31	82189.55	166423.94	93892.45	4.61E-03
350.67	0.0030	0.9970	16.1397	0.9980	101067.09	69122.21	165642.25	93510.92	4.92E-03
350.43	0.0030	0.9970	16.1397	0.9980	100299.90	1061095.92	164207.09	92809.74	4.91E-03
350.37	0.0041	0.9959	15.4222	0.9972	102359.31	1059468.96	163849.91	92635.10	6.56E-03
349.20	0.0055	0.9945	14.5894	0.9961	101045.12	81159.06	157012.08	89280.84	8.55E-03
348.45	0.0058	0.9942	14.4216	0.9959	99096.60	4988063.67	152754.19	87181.47	8.94E-03
346.92	0.0134	0.9866	11.1165	0.9890	102508.19	1388123.96	144363.70	83019.38	1.89E-02
346.21	0.0190	0.9810	9.4784	0.9831	103579.33	5059475.35	140601.74	81142.00	2.58E-02
344.11	0.0276	0.9724	7.7123	0.9734	99394.15	3747520.89	129946.80	75784.61	3.61E-02
					Total	18358432.20			
Species	A	B	C						
methanol	11.9673	3626.55	-34.29						
benzene	9.2806	2788.51	-52.36						

By using three different activity models for methanol-benzene system, we were able to obtain three final sum of objective function data. The activity models used are three-suffix Margules equation, Van Laar equation and Wilson equation. Table 4.1, 4.2, 4.3 above shows the data obtained in Excel.

Three-suffix Margules equation:

$$RT \ln \gamma_a = (A + 3B)x_b^2 - 4Bx_b^3$$

$$RT \ln \gamma_b = (A - 3B)x_a^2 + 4Bx_a^3$$

Van Laar equation:

$$RT \ln \gamma_a = A \left(\frac{Bx_b}{Ax_a + Bx_b} \right)^2$$

$$RT \ln \gamma_b = B \left(\frac{Ax_a}{Ax_a + Bx_b} \right)^2$$

Wilson equation:

$$\ln \gamma_a = -\ln(x_a + Ax_b) - x_b \left(\frac{B}{x_b + Bx_a} - \frac{A}{x_a + Ax_b} \right)$$

$$\ln \gamma_b = -\ln(x_b + Bx_a) - x_a \left(\frac{A}{x_a + Ax_b} - \frac{B}{x_b + Bx_a} \right)$$

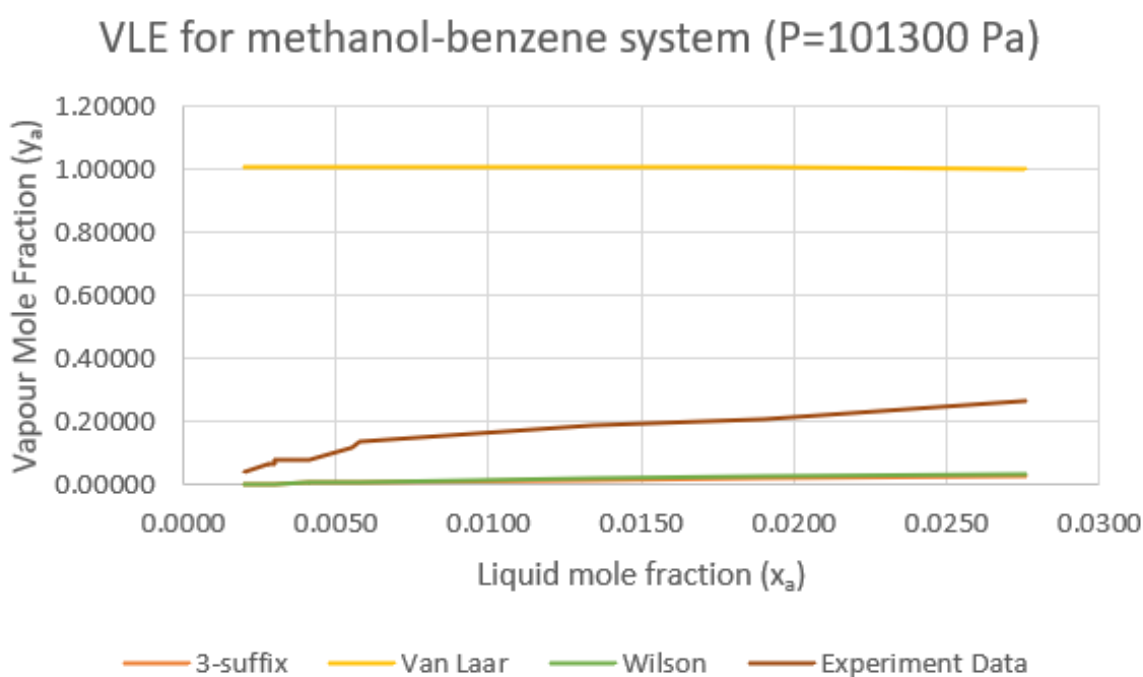
In three-suffix Margules model, γ_a fluctuates around 13.8 while temperature decreases and has a peak of 13.9223 at 348.45 K. On the other hand, γ_b slightly increases while temperature decreases. Besides that, in Van Laar model, γ_a and γ_b fluctuate around 1.01 and around 1.0 respectively as the temperature decreases. Moreover, in Wilson model γ_a and γ_b gradually decreases with temperature as when temperature lowers in pressure constant conditions, liquid mole fraction of methanol (x_a) and benzene (x_b) both increases.

(e)

2.5 Equilibrium Vapour Mole Fraction & Suitability of Models for Methanol-Benzene System

Equation used to calculate vapour mole fraction (y_a)

$$y_a = \frac{x_a P_{a,sat}}{P_{calc}}$$



The vapour-liquid equilibrium (VLE) describes the distribution of a chemical species between the vapour phase and a liquid phase. In mixtures containing two or more components, the concentration of each component is often expressed as mole fractions, and in this case are methanol and benzene. The mole fraction of a given component of a mixture in a particular phase (either the vapour or the liquid phase) is the number of moles of that component in that phase divided by the total number of moles of all components in that phase. For each component in a binary mixture, one could make a vapor-liquid equilibrium diagram. Such a diagram would graph liquid mole fraction on a horizontal axis and vapour mole fraction on a vertical axis. In such VLE diagrams. By comparing the vapour mole fraction from the experimental data from the literature with the collected data, observations clearly showed that, among 3 activity models, Wilson and Three-Suffix Margules activity model has the closest

data to the data harvested from literature. It indicates that Three-Suffix Margules and Wilson activity model are most suitable for simple liquid mixture with similarity of the molar volume to its components.

3.0 Part 2: UNIQUAC activity model for Methanol- Benzene System

This simulation about VLE data for methanol-benzene system based on UNIQUAC activity model which can be shifted at different pressure in a pressure-swing distillation is saved inside of the Aspen Plus simulation file.

Conclusion

In conclusion, the percentage error of the pressure is 0.33%. The highest and lowest values for the percentage error of the 10 temperature values are 0.22% and 0.01% respectively. For the percentage error of the 10 values of liquid mole fraction and the other 10 values of vapour mole fraction are all 0%.

Peng Robinson Equation of State is applied in question 1(b). Methanol and benzene are binary mixtures. The fugacity coefficient of methanol in 351.76 K (highest temperature in set of data) in liquid phase is 2.2339 which is far from ideal condition while it at vapour phase is 0.9864, quite near to ideal condition. The fugacity coefficient of benzene in 351.76 K at liquid phase is 0.9311 while at vapour phase is 0.9710. On the other hand, the fugacity coefficient of methanol in 344.11 K (lowest temperature in set of data) at liquid phase is 0.5442 while at vapour phase is 0.9837. For benzene at 344.11 K in liquid phase is 0.7367 while at vapour phase at 0.9696.

The equation of $\gamma_i \hat{\phi}_1^v = x_i \hat{\phi}_1^l$ is applied to find out the estimated value of vapour mole fraction of methanol and benzene. After calculating the estimated vapour mole fraction, we found out that the estimated value of the vapour mole fraction for methanol that we obtained has a big difference from the experimental value, while benzene also has a slight difference. In conclusion, the Peng-Robinson EOS is not suitable for this system.

By using Excel to calculate the data with three-suffix Margules model, Van Laar model and Wilson model we can observe that in Van Laar model fluctuates around 1 where else three-suffix Margules model and Wilson model generally decrease with the temperature.

By plotting the y-x graph of vapour mole fraction (y_a) against liquid mole fraction (x_a), it is clearly observed that Three-Suffix Margules and Wilson activity models are the most conducive as compared to the experiment data from the literature. Both activity models gave a better relation between change of mole fraction with partial pressure of a component in a liquid mixture. However, Wilson activity model is not suitable as methanol and benzene are miscible.

References

DDBST GmbH (2022). Vapor-Liquid Equilibrium Data Set 39. *Vapor-Liquid Equilibrium Data of Benzene + Methanol from Dortmund Data Bank*. [online] Ddbst.com. Available at: <http://www.ddbst.com/en/EED/VLE/VLE%20Benzene%3BMethanol.php>. [Accessed on 2 April 2022]