

Exercise 3 – Thermodynamics

1 Introduction

Vapour liquid equilibrium (VLE) simulations were carried out for both binary and ternary mixtures of benzene, cyclohexane and acetone. The Wilson activity coefficient model was used in order to model the non-ideal mixtures [1].

Reliable VLE predictions offer insight in designing distillation column operations for the purification of compounds such as cyclohexane and benzene, which are subsequently used in the polymer manufacturing industry.

In the remainder of this report the methodology employed is discussed, the simulation results are analysed, and recommendations are made regarding the efficient separation of mixtures of cyclohexane and benzene into pure components. In addition, as far as reliability is concerned, the simulations are compared to those that UniSim would predict for this system using the Wilson activity coefficient model.

2 Modelling VLE for benzene-cyclohexane at 50 °C

Experimental data provided at 50 °C was used in order to optimise Wilson parameters for predicting benzene-cyclohexane VLE. Table 1 displays the calculated molar volumes (\underline{V}) of the 3 species at temperatures of 20, 50 and 100 °C respectively [1]. In addition, table 2 reports the optimised Wilson parameters ($\lambda_{12}-\lambda_{11}$) & ($\lambda_{21}-\lambda_{22}$) as well as the RMS error of the fit to experimental data.

Table 1: RMM values and molar volumes at 3 different temperatures for the 3 components

Component	Benzene	Cyclohexane	Acetone
RMM / g mol ⁻¹	78.11	84.16	58.08
\underline{V} (20 °C) / 10 ⁻⁵ m ³ mol ⁻¹	8.886	10.775	7.342
\underline{V} (50 °C) / 10 ⁻⁵ m ³ mol ⁻¹	9.222	11.206	7.713
\underline{V} (100 °C) / 10 ⁻⁵ m ³ mol ⁻¹	9.850	11.954	8.393

Table 2: Optimised Wilson parameter values for benzene-cyclohexane at 50 °C and RMS error of fit

$(\lambda_{12}-\lambda_{11})$ / J mol ⁻¹	$(\lambda_{21}-\lambda_{22})$ / J mol ⁻¹	RMS error of fit / Pa
822.65	526.32	96.45

In modelling the system, equation 1 was employed. Partial fugacity coefficients of unity were assumed and the Poynting correction was neglected, because of the low pressures involved. In equation 1, i refers to a component. For the purposes of this investigation $i = 1, 2, 3$ for benzene, cyclohexane and acetone respectively. P^{sat} values were estimated using the Antoine equation and activity coefficients (γ_i) were calculated using the Wilson model [1].

$$P * \sum_i(y_i) = \sum_i(\gamma_i * P_i^{\text{sat}} * x_i) \quad (1)$$

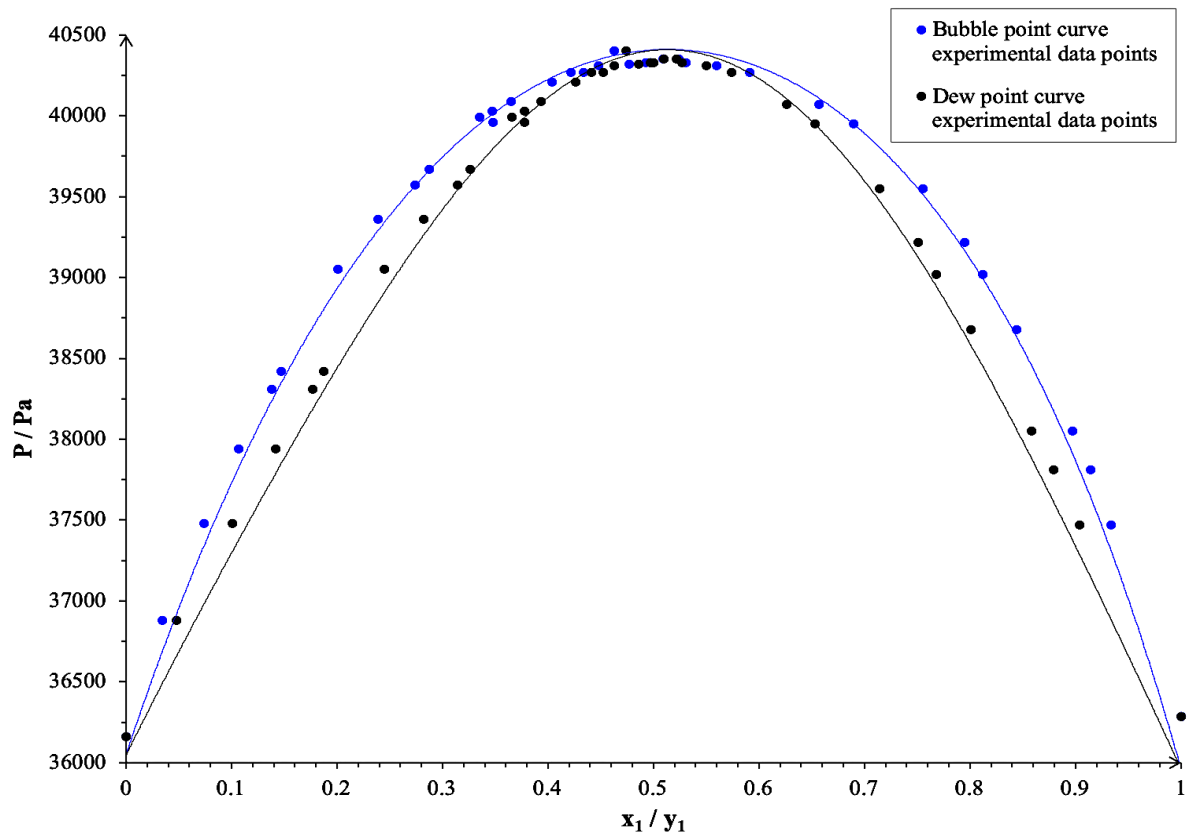


Figure 1: Plots of predicted bubble and dew point curve fits for the benzene-cyclohexane mixture at 50 °C

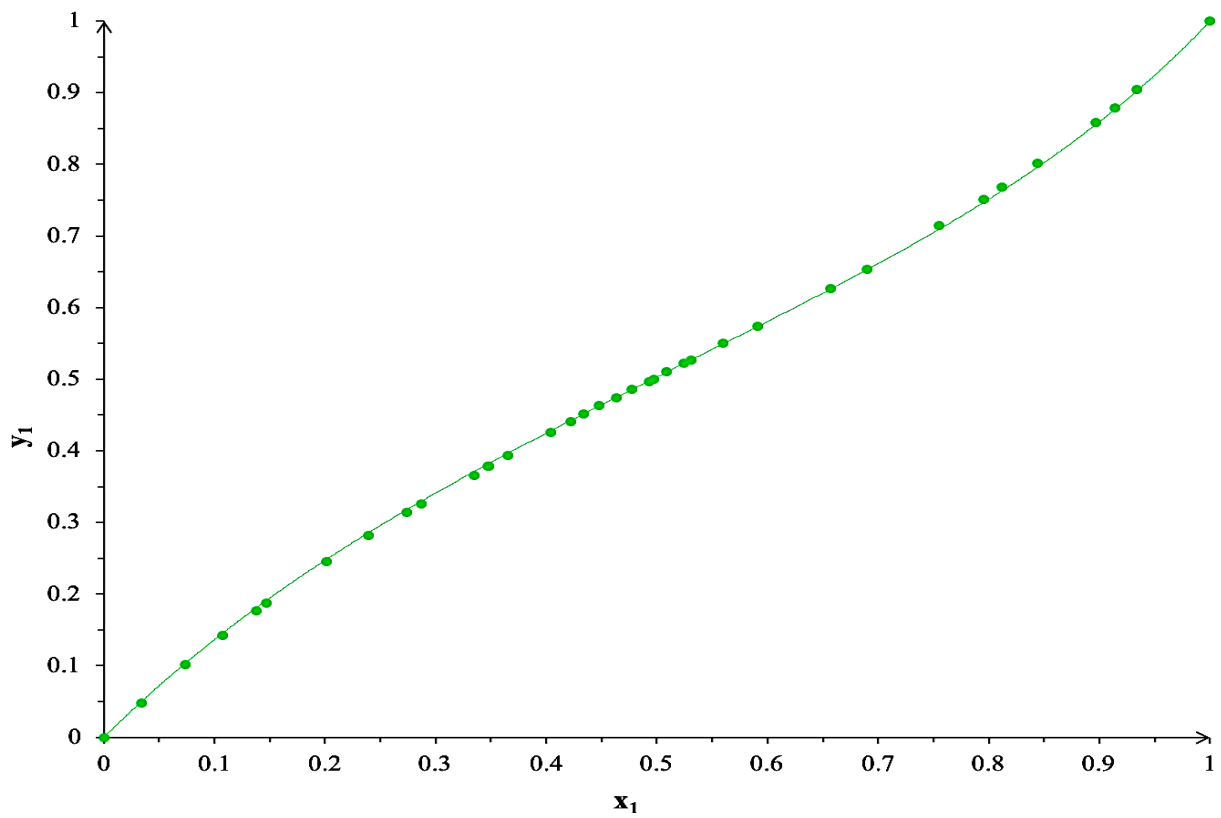


Figure 2: Plot of y_1 vs x_1 predicted curve for the benzene-cyclohexane mixture along with the experimental data points at 50 °C

Figure 1 depicts the bubble and dew point predicted curves and their fit to experimental data at 50 °C. In addition, figure 2 depicts the y_1 vs x_1 predicted curve and its fit to experimental data. From figure 1 it's clear that the benzene-cyclohexane mixture displays a maximum boiling pressure azeotrope at 50 °C. There's a certain positive deviation from Raoult's law [3]. Figure 2 is also indicative of this positive deviation from ideality when comparing the plot to the $y_1 = x_1$ line.

3 Modelling VLE for benzene-acetone at 50 °C

Using the same assumptions as for the benzene-cyclohexane mixture as well as equation 1, Wilson parameters were optimised for the benzene-acetone mixture. The Wilson parameters and RMS error of the fit to experimental data [1] are tabulated in table 3.

Table 3: Optimised Wilson parameter values for benzene-acetone at 50 °C and RMS error of fit

$(\lambda_{13}-\lambda_{11}) / \text{J mol}^{-1}$	$(\lambda_{31}-\lambda_{33}) / \text{J mol}^{-1}$	RMS error of fit / Pa
112.59	1175.15	250.92

Figure 3 is indicative of positive deviation from Raoult's law, as far as the benzene-acetone mixture is concerned. The system doesn't form an azeotrope which is also clear when comparing the curve in figure 4 to the $y_1 = x_1$ line.

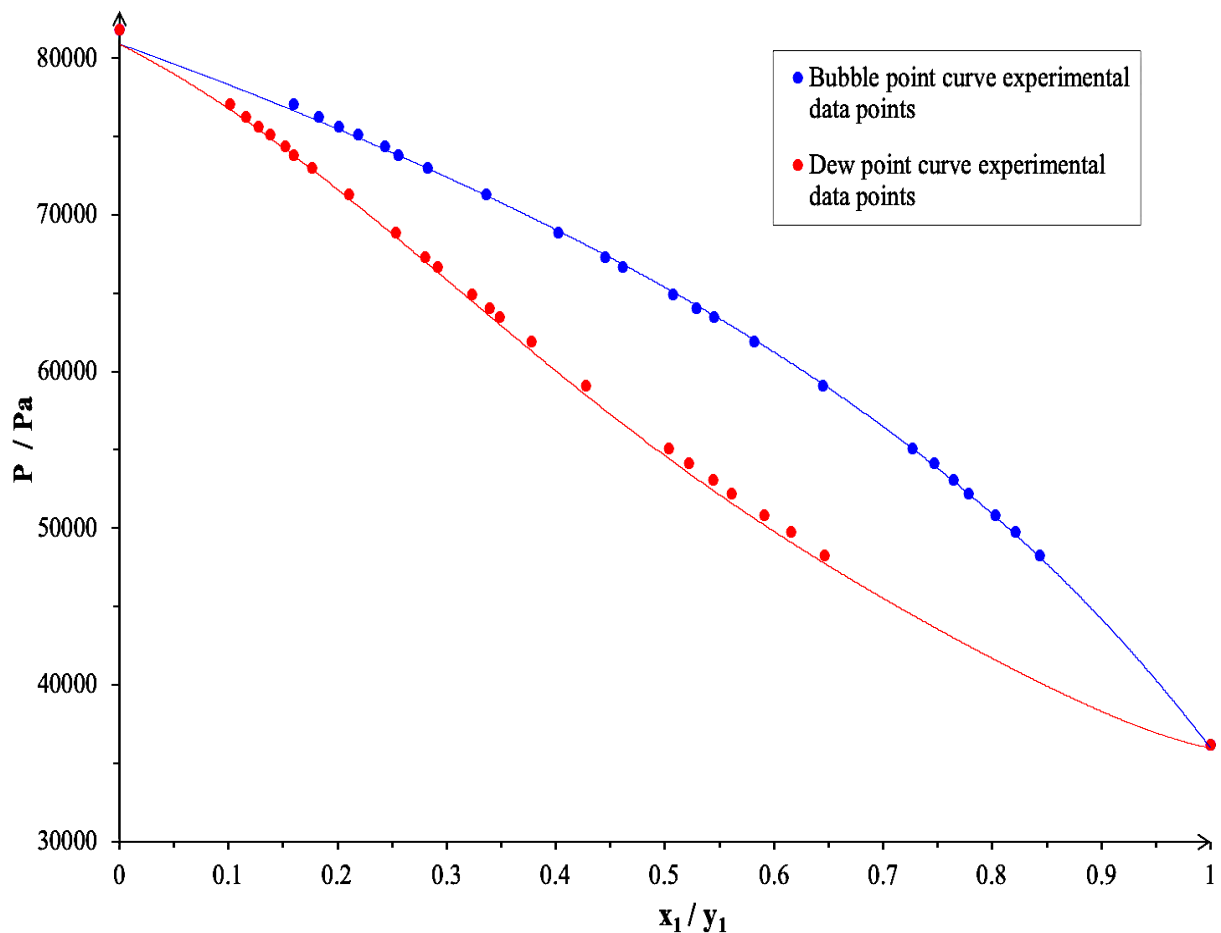


Figure 3: Plots of predicted bubble and dew point curve fits for the benzene-acetone mixture at 50 °C

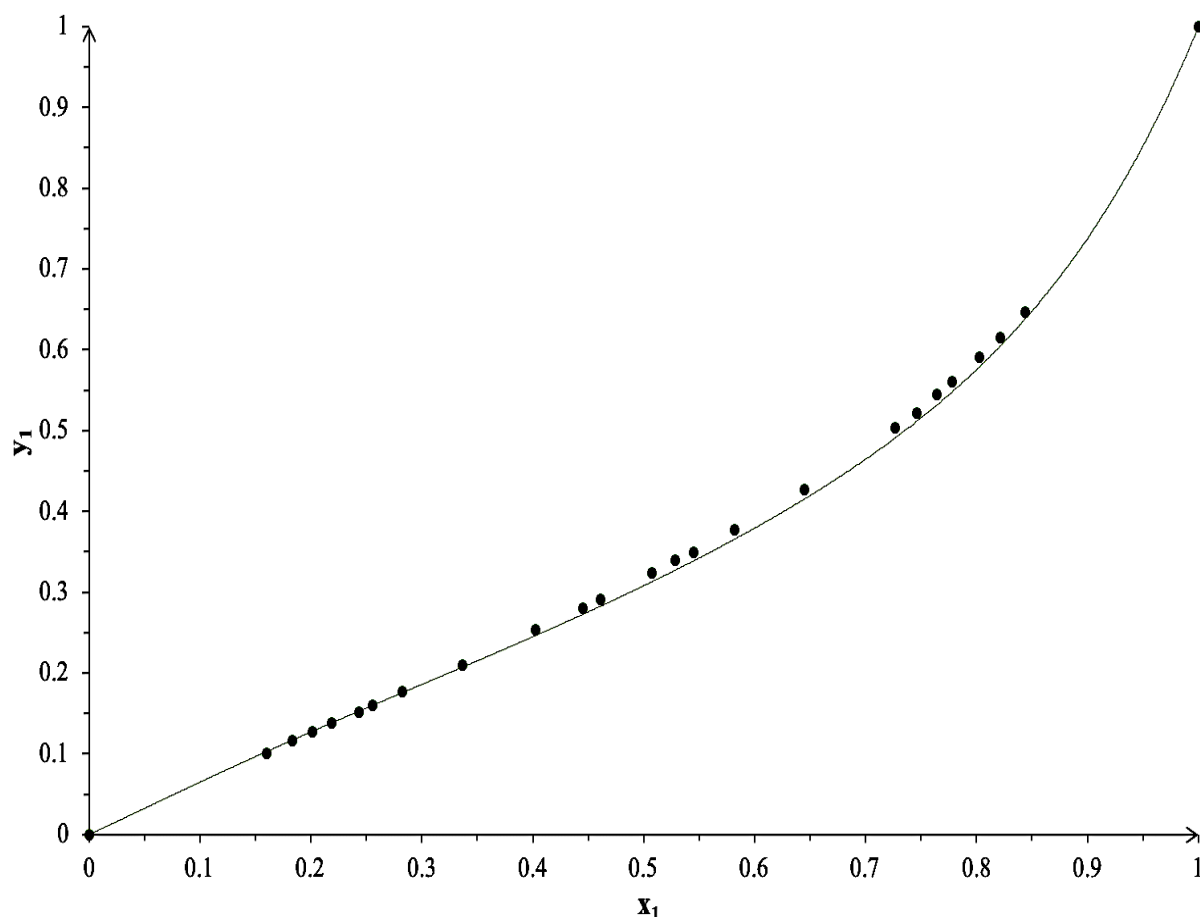


Figure 4: Plot of y_1 vs x_1 predicted curve for the benzene-acetone mixture along with the experimental data points at 50 °C

4 Modelling VLE for cyclohexane-acetone at 50 °C

Wilson parameters for the cyclohexane-acetone mixture were also optimised using equation 1 and the same assumptions as those employed in modelling the other 2 binary mixtures. The parameters are reported in table 4 along with the RMS error of the fit to experimental data [1].

Table 4: Optimised Wilson parameter values for cyclohexane-acetone at 50 °C and RMS error of fit

$(\lambda_{23}-\lambda_{22}) / \text{J mol}^{-1}$	$(\lambda_{32}-\lambda_{33}) / \text{J mol}^{-1}$	RMS error of fit / Pa
2119.37	3777.64	229.20

Figure 5 is indicative of the fact that a maximum boiling pressure azeotrope is formed in the cyclohexane-acetone mixture. The system displays more severe non-ideal behaviour when compared to the benzene-cyclohexane binary mixture. This is also clear from the plot in figure 6 when compared to the $y_2=x_2$ line.

The Wilson model is still good enough for predicting VLE for this system because liquid-liquid separation doesn't occur between cyclohexane and acetone [3].

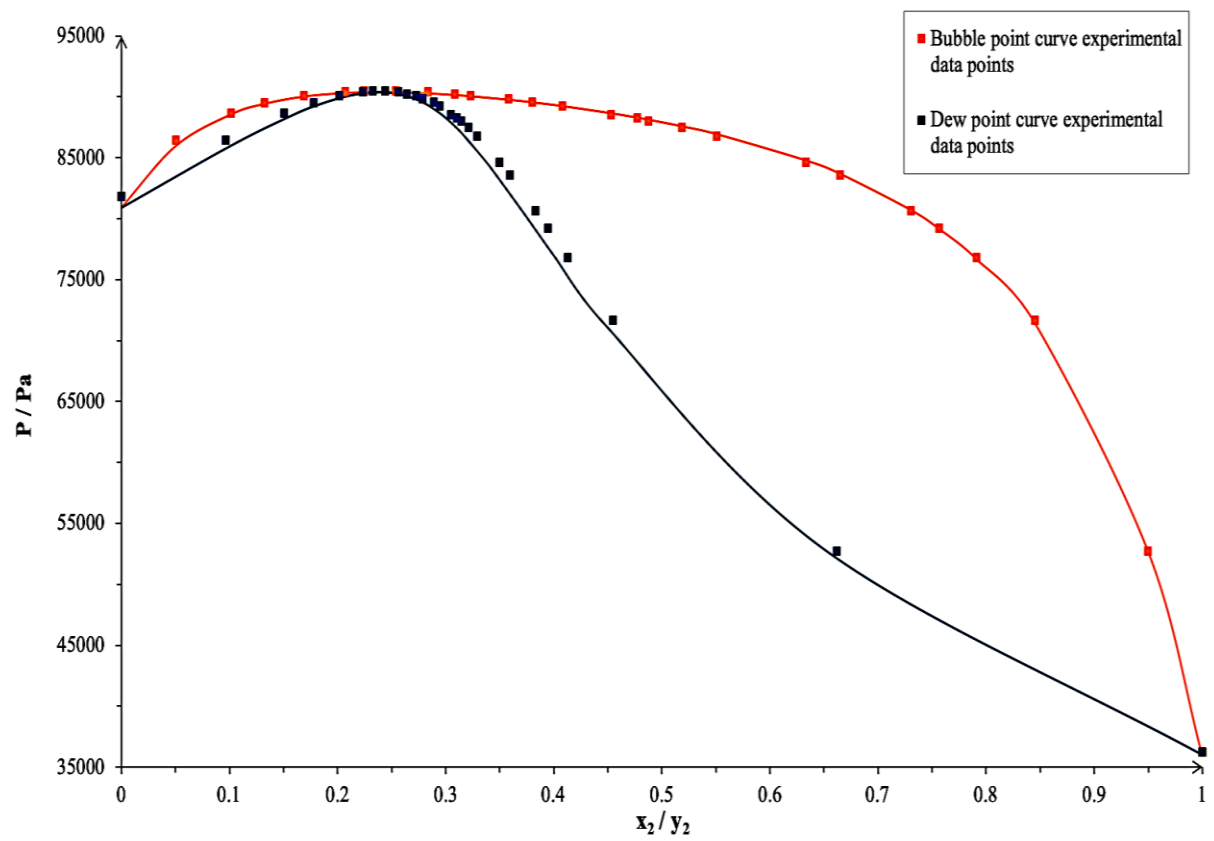


Figure 5: Plots of predicted bubble and dew point curve fits for the cyclohexane-acetone mixture at 50 °C

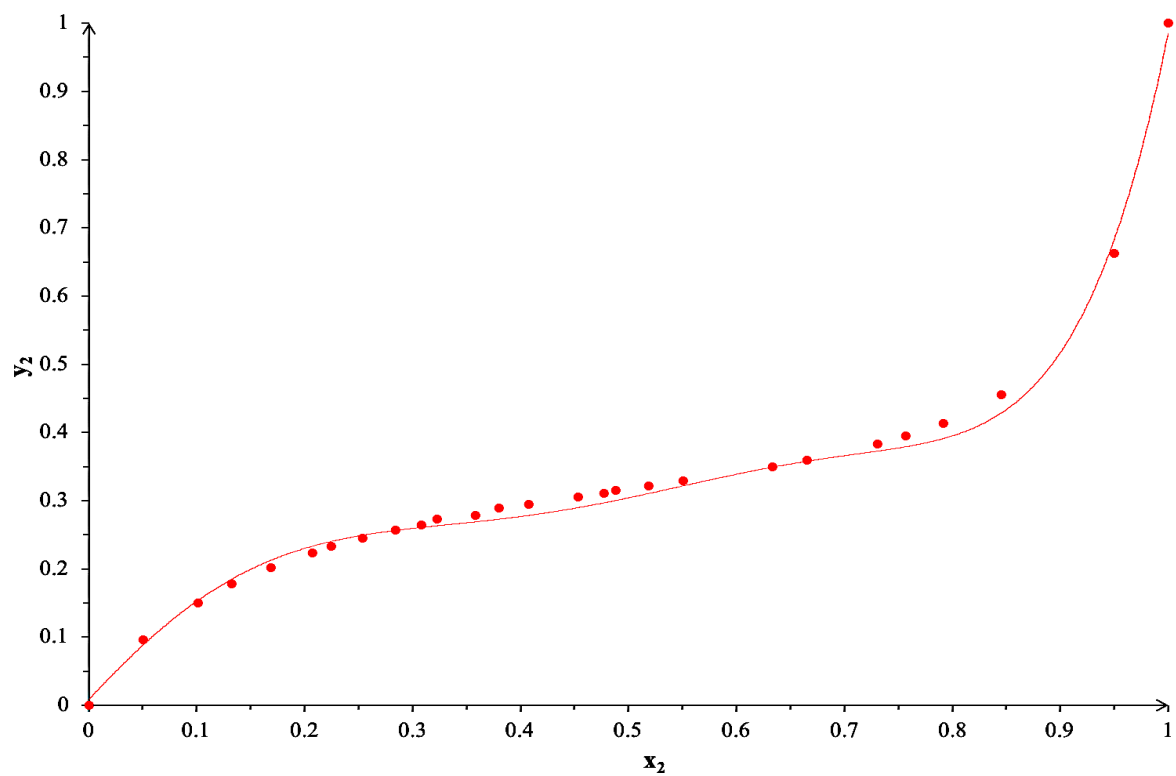


Figure 6: Plot of y_2 vs x_2 predicted curve for the cyclohexane-acetone mixture along with the experimental data points at 50 °C

5 Predicting VLE for ternary mixtures of benzene, cyclohexane and acetone at 50 °C

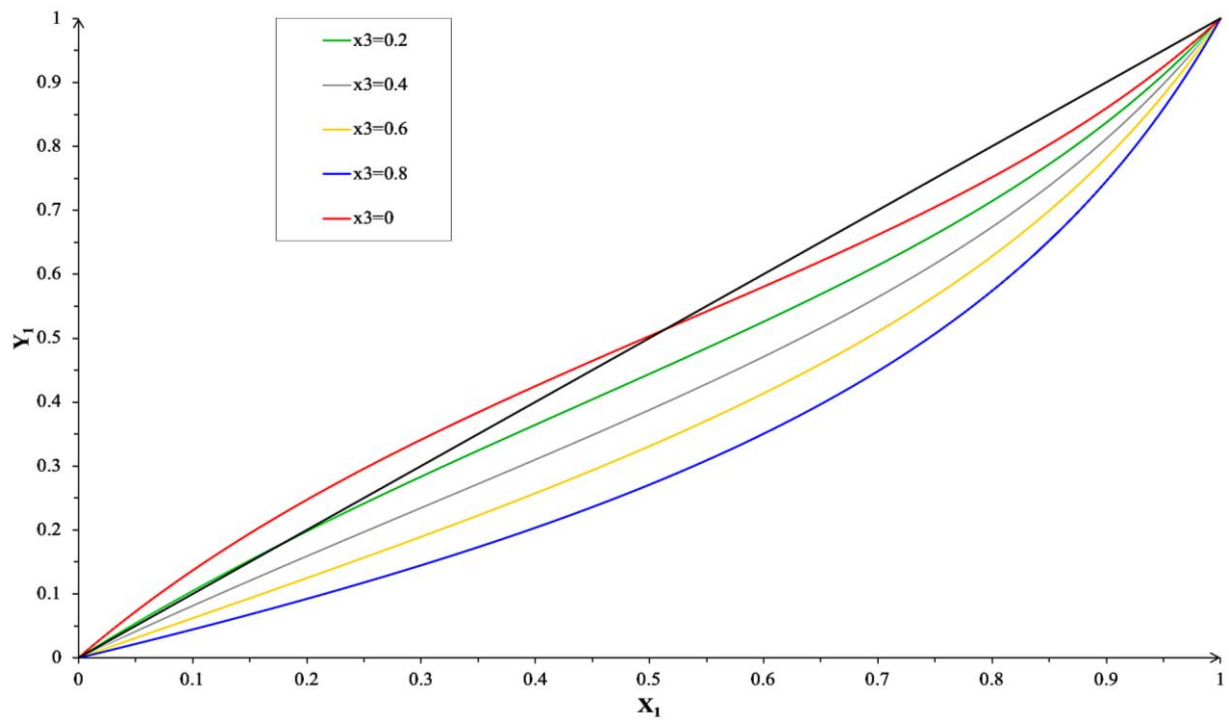


Figure 7: Plots of Y_1 vs X_1 predicted curves at fixed x_3 for the ternary system at 50 °C including the $Y_1 = X_1$ black line

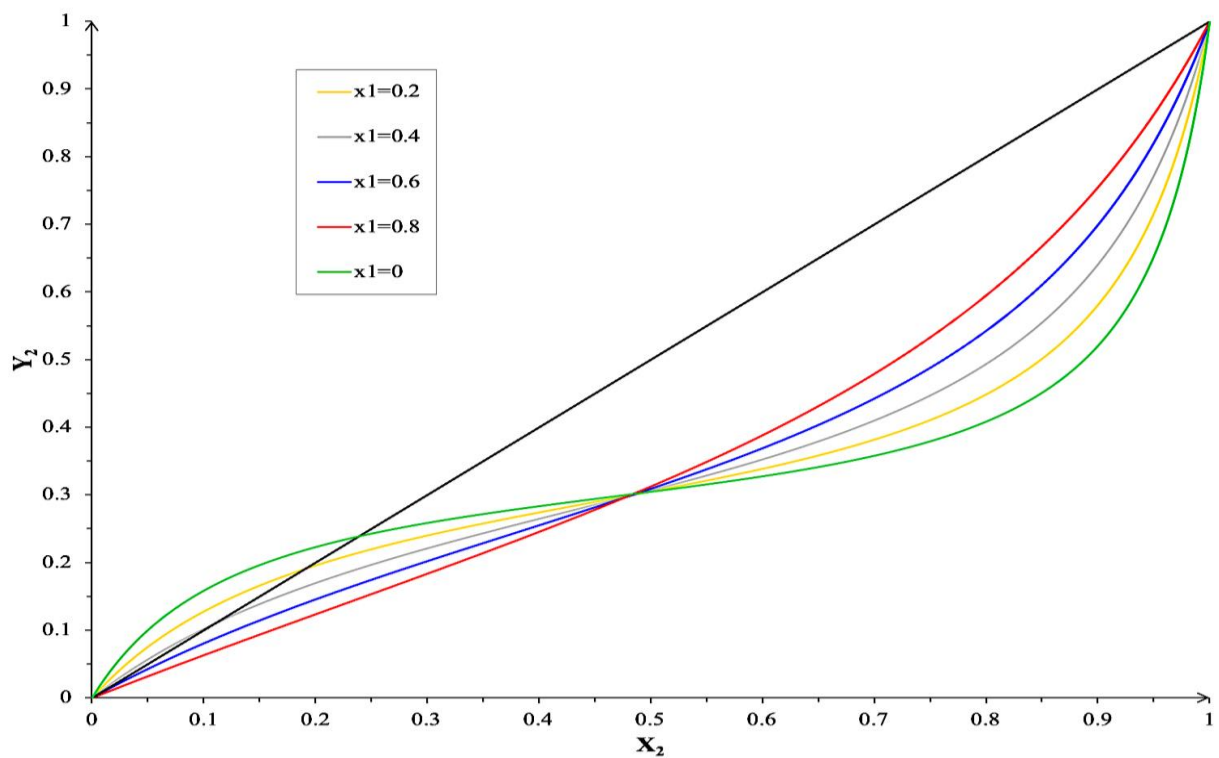


Figure 8: Plots of Y_2 vs X_2 predicted curves at fixed x_1 for the ternary system at 50 °C including the $Y_2 = X_2$ black line

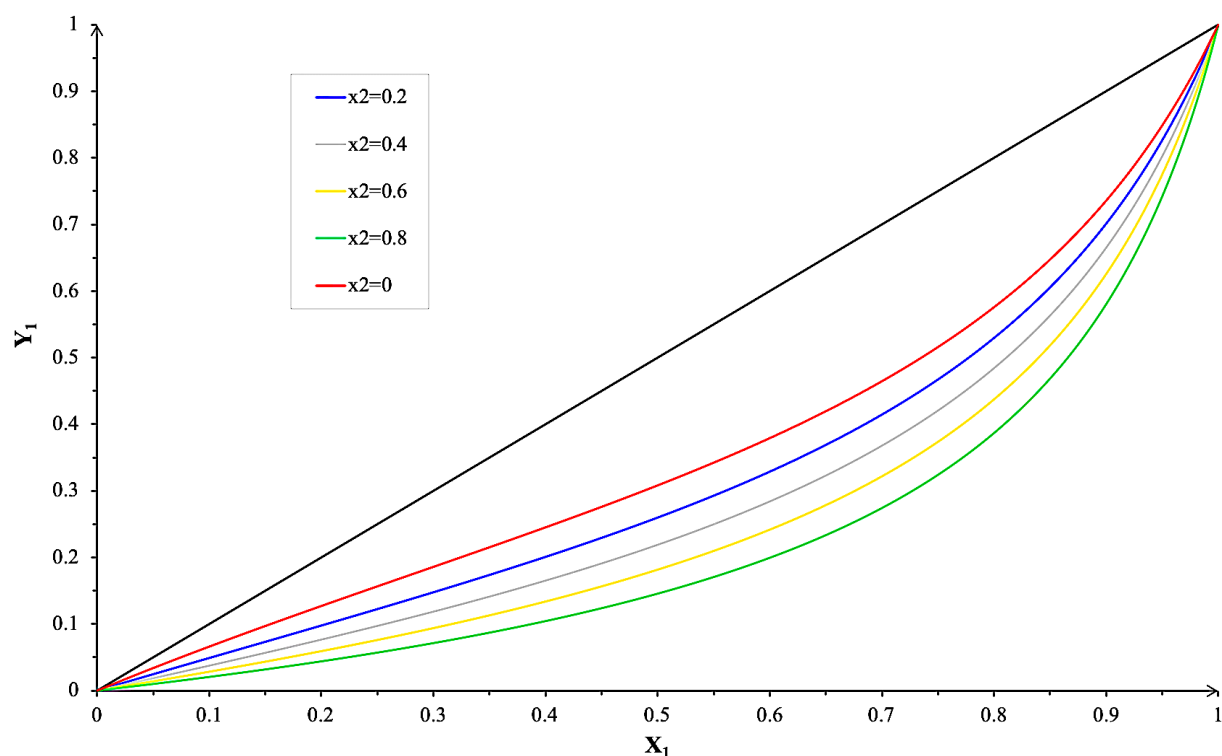


Figure 9: Plots of Y_1 vs X_1 predicted curves at fixed x_2 for the ternary system at 50 °C including the $Y_1 = X_1$ black line

The ternary system of benzene-cyclohexane-acetone was modelled at 50 °C using the optimised Wilson binary parameters [1]. In figure 7, Y_1 and X_1 are acetone-free parameters. Similarly, in figures 8 and 9, Y_2 , X_2 are benzene-free and Y_1 , X_1 are cyclohexane-free parameters respectively [1].

Based on the results depicted in figures 7 and 8, the ternary system clearly exhibits (maximum boiling pressure) binary azeotrope formation. Figure 9 is indicative of the fact that at fixed x_2 , the ternary system doesn't display a binary azeotrope which makes sense when compared to the binary system predictions of figures 1, 3 and 5.

A binary azeotrope is formed between benzene and cyclohexane when fixing x_3 in the range $0 \leq x_3 \leq 0.2$, according to the plots in figure 7 including the $Y_1 = X_1$ line. Moreover, a binary azeotrope is formed between cyclohexane and acetone when fixing x_1 in the range $0 \leq x_1 \leq 0.4$, according to the plots in figure 8.

A ternary diagram would yield a clearer picture regarding the range of conditions at which binary azeotropes form in the ternary system. Nevertheless, considering the results in figures 7, 8 & 9, there's strong evidence suggesting that a ternary azeotrope doesn't form in the ternary mixture.

6 Predictions for ternary mixtures of benzene, cyclohexane and acetone at 1 bara

In performing simulations for the binary systems and ternary mixture at 1 bara, linear interpolation was employed in the form of equation 2. The T range of $50 \leq T \leq 100$ °C was

used when performing simulations using linearly interpolated molar volumes. In equation 2, $\underline{V}_i(T)$ refers to the molar volume of component i at the given T , where $i = 1, 2, 3$ [1].

$$\underline{V}_i(T) = \underline{V}_i(373\text{ K}) - \frac{373-T}{373-323} * [\underline{V}_i(373\text{ K}) - \underline{V}_i(323\text{ K})] \quad (2)$$

Table 5: T_{sat} for each pure component at 1 bara

Component	Benzene	Cyclohexane	Acetone
$T_{\text{sat}} (1 \text{ bara}) / \text{K}$	352.8	353.4	329.1

According to table 5, acetone is the more volatile component (MVC). In addition, figures 10, 11 & 12 display the bubble and dew point plots for each of the binary mixtures explored. An iterative scheme incorporating the Antoine equation [1] was employed in order to construct the curves in each of figures 10, 11 & 12.

Moreover, figure 13 depicts plots of $Y_1 = y_1/(y_1+y_2)$ vs $X_1 = x_1/(x_1+x_2)$ at fixed x_3 , for the ternary mixture. According to figure 13, a binary azeotrope between benzene and cyclohexane forms at slightly higher X_1 as opposed to what happens at 50 °C.

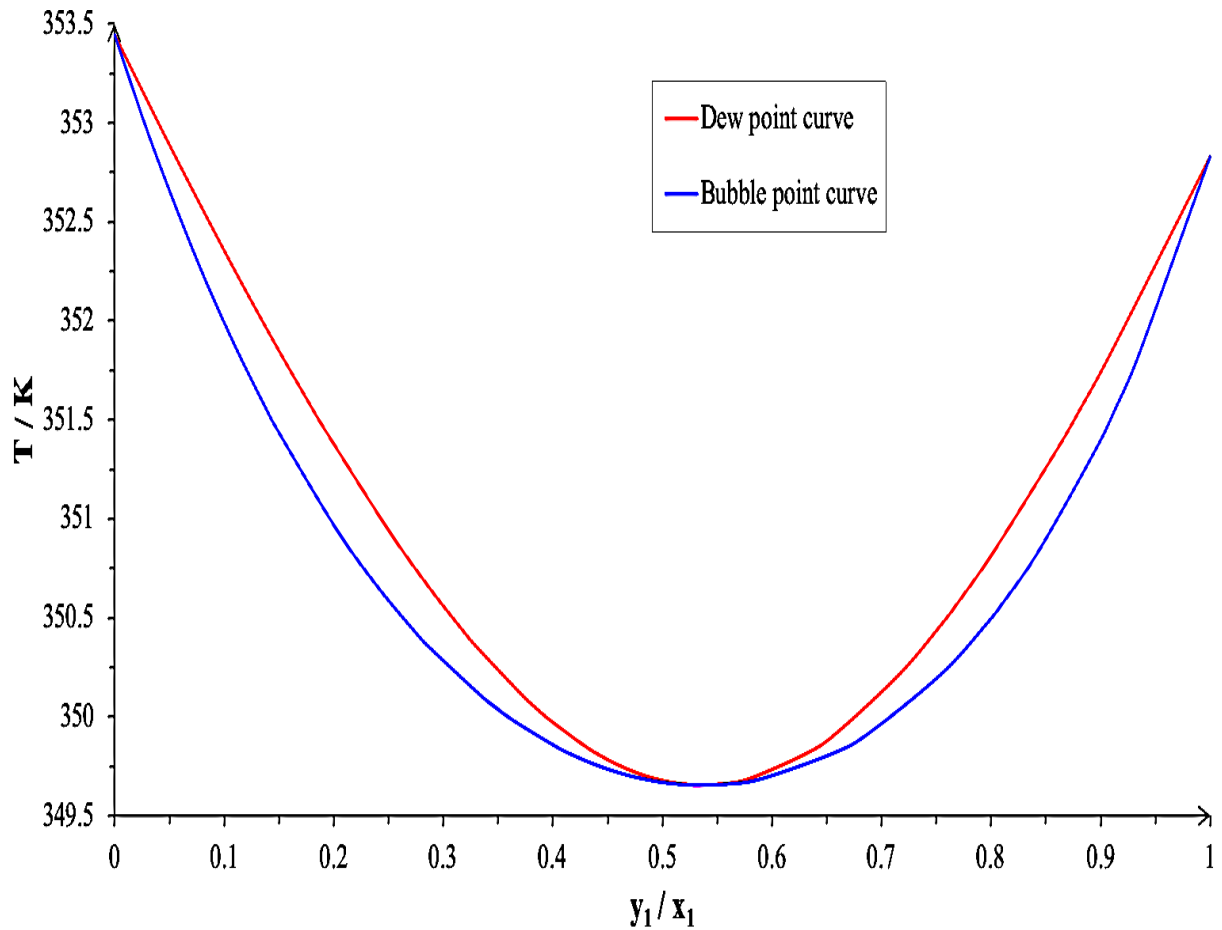


Figure 10: Plots of predicted bubble and dew point curve fits for the benzene-cyclohexane binary mixture at 1 bar

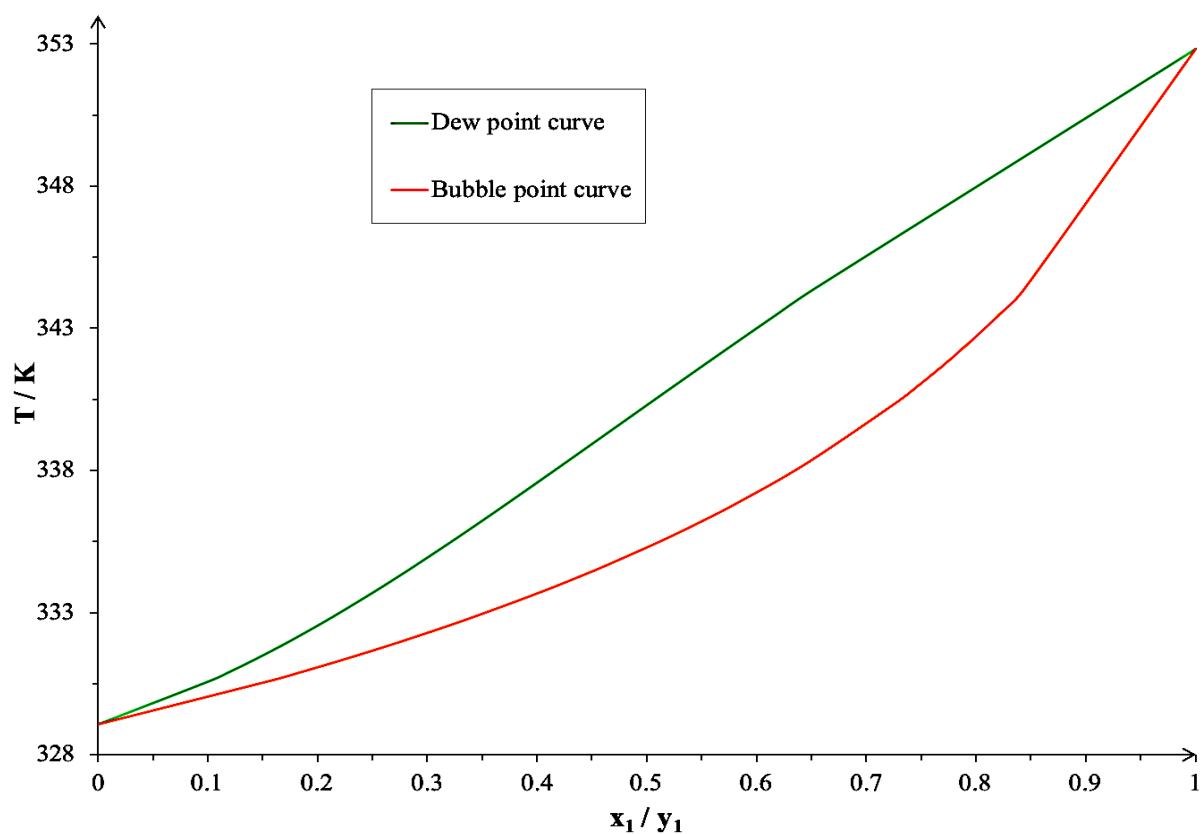


Figure 11: Plots of predicted bubble and dew point curve fits for the benzene-acetone binary mixture at 1 bar

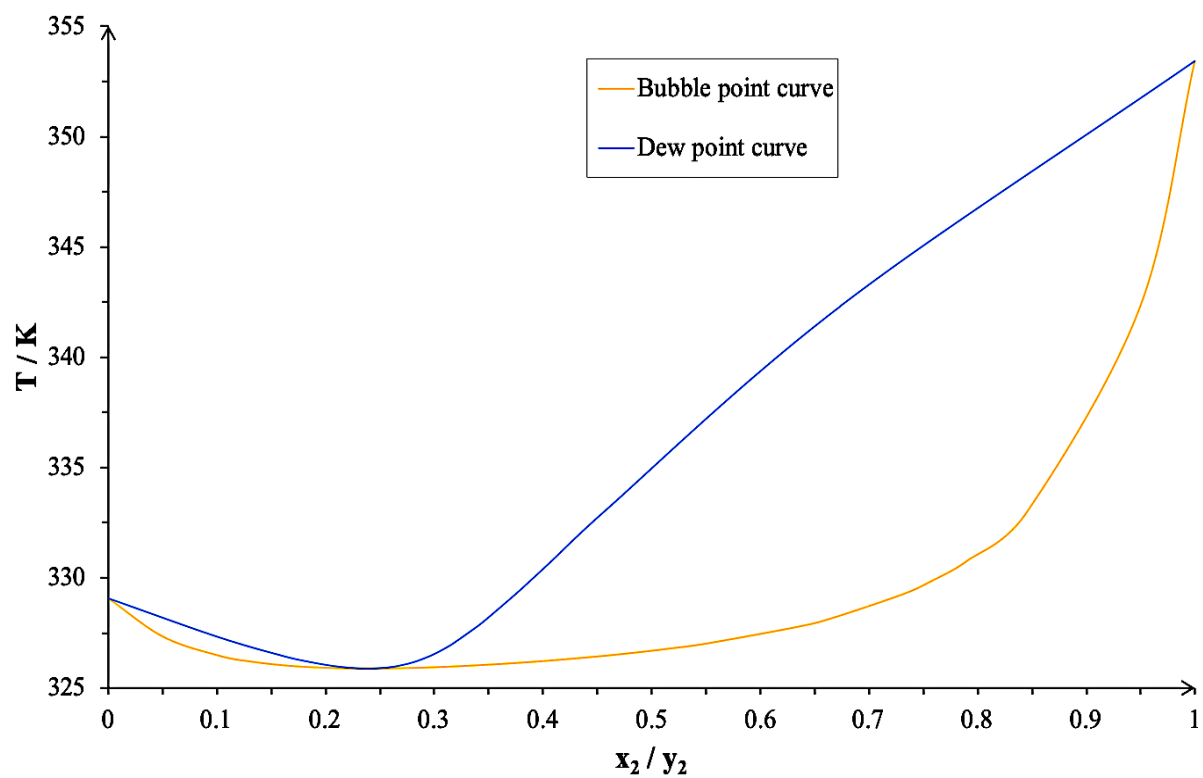


Figure 12: Plots of predicted bubble and dew point curve fits for the cyclohexane-acetone binary mixture at 1 bar

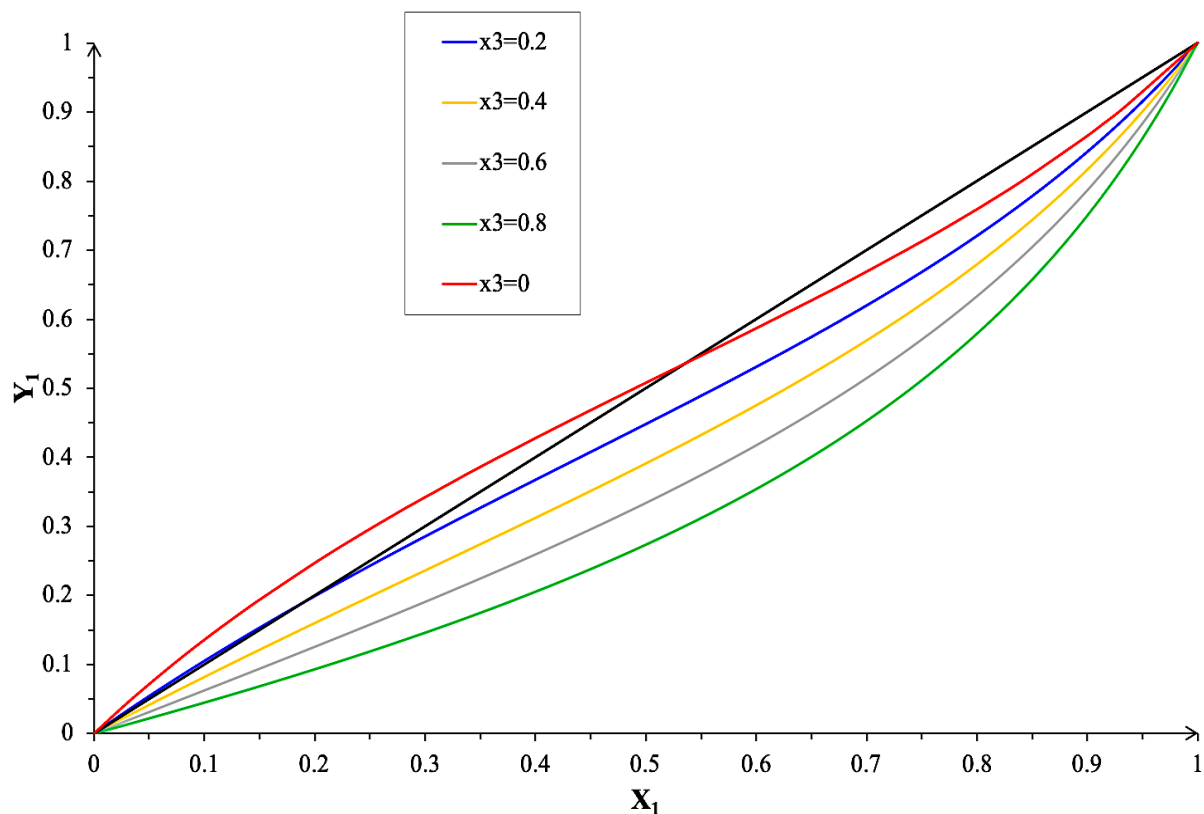


Figure 13: Plots of Y_1 vs X_1 predicted curves for at fixed x_3 for the ternary system at 1 bara including the $Y_1 = X_1$ black line

For a distillation column operating at total reflux and 1 bara fixed pressure, table 6 tabulates the temperatures estimated for a set of stages along the column. The stages were assumed to be far from the feed entry stage. Using the limiting situation expressed in the form of equation 3 which relates adjacent stream compositions and by taking stage 1 with $x_1 = 0.8$, $x_2 = 0.198$ and $x_3 = 0.002$ as the starting point, compositions for higher column stages were estimated. These are tabulated in table 6 [1].

$$y_{i, \text{tray } n} = x_{i, \text{tray } n+1} \quad (3)$$

Table 6: Predicted T and composition on 10 distillation column stages for which the distillation column is assumed to operate at 1 bara fixed pressure and total reflux

Stage	T / K	x_1	x_2	x_3	y_1	y_2	y_3
1	350.3	0.800	0.198	0.002	0.755	0.238	0.007
2	349.6	0.755	0.238	0.007	0.702	0.273	0.025
3	347.9	0.702	0.273	0.025	0.620	0.292	0.088
4	343.3	0.620	0.292	0.088	0.471	0.277	0.253
5	336.0	0.471	0.277	0.253	0.276	0.233	0.490
6	330.6	0.276	0.233	0.490	0.139	0.209	0.652
7	328.1	0.139	0.209	0.652	0.068	0.209	0.723
8	326.9	0.068	0.209	0.723	0.033	0.217	0.750
9	326.4	0.033	0.217	0.750	0.016	0.226	0.759
10	326.1	0.016	0.226	0.759	0.007	0.232	0.761

According to table 6, cyclohexane is not undergoing efficient separation. It's cycling in composition as opposed to the changes the other two species are undergoing.

Taking into consideration the simulations performed, a mixture of benzene and cyclohexane can theoretically be separated using pressure-swing distillation. Acetone would be administered in the feed mixture at a mole fraction in the range $0.2 < x_3 < 1$. The first distillation column would operate at a pressure of 1 bar. At the stage where cyclohexane would start forming an azeotrope, an additional feed of pure acetone would be introduced in the first column. The distillate of the first column would then act as feed for the second column which would operate at 2-3 bar. The additional acetone would break the azeotrope in the first column and the higher pressure in the second column would ensure purification of cyclohexane by lowering its azeotropic composition (pressure-sensitive azeotrope) [2, 3]. Extractive distillation using a high boiling-point entrainer can also be considered for purification purposes.

The suggested purification scheme is likely to be more practical for benzene-rich mixtures, according to the simulations performed. In benzene rich mixtures there's greater flexibility in terms of avoiding azeotrope formation due to the small quantities of cyclohexane involved. In cyclohexane-rich mixtures the opposite is true and as a result, the suggested scheme may not be practical for purification purposes [3].

7 Discussion of calculation method

The simulations conducted at 50 °C and 1 bara are likely to be less reliable than those that UniSim would predict using the Wilson activity coefficient model. UniSim has a more extensive directory of VLE data (smaller interval widths) and at different pressures and temperatures as well. As a result, it performs VLE simulations using Wilson parameters that are less likely to have been extensively extrapolated to different temperatures and pressures as opposed to the assumptions employed in the spreadsheet simulations.

UniSim is more likely to evaluate adjusted Wilson parameters based on more accurate pressure or temperature dependencies, even though these might be minor. On the other hand, for the spreadsheet simulations, Wilson parameters were estimated using data at a single fixed temperature.

8 References

- [1] CET IIA, Exercise 3-Thermodynamics MT 2019, CEB Department, University of Cambridge, handout pp 5-9.
- [2] CET IIA, Separation Processes 2, course handout 5, CEB Department, University of Cambridge, pp 7-11.
- [3] Perry, Robert H. and Don W. Green, Perry's Chemical Engineer's Handbook, New York: McGraw-Hill, 2008, 7th edition, chapter 4 pp 4-35.