CHEG 325-010 Spring 2020 Final Project Assignment - Part 1

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The assigned mixture was n-heptane and ethylbenzene mixture. It was found that both chemical compounds were non-polar [1] [2]. Ethylbenzene is a commercial chemical used to make other chemicals, such as components of automotive and aviation fuels. Moreover, it is also used in paints and wood stains, mainly as arts and crafts finish [3]. Meanwhile for n-heptane, it is widely used in industry as functional fluids in closed systems and solvents for cleaning and degreasing. Consumer wise, it is produced as ink, toner and colorant products used in printers, and also as automotive care products [4].

Two thermodynamic activity coefficient models that are used to fit the experimental data obtained [5], are the Wilson and Van Laar model. The Van Laar model took into account the more complicated systems with dissimilar molecules, where the activity coefficient for each species would not be mirror images of each other (unsymmetric). However, the Wilson model acknowledged the ratio of a species to the other molecules surrounding any molecule depends on the differences in sizes and energies of interaction of the molecules, unlike the Van Laar model [6]. The general equation to calculate activity coefficient for each model is as shown below [7]:

Wilson model:

$$ln\,\gamma_i = 1 - ln\left(\sum_j^c A_{ij}x_j\right) - \sum_j^c \frac{A_{ji}x_j}{\sum_k^c A_{jk}x_k}$$

$$ln\,A_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij}\,ln\,T + d_{ij}T + \frac{e_{ij}}{T^2}$$

$a_{ij}, b_{ij}, c_{ij}, d_{ij}, e_{ij}$ are unsymmetrical

Van Laar model:

$$ln\,\gamma_i = A_i(1-z_i)^2\left[1 + C_i z_i\left(z_i - \tfrac{2}{3}\right) + 2z_i\left(\frac{A_iB_i}{|A_iB_i|} - 1\right)\right]$$

$$z_i = \frac{|A_i|x_i}{|A_i|x_i + |B_i|(1-x_i)}$$

$$A_i = \frac{\sum_j^c x_j A_{ij}}{(1-x_i)},\; B_i = \frac{\sum_j^c x_j A_{ji}}{(1-x_i)},\; C_i = \frac{\sum_j^c x_j C_{ij}}{(1-x_i)}$$

$$A_{ij} = a_{ij} + \frac{b_{ij}}{T},\; C_{ij} = c_{ij} + \frac{d_{ij}}{T},\; C_{ij} = C_{ji},\; A_{ii} = B_{ii} = C_{ii} = 0$$

a_{ij}, b_{ij} are unsymmetrical

In order to fit the VLE data obtained experimentally, the binary parameters for each model has to be specified before a regression analysis is performed on the data. For Wilson model, only $a_{ij/ji}$ and $c_{ij/ji}$ were specified, making $b_{ij/ji} = d_{ij/ji} = e_{ij/ji} = 0$ by default. Making n-heptane and ethylbenzene species 1 and 2 respectively, it was obtained that $a_{12} = -0.467 \pm 7.808$, $a_{21} = 2.729 \pm 2.908$, $c_{12} = -0.00093 \pm 1.30112\,K$, and $c_{21} = -0.0025 \pm 0.4868\,K$, written in terms of values ± standard deviation. The residual root mean square error (RSME) is 1.65139.

For Van Laar model, only $a_{ij/ji}$ and c_{ij} were specified, making $b_{ij/ji} = d_{ij} = 0$ by default. It was computed that $a_{12} = -2.106 \pm 0.029$, $a_{21} = 8.011 \pm 0.077$, and $c_{12} = c_{21} = 4.104 \pm 0.865$, with RSME of 6.18016.

For each model, when deciding which binary parameters to specify for the regression, trial and error analysis was conducted multiple times for the associated parameters, by doing inferences based on the resulting standard deviation (SD) of each parameter. If the SD is too large compared to its value, it was removed from the specification and remained those who had it small, or add other parameters unspecified previously. The SD has an overall impact on RSME, where the lower the RSME value is, the better the given model fits the experimental data, as the data is closely aligned with the regression fit [8]. In this given system, Wilson model best fits the experimental data than Van Laar model, as it has a lower RSME value. Due to that, the Wilson model is used for the rest of the analysis of this mixture. A T-xy and y-x plot for both models are as shown in Figure 1 - 4 in the following page.

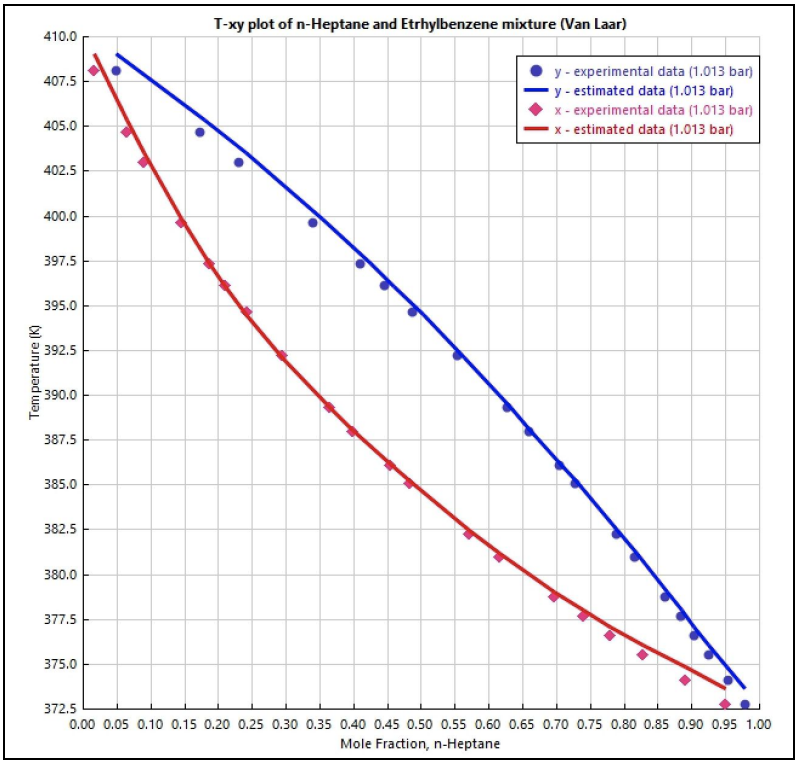

Figure 1: T-xy plot of the mixture with Van Laar Model

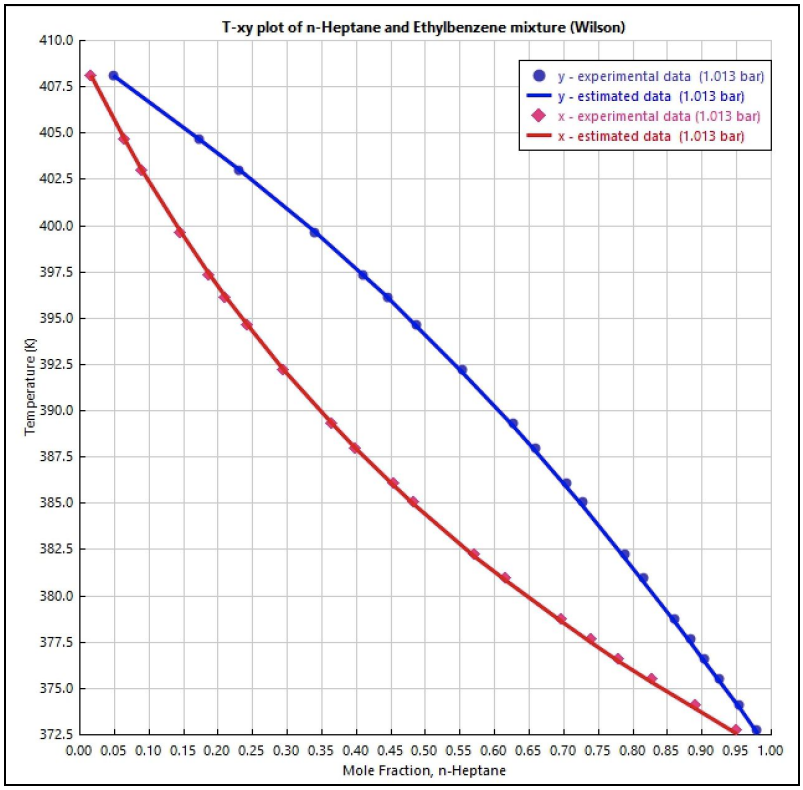

Figure 2: T-xy plot of mixture with Wilson Model

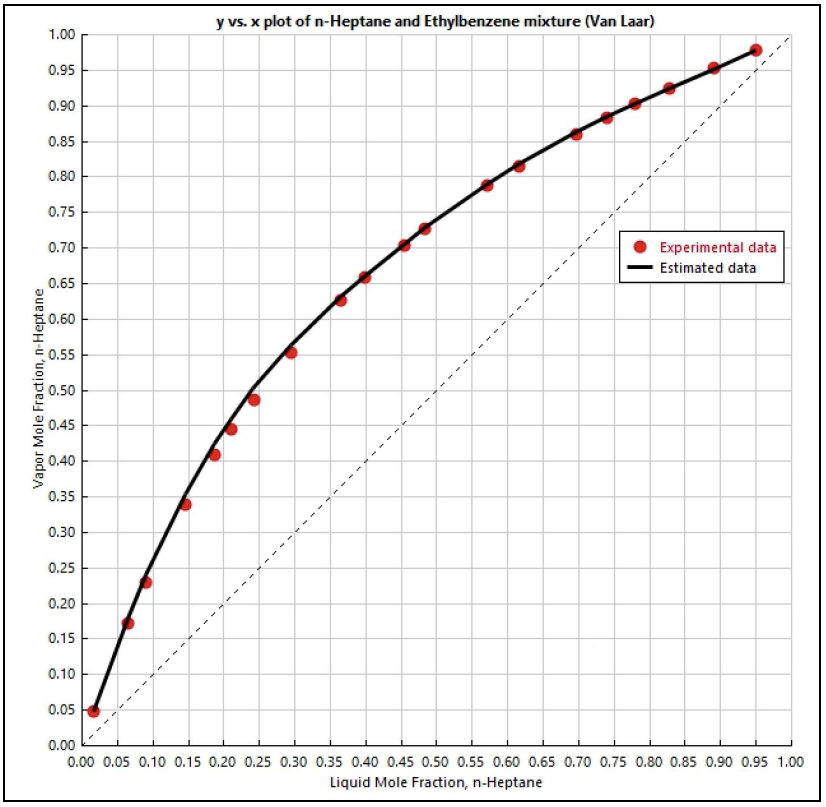

Figure 3: y-x plot of mixture with Van Laar Model

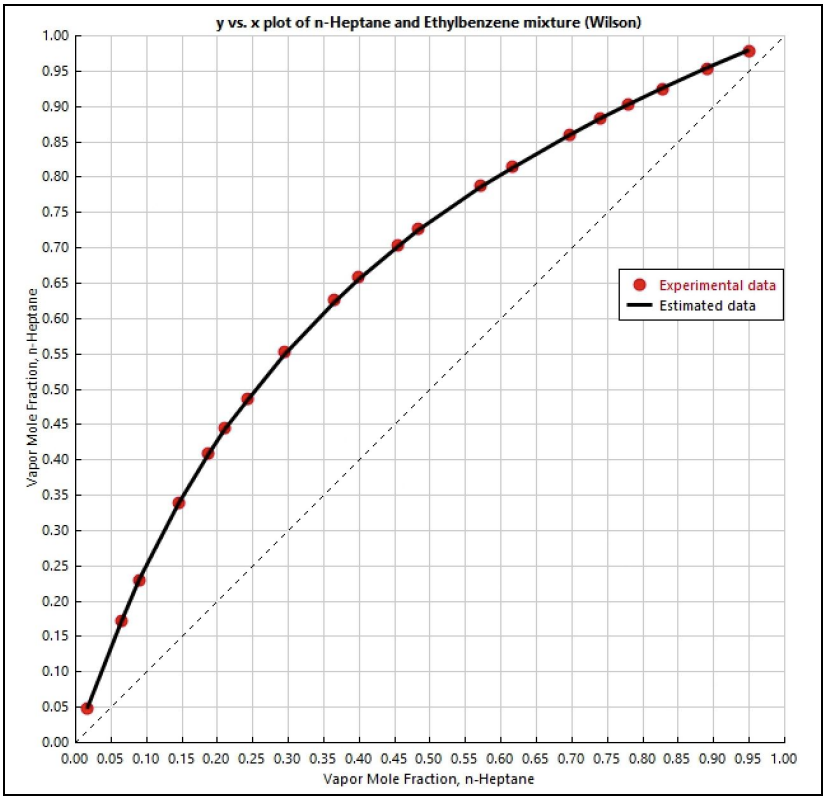

Figure 4: y-x plot of mixture with Wilson Model

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