Example 05.19 VLLE of n-Butanol - Water at 50°C Using UNIQUAC

problem:

Calculate the miscibility gap for the system n-butanol (1) water (2) at 50°C and additionally the corresponding pressure and vapor phase composition using the UNIQUAC equation with the help of the UNIQUAC-parameters fitted to VLE data*. An ideal vapor phase can be assumed

* J. Gmehling, U. Onken, et al. Vapor-Liquid Equilibrium Data Collection, DECHEMA Chemistry Data Series, Vol. I, 37 parts, Frankfurt starting 1977

general constants and definitions:

$cm := 0.01m \qquad R_{gas} := 8.31433 \frac{J}{K \cdot mol}$

$kPa := 1000Pa \qquad bar := 10^5 Pa \qquad dm := 0.1m$

input data

$n_{comp} := 2 \qquad i := 1 .. n_{comp} \qquad j := 1 .. n_{comp}$

Relative VdW volumes and surfaces: $r := \begin{pmatrix} 3.4543 \\ 0.92 \end{pmatrix} \qquad q := \begin{pmatrix} 3.052 \\ 1.4 \end{pmatrix}$

UNIQUAC binary interaction parameters: $\Delta u := \begin{pmatrix} 0 & 129.7 \\ 489.6 & 0 \end{pmatrix} \frac{cal}{mol}$

Pure component vapor pressures: $Ps := \begin{pmatrix} 4.61 \\ 12.36 \end{pmatrix} kPa$

Temperature: $Temp := (50 + 273.15)K$

Solution

The following function is used to calculate activity coefficients using the UNIQUAC model:

$$\gamma_{calc}(x, Temp) := \left| \begin{array}{l} \text{for } i \in 1..n_{comp} \\ \quad \text{for } j \in 1..n_{comp} \\ \qquad \tau_{i,j} \leftarrow e^{\frac{-\Delta u_{i,j}}{R_{gas} \cdot Temp}} \\ R \leftarrow \sum_{j=1}^{n_{comp}} r_j \cdot x_j \\ Q \leftarrow \sum_{j=1}^{n_{comp}} q_j \cdot x_j \\ \text{for } i \in 1..n_{comp} \\ \quad \left| \begin{array}{l} V_i \leftarrow \frac{r_i}{R} \\ F_i \leftarrow \frac{q_i}{Q} \end{array} \right. \\ \text{for } i \in 1..n_{comp} \\ \quad \left| \begin{array}{l} \ln\gamma_i \leftarrow 1 - V_i + \ln(V_i) - 5 \cdot q_i \cdot \left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \ldots \\ \qquad + q_i \cdot \left(1 - \ln\left(\frac{\sum_{j=1}^{n_{comp}} q_j \cdot x_j \cdot \tau_{j,i}}{Q}\right) - \sum_{j=1}^{n_{comp}} \frac{q_j \cdot x_j \cdot \tau_{i,j}}{\sum_{k=1}^{n_{comp}} q_k \cdot x_k \cdot \tau_{k,j}}\right) \\ \gamma_i \leftarrow \exp(\ln\gamma_i) \end{array} \right. \\ \gamma \end{array} \right.$$

$$\gamma_{calc}\left[\begin{pmatrix} .5 \\ .5 \end{pmatrix}, Temp\right] = \begin{pmatrix} 1.271 \\ 2.133 \end{pmatrix}$$

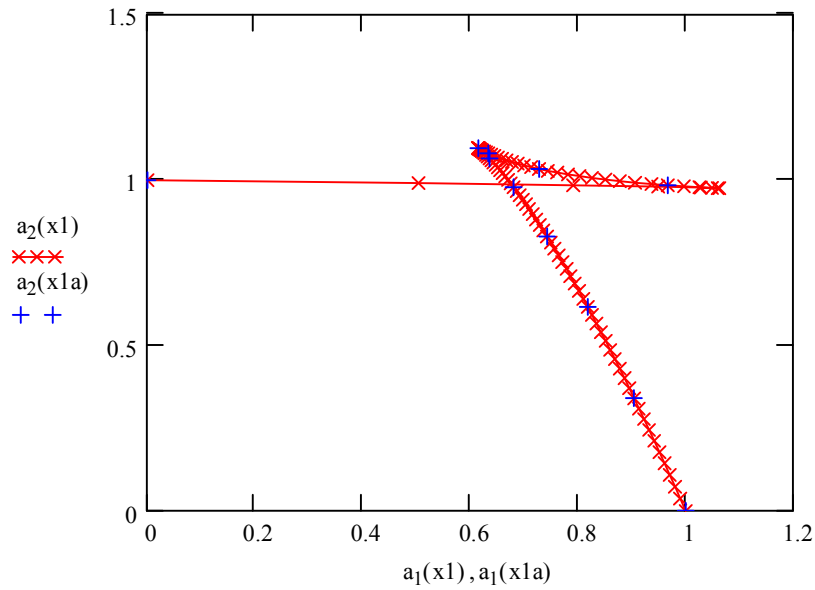
To plot the activity of component 2 vs. the activity of component 1, the following two functions are defined:

$$a_1(x1) := x1 \cdot \gamma_{calc}\left[\begin{pmatrix} x1 \\ 1 - x1 \end{pmatrix}, Temp\right]_1$$

$$a_2(x1) := (1 - x1) \cdot \gamma_{calc}\left[\begin{pmatrix} x1 \\ 1 - x1 \end{pmatrix}, Temp\right]_2$$

For convenience, the representation in the following plot contains a curve, red "x" every 1 mol% and a blue "+" every 10 mol%.

$x1 := 0.0, 0.01 .. 1$ $\qquad$ $x1a := 0, 0.1 .. 1$



The immiscible region should be between about x_1'=0.405 and x_1"=0.984.

$x_{1p} := 0.016$ $\qquad$ $x_{1pp} := 0.595$

The exact solution can be found by solving the isoactivity criterion for both components:

Given

$$a_1(x_{1p}) = a_1(x_{1pp}) \qquad a_2(x_{1p}) = a_2(x_{1pp})$$

$$res := Find(x_{1p}, x_{1pp})$$

$$res = \begin{pmatrix} 0.01528 \\ 0.59256 \end{pmatrix} \qquad x_{1p} := res_1 \qquad x_{1pp} := res_2$$

The result should be verified:

$$a_1(x_{1p}) - a_1(x_{1pp}) = -3.865 \times 10^{-9} \qquad a_2(x_{1p}) - a_2(x_{1pp}) = 5.294 \times 10^{-11}$$

The values of the activity coefficients for the liquid-liquid phase boundaries are:

$$x(x_1) := \begin{pmatrix} x_1 \\ 1 - x_1 \end{pmatrix} \qquad \gamma_{calc}(x(x_{1p}), Temp) = \begin{pmatrix} 44.252 \\ 1.003 \end{pmatrix}$$

$$\gamma_{calc}(x(x_{1pp}), Temp) = \begin{pmatrix} 1.141 \\ 2.424 \end{pmatrix}$$

The total pressure above these mixtures is:

$$P_{calc}(x) := \left| \begin{array}{l} \gamma \leftarrow \gamma_{calc}(x, Temp) \\ P_{calc} \leftarrow \sum_j x_j \cdot \gamma_j \cdot Ps_j \end{array} \right.$$

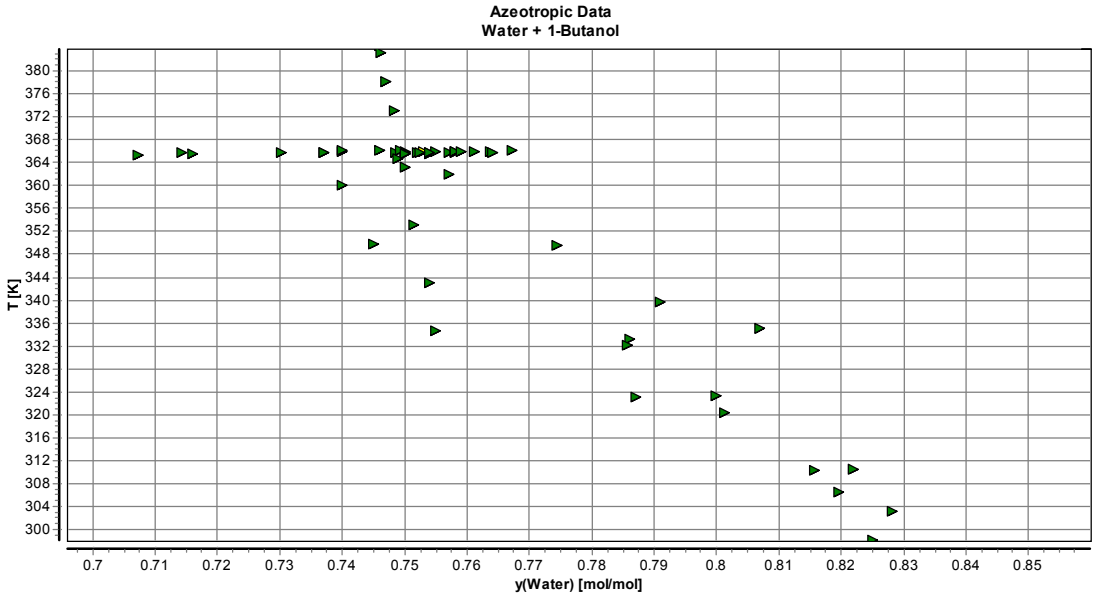
$$P_{calc}(x(x_{1p})) = 0.15325 \text{ bar} \qquad P_{calc}(x(x_{1pp})) = 0.15325 \text{ bar}$$

The vapor phase composition can be calculated via the following function:

$$y_{calc}(x) := \left| \begin{array}{l} \gamma \leftarrow \gamma_{calc}(x, Temp) \\ \text{for } j \in 1..n_{comp} \\ \quad P_j \leftarrow x_j \cdot \gamma_j \cdot Ps_j \\ P_{total} \leftarrow \sum_{j=1}^{n_{comp}} P_j \\ \dfrac{P}{P_{total}} \end{array} \right.$$

$$y_{calc}(x(x_{1p})) = \begin{pmatrix} 0.20346 \\ 0.79654 \end{pmatrix} \qquad y_{calc}(x(x_{1pp})) = \begin{pmatrix} 0.20346 \\ 0.79654 \end{pmatrix}$$

Identical results are obtained for both mixtures. As these are in thermal, mechanical and thermodynamic equilibrium, they must be in equilibrium with the same vapor phase. As the vapor phase mole fraction of component 1 lies between its mole fractions in the two liquid phases, the calculation yields a heterogeneous azeotrop at a liquid and vapor mole fraction of 0.20346. Literature data from the DDB (Version 2011) are shown in the plot below. Please note the different order of the components. The calculated value closely matches the literature information.


Azeotropic Data
Water + 1-Butanol
T [K]
380
376
372
368
364
360
356
352
348
344
340
336
332
328
324
320
316
312
308
304
300
0.7
0.71
0.72
0.73
0.74
0.75
0.76
0.77
0.78
0.79
0.8
0.81
0.82
0.83
0.84
0.85
y(Water) [mol/mol]