Example 05.20 Liquid-Liquid Equilibrium for the System Water – Ethanol – Benzene K-Factor Method UNIQUAC

problem: Calculate the liquid-liquid equilibrium composition for the system water (1) - ethanol (2) - benzene (3) for the following feed stream: n_1 = 1 mol, n_2 = 0.3 mol, and n_3 = 1 mol at 25 °C with the help of the UNIQUAC model.

general constants and definitions:

$$R_{gas} := 8.31433 \frac{J}{K \cdot mol}$$

input data

Components:
1 - water
2 - ethanol
3 - benzene

$water := 1$
$ethanol := 2$
$benzene := 3$

$n_{comp} := 3$
$i := 1 .. n_{comp}$
$j := 1 .. n_{comp}$
$k := 1 .. n_{comp}$

$Temp := (273.15 + 25)K$

UNIQUAC parameters:

$$r := \begin{pmatrix} 0.92000 \\ 2.10550 \\ 3.18780 \end{pmatrix} \quad q := \begin{pmatrix} 1.40000 \\ 1.97200 \\ 2.40000 \end{pmatrix} \quad \Delta u := \begin{pmatrix} 0 & 526.02 & 309.64 \\ -318.06 & 0 & -91.532 \\ 1325.1 & 302.57 & 0 \end{pmatrix} K$$

Solution

In the first step a convenient function to convert the mole flow vector into a mol fraction vector is defined:

$$x(nn) := \frac{nn}{\sum_{k=1}^{n_{comp}} nn_k}$$

The interaction parameter matrix Δu is converted to the τ matrix only once as temperature is constant in the calculation:

$$\tau_{i,j} := \exp\left(\frac{-\Delta u_{i,j}}{Temp}\right) \qquad \tau = \begin{pmatrix} 1.00000 & 0.17131 & 0.35397 \\ 2.90600 & 1.00000 & 1.35934 \\ 0.01174 & 0.36247 & 1.00000 \end{pmatrix}$$

The following functions yield the logarithmic activity coefficient and activity coefficient vector using the UNIQUAC equation (Table 5.6):

$$\ln\gamma(x,i) := 1 - \frac{r_i}{\sum_k r_k \cdot x_k} + \ln\left(\frac{r_i}{\sum_k r_k \cdot x_k}\right) - 5 \cdot q_i \cdot \left[1 - \frac{r_i \cdot \left(\sum_k q_k \cdot x_k\right)}{q_i \cdot \left(\sum_k r_k \cdot x_k\right)} + \ln\left[\frac{r_i \cdot \left(\sum_k q_k \cdot x_k\right)}{q_i \cdot \left(\sum_k r_k \cdot x_k\right)}\right]\right] \ldots$$
$$+ q_i \cdot \left(1 - \ln\left(\sum_k \frac{x_k \cdot q_k \cdot \tau_{k,i}}{\sum_j q_j \cdot x_j}\right) - \sum_k \frac{x_k \cdot q_k \cdot \tau_{i,k}}{\sum_j q_j \cdot x_j \cdot \tau_{j,k}}\right)$$

$$\gamma(x,i) := \exp(\ln\gamma(x,i))$$

As an example, activity coefficients for the components in the feed stream are calculated:

$$n_{feed} := \begin{pmatrix} 1 \\ 0.3 \\ 1 \end{pmatrix} \qquad x(n_{feed}) = \begin{pmatrix} 0.43478 \\ 0.13043 \\ 0.43478 \end{pmatrix} \qquad \gamma(x(n_{feed}), i) =$$

3.74666
0.32259
3.02346

For the K-factor method, an initial estimation of the mole flows in the first liquid outlet stream is required:

$$n_1 := n_{feed} - \begin{pmatrix} 0.9 \cdot n_{feed_1} \\ n_{feed_2} \\ 0.1 \cdot n_{feed_3} \end{pmatrix} \qquad n_1 = \begin{pmatrix} 0.10000 \\ 0.00000 \\ 0.90000 \end{pmatrix} \qquad x(n_1) = \begin{pmatrix} 0.10000 \\ 0.00000 \\ 0.90000 \end{pmatrix}$$

The iterative K-factor method can be programmed into a simple function:

$$eps := 0.00000000000001$$

$$n_{1f}(n_{feed}, n_1, eps) := \left| \begin{array}{l} dev \leftarrow 1 \\ \text{while } dev > eps \\ \quad \left| \begin{array}{l} n_2 \leftarrow n_{feed} - n_1 \\ n_{1old} \leftarrow n_1 \\ \text{for } i \in 1 .. n_{comp} \\ \quad n_{1_i} \leftarrow \dfrac{n_{feed_i}}{1 + \dfrac{\gamma(x(n_1), i) \cdot \sum_{j=1}^{n_{comp}} n_{2_j}}{\gamma(x(n_2), i) \cdot \sum_{j=1}^{n_{comp}} n_{1_j}}} \\ dev \leftarrow \sum_i \left(n_{1old_i} - n_{1_i}\right)^2 \end{array} \right. \\ n_1 \end{array} \right.$$

Now the K-factor function is used to calculate the mole flows in the first liquid outlet stream. The second liquid stream is found by solving the mass balance:

$$n_1 := n_{1f}(n_{feed}, n_1, eps) \qquad n_1 = \begin{pmatrix} 0.02012 \\ 0.08473 \\ 0.98718 \end{pmatrix} \qquad x(n_1) = \begin{pmatrix} 0.01842 \\ 0.07759 \\ 0.90399 \end{pmatrix}$$

$$n_2 := n_{feed} - n_1 \qquad n_2 = \begin{pmatrix} 0.97988 \\ 0.21527 \\ 0.01282 \end{pmatrix} \qquad x(n_2) = \begin{pmatrix} 0.81118 \\ 0.17821 \\ 0.01061 \end{pmatrix}$$

In the last step, the result is verified by applying the isoactivity criterion. The sum of squared deviations in activity between the outlet streams over all components should result in a very small number:

$$a1_i := \gamma(x(n_1), i) \cdot x(n_1)_i \qquad a2_i := \gamma(x(n_2), i) \cdot x(n_2)_i$$

$$\sum_j \left(a1_j - a2_j\right)^2 = 1.16192 \times 10^{-12}$$