Example 05.03 Activity Coefficients from Experimental xyPT-Data

problem: Calculate the activity coefficients for the system ethanol (1) - water (2) at theta = 70 °C from experimental VLE data at a given composition.

general constants and definitions:

$kPa := 1000Pa \qquad dm := 0.1m \qquad R := 8.31433 \frac{J}{K \cdot mol}$

input data

$ncomp := 2 \qquad i := 1..ncomp \qquad j := 1..ncomp$

Liquid and vapor mole fractions, temperature, pressure

$$x_1 := 0.252 \qquad x_{ncomp} := 1 - \sum_{i=1}^{ncomp-1} x_i \qquad x = \begin{pmatrix} 0.252 \\ 0.748 \end{pmatrix}$$

$$y_1 := 0.552 \qquad y_{ncomp} := 1 - \sum_{i=1}^{ncomp-1} y_i \qquad y = \begin{pmatrix} 0.552 \\ 0.448 \end{pmatrix}$$

$T := (273.15 + 70)K \qquad P := 62.39kPa$

Vapor pressure of the pure components

$$\left(\left[P^S\right]\right)_1 := 72.30kPa \qquad \left(\left[P^S\right]\right)_2 := 31.09kPa$$

Liquid molar volume

$$v_1 := 0.06195 \frac{dm^3}{mol} \qquad v_2 := 0.01842 \frac{dm^3}{mol}$$

Virial coefficients at theta = 70°C

$$B_{1,1} := -1100 \frac{cm^3}{mol} \qquad B_{1,2} := -850 \frac{cm^3}{mol} \qquad B_{2,2} := -650 \frac{cm^3}{mol} \qquad B_{2,1} := B_{1,2}$$

$$B = \begin{pmatrix} -1100 & -850 \\ -850 & -650 \end{pmatrix} \frac{cm^3}{mol}$$

Solution a) neglecting the real vapor phase behavior and the Poynting correction

$$\gamma_i := \frac{y_i \cdot P}{x_i \cdot \left(\left[P^S\right]\right)_i} \qquad \gamma = \begin{pmatrix} 1.89 \\ 1.202 \end{pmatrix}$$

Solution b) taking into account the real vapor phase behavior using the Virial equation and using the Poynting correction

The second virial coefficient of the mixture is calculated by:

$$B_{mix} := \sum_i \sum_j y_i y_j B_{i,j} \qquad B_{mix} = -886.035 \frac{cm^3}{mol}$$

Calculation of the fugacity coefficients of the components in the mixture:

$$\left(\left[\ln\phi^V\right]\right)_i := \left(2 \sum_j y_i B_{i,j} - B_{mix}\right) \frac{P}{R \cdot T} \qquad \left[\ln\phi^V\right] = \begin{pmatrix} -0.02770 \\ -0.01001 \end{pmatrix}$$

$$\left[\phi^V\right] := e^{\left[\ln\phi^V\right]} \qquad \left[\phi^V\right] = \begin{pmatrix} 0.973 \\ 0.990 \end{pmatrix}$$

Calculation of the fugacity coefficients of the pure components in the saturated state:

$$\left(\left[\ln\phi^S\right]\right)_i := \frac{B_{i,i} \left(\left[P^S\right]\right)_i}{R \cdot T} \qquad \left[\ln\phi^S\right] = \begin{pmatrix} -0.02788 \\ -0.00708 \end{pmatrix}$$

$$\left[\phi^S\right] := e^{\left[\ln\phi^S\right]} \qquad \left[\phi^S\right] = \begin{pmatrix} 0.973 \\ 0.993 \end{pmatrix}$$

Calculation of the Poynting factor:

$$Poy_i := e^{v_i \frac{\left[P - \left(\left[P^S\right]\right)_i\right]}{R \cdot T}} \qquad Poy = \begin{pmatrix} 0.9998 \\ 1.0002 \end{pmatrix}$$

Calculation of the activity coefficients

$$\gamma_i := \frac{y_i \cdot P \cdot \left(\left[\phi^V\right]\right)_i}{x_i \cdot Poy_i \cdot \left(\left[P^S\right]\right)_i \cdot \left(\left[\phi^S\right]\right)_i} \qquad \gamma = \begin{pmatrix} 1.891 \\ 1.198 \end{pmatrix}$$

In this low pressure case, the real vapor phase behavior and the Poynting correction are not very important. Things become different if higher pressures are involved.