Example 05.08 **Activity Coefficient of the Monomer in a Polymer Using the Athermal Flory-Huggins Equation**

problem: Calculate the activity coefficient of the monomer in a polymer using the athermal Flory-Huggins equation. For the calculation the following volumes should be used:

v_1 = 70 cm^3/mol v_2 = 70000 cm^3/mol

general constants and definitions:

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

input data

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

Liquid molar volumes of the components

$$v := \begin{pmatrix} 70 \\ 70000 \end{pmatrix} \frac{cm^3}{mol}$$

Solution

Using equation 5.33, the activity coefficient can be calculated from the volume fractions θ of the components in the mixture:

$$\ln(\gamma_i) = \ln\left(\frac{\theta_i}{x_i}\right) + 1 - \frac{\theta_i}{x_i}$$

For the activity coefficient, the following expression results:

$$\gamma_i = \exp\left(\ln\left(\frac{\theta_i}{x_i}\right) + 1 - \frac{\theta_i}{x_i}\right)$$

The surface fraction vector is calculated from the mole fraction vector via:

$$\theta(x,i) := \frac{x_i \cdot v_i}{\sum_{j=1}^{ncomp} x_j \cdot v_j}$$

Simplification of the expression for the activity coefficient leads to:

$$\gamma(x,i) := \frac{\theta(x,i)}{x_i} \cdot \exp\left(1 - \frac{\theta(x,i)}{x_i}\right)$$

To avoid the singularity at the pure components, the following function V should be used, which provides identical values without the singularity.

$$V_i = \frac{\theta_i}{x_i} \qquad V(x,i) := \frac{v_i}{\sum_{j=1}^{ncomp} x_j \cdot v_j}$$

$$\gamma(x,i) := V(x,i) \cdot \exp(1 - V(x,i))$$

Calculation should be performed for a monomer mole fraction of 0.2:

$$x_1 := 0.2 \qquad x_2 := 1. - x_1 \qquad x = \begin{pmatrix} 0.2 \\ 0.8 \end{pmatrix}$$

This results in the following volume fractions:

$\theta(x,i) =$

0.0002499
0.9997501

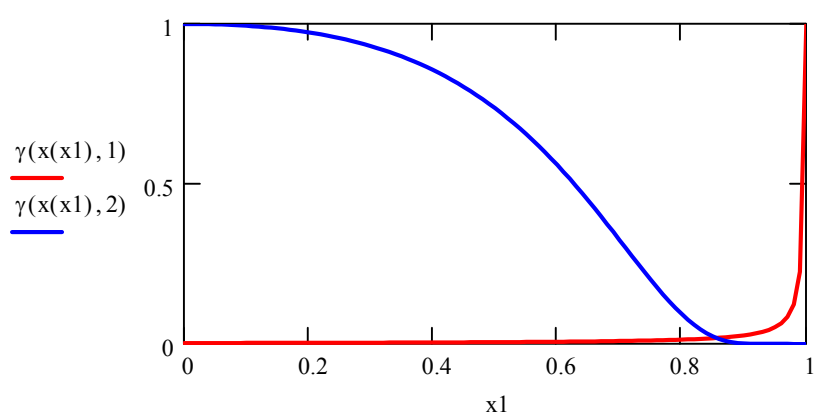
The following values for the activity coefficients can be found:

$$\gamma(x,1) = 3.393 \times 10^{-3}$$

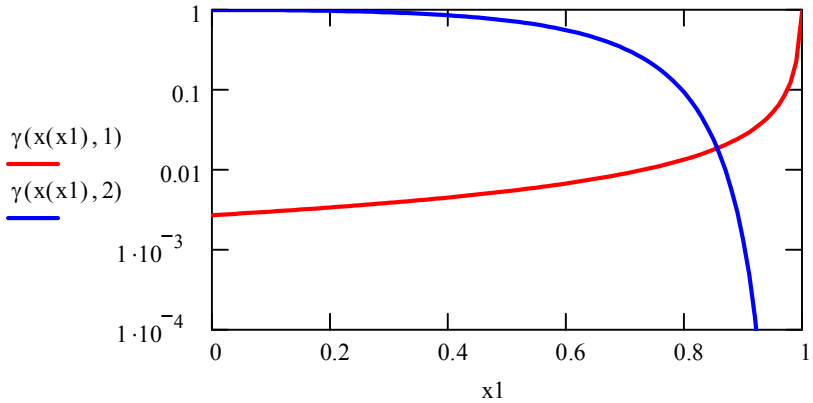
$$\gamma(x,2) = 0.974$$

The same function can now be used to plot the activity coefficients as function of composition:

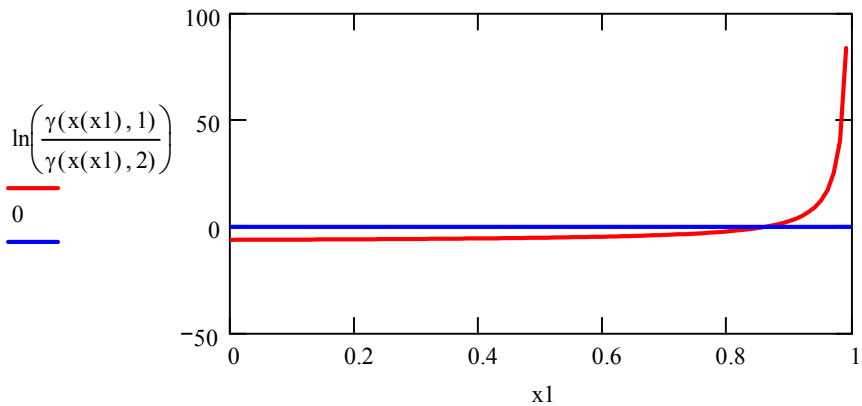
$$x(x1) := \begin{pmatrix} x1 \\ 1 - x1 \end{pmatrix} \qquad x1 := 0, 0.01 .. 1$$



Or in logarithmic form:



Plotting the logarithm of the ratio of the activity coefficients as function of concentration leads to:



The curvature above is very typically for strongly assymetric systems with negative deviation from Raoult's Law.