Problem 14-13 Influence of the surface curvature on solubility

At the temperature of 322 K a solid substance in the form of large crystals dissolves to form a saturated solution of concentration 5.2 wt. %. If we will dissolve the same substance at the same temperature in the same solvent ($\rho^{(\ell)}$ = 0.823 g cm^{-3}), but in the form of small approximately spherical particles, the solubility will change. The interfacial tension solid/saturated solution is 62 mN m^{-1}, the studied substance does not dissociate on dissolving and its molar mass is M = 136 g mol^{-1}. Specific area of the small particles is 4.22 m^2/g. Calculate the percentage change in solubility.

[100 ($c_r - c_\infty$)/c_∞ = 0.89 % (c_r = 5.2463 wt. %)]

Solution:

T = 322 K

c_∞ = 5.2 wt. %

M = 136 g mol^{-1} = 0.136 kg mol^{-1}

A_{sp} = 4.22 m^2 g^{-1} = 4220 m^2 g^{-1}

$\gamma_{\ell s}$ = 62 mN m^{-1} = 0.062 N m^{-1}

$\rho^{(\ell)}$ = 0.823 g cm^{-3} = 823 kg m^{-3}

$$\ln\frac{c_r}{c_\infty} = \frac{2\cdot\gamma_{\ell s}\cdot V_m^{(s)}}{RT\cdot r} = \frac{2\cdot\gamma_{\ell s}\cdot M}{RT\cdot\rho^{(s)}\cdot r}$$

where $$A_{sp} = \frac{A_i}{m_i} = \frac{4\cdot\pi\cdot r^2}{\frac{4}{3}\cdot\pi\cdot r^3\cdot\rho^{(s)}} = \frac{3}{r\cdot\rho^{(s)}} \quad\Rightarrow\quad r\cdot\rho^{(s)} = \frac{3}{A_{sp}}$$

$$\ln\frac{c_r}{c_\infty} = \frac{2\cdot\gamma_{\ell s}\cdot M\cdot A_{sp}}{RT\cdot 3} \qquad \left[\frac{(\text{N m}^{-1})\cdot(\text{kg mol}^{-1})\cdot(\text{m}^2\ \text{kg}^{-1})}{(\text{N m mol}^{-1}\ \text{K}^{-1})\cdot\text{K}} = 1\right]$$

$$= \frac{2\cdot 0.062\cdot 0.136\cdot 4220}{8.314\cdot 322\cdot 3} = 0.008861$$

$$\frac{c_r}{c_\infty} = e^{0.008861} = 1.0089$$

$$c_r = c_\infty\cdot 1.0089 = 5.2\cdot 1.0089 = 5.2463 \text{ hm.\%}$$

$$\Delta_{\%} = 100\cdot\frac{c_r - c_\infty}{c_\infty} = 100\cdot\left(\frac{c_r}{c_\infty} - 1\right) = 100\cdot(1.0089 - 1) = 0.89\ \%$$