Problem 14-11 Kelvin equation – concave surface

The surface tension of nitrobenzene is 39 mN m^{-1}, its molar volume 102.2 cm^3 mol^{-1}, and the equilibrium vapour pressure at the temperature of 303 K has the value p^s_∞ = 2.271 kPa. At this temperature calculate the vapour pressure above the meniscus of nitrobenzene

(a) in a thin capillary of diameter 0.46 μm, which is completely wetted by nitrobenzene ($\theta = 0°$),

(b) in a capillary of the same diameter but made from a material, which is not completely wetted by nitrobenzene ($\theta = 55°$).

[(a) p^s_r = 2.24 kPa, (b) p^s_r = 2.253 kPa]

Solution:

V_m = 102.2 cm^3 mol^{-1} = 102.2·10^{-6} m^3 mol^{-1}

T = 303 K

$\mathcal{D}$ = 0.46 μm =·4.6 10^{-7} m

$\mathcal{R}$ = 2.3·10^{-7} m

p^s_∞ = 2.271 kPa

(a) $\theta = 0°$, $r = R$

$$\ln\frac{p^s_r}{p^s_\infty} = -\frac{2\cdot\gamma\cdot V^\ell_m}{RT\cdot r}$$

$$\ln\frac{p^s_r}{p^s_\infty} = -\frac{2\cdot 0.039\cdot 102.2\cdot 10^{-6}}{8.314\cdot 303\cdot 2.3\cdot 10^{-7}} = -0.0137583$$

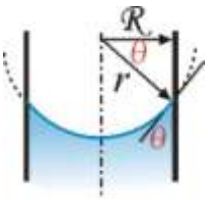
$$p^s_r = p^s_\infty\cdot e^{-0.0137583} = 2.271\cdot 0.986336 = 2.24 \text{ kPa}$$

$$100\cdot\frac{p^s_\infty - p^s_r}{p^s_\infty} = 100\cdot\frac{2.240-2.271}{2.271} = -1.365\ \%$$

(b) $\theta = 55°$, $r = \mathcal{R}/\cos\theta$

$$\ln\frac{p^s_r}{p^s_\infty} = -\frac{2\cdot\gamma\cdot V^\ell_m}{RT\cdot r} = -\frac{2\cdot\gamma\cdot V^\ell_m}{RT\cdot\mathcal{R}}\cdot\cos\theta$$

$$\ln\frac{p^s_r}{p^s_\infty} = -\frac{2\cdot 0.039\cdot 102.2\cdot 10^{-6}}{8.314\cdot 303\cdot 2.3\cdot 10^{-7}}\cdot\cos 55 = -0.0078914$$



$$p^s_r = p^s_\infty\cdot e^{-0,0078914} = 2.271\cdot 0.99214 = 2.253 \text{ kPa}$$

$$100\cdot\frac{p^s_\infty - p^s_r}{p^s_\infty} = 100\cdot\frac{2.253-2.271}{2.271} = -0.793\ \%$$