5.15 Quantification of osmosis (ideal systems): Van’t Hoff equation

To quantify osmosis we start from the equilibrium condition

$$\mu_A^*(p) = \mu_A(solution, p+\pi) = \mu_A^*(p+\pi) + RT\,\ln a_A \tag{5.47}$$

To calculate $\mu_A^*(p+\pi)$ we use the pressure dependence of $G_{A,m}$

$$\begin{aligned} \left(\frac{\partial \mu_A^*}{\partial p}\right)_T &= \left(\frac{\partial G_{A,m}}{\partial p}\right)_T = V_{A,m}^* \quad \Rightarrow \quad \int_p^{p+\pi} d\mu_A^* = \int_p^{p+\pi} V_{A,m}^* dp \\ \mu_A^*(p+\pi) &= \mu_A^*(p) + V_{A,m}^* \int_p^{p+\pi} dp = \mu_A^*(p) + V_{A,m}^*\,\pi \quad \text{assuming } V_{A,m}^* \text{ independent of } p \end{aligned} \tag{5.48}$$

Including this result into the equilibrium condition of Eq. (5.47) we find

$$\begin{aligned} \mu_A^*(p) &= \mu_A(solution, p+\pi) + RT\,\ln a_A = \mu_A^*(p) + V_{A,m}^*\,\pi + RT\,\ln a_A \\ \Rightarrow -V_{A,m}^*\,\pi &= RT\,\ln a_A \end{aligned} \tag{5.49}$$

i.e. the activity of the solvent can be determined from measurements of π.
Using the approximations for Raoult’s standard state applied to $RT\,\ln a_A$ we get

$$\begin{aligned} RT\,\ln a_A \approx &\; RT\,\ln x_A = RT\,\ln(1-x_B) \approx -RT\,x_B = -RT\,\frac{n_B}{n_A+n_B} \approx -RT\,\frac{n_B}{n_A} \\ \Rightarrow -\pi\,V_{A,m}^* = -\pi\frac{V_A^*}{n_A} = &\; RT\,\ln a_A \approx -RT\,\frac{n_B}{n_A} \quad \Rightarrow \quad \pi V_A^* = n_B\,RT \end{aligned} \tag{5.50}$$

Rewriting Eq. (5.50) we get the van’t Hoff equation

$$\pi = \frac{n_B}{V_A^*}RT = \frac{m_B}{M_B\,V_A^*}RT = \frac{RT}{M_B}\frac{m_B}{V_A^*} = \frac{RT}{M_B}c_B \tag{5.51}$$

here c_B is a modified concentration in [g/cm^3].
Measuring the osmotic pressure π as a hydrostatic pressure $\rho_A\,g\,h$ (ρ_A: density of the solvent) we get a generalization of Eq. (5.51) by a virial approach

$$\begin{aligned} \pi = \rho_A\,g\,h = &\; \frac{RT}{M_B}c_B\left(1 + \frac{B\,c_B}{M_B} + \cdots\right) \\ \Rightarrow \quad \frac{h}{c_B} = &\; \frac{RT}{\rho_A\,g\,M_B} + \left(\frac{RT\,B}{\rho_A\,g\,M_B^2}\right)c_B + \cdots \end{aligned} \tag{5.52}$$

Plotting of h/c_B against c_B typically gives a straight line as shown in Fig. 5.14 . The extrapolation of this line to $c_B = 0$ allows to calculate $RT/\rho_A\,g\,M_B$ and thus finally M_B. The B parameter contains additional information about the intermolecular interactions.

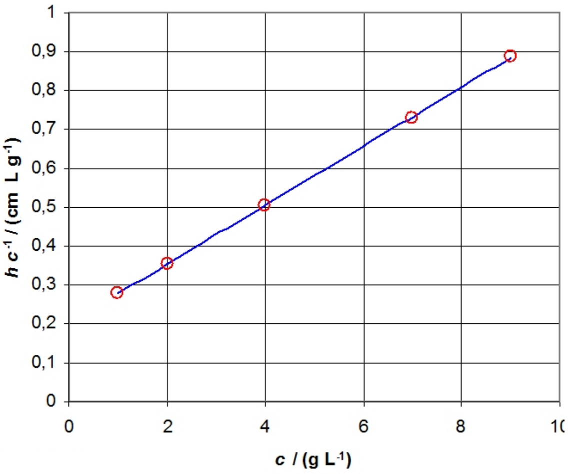

Figure 5.14: Representation of measured data according to Eq. (5.52).