

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

To quantify osmosis we start from the equilibrium condition

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

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

$$\left(\frac{\partial \mu_A^*}{\partial p}\right)_T = \left(\frac{\partial G_{A,m}}{\partial p}\right)_T = V_{A,m}^* \Rightarrow \int_p^{p+\pi} d\mu_A^* = \int_p^{p+\pi} V_{A,m}^* dp \quad (5.48)$$

$$\mu_A^*(p + \pi) = \mu_A^*(p) + V_{A,m}^* \int_p^{p+\pi} dp = \mu_A^*(p) + V_{A,m}^* \pi \quad \text{assuming } V_{A,m}^* \text{ independent of } p$$

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

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

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

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

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

$$\pi = \frac{n_B}{V_A^*} RT = \frac{m_B}{M_B V_A^*} RT = \frac{RT m_B}{M_B V_A^*} = \frac{RT}{M_B} c_B \quad (5.51)$$

here c_B is a modified concentration in $[\text{g}/\text{cm}^3]$.

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

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

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.

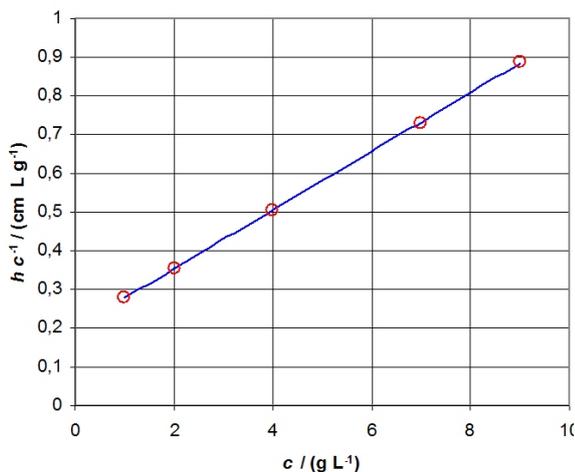


Figure 5.14: Representation of measured data according to Eq. (5.52).