[pex56] Donnan equilibrium between ionic polymer and solvent

Consider ionic polymers in solution confined to one chamber (p) of a container separated from a chamber (s) with solvent by a semi-permeable wall as shown. The polymer contains positive ionic groups and salt has been added to the solvent. All ions except the polymers are free to migrate between compartments. The number density of (positive) bound charges is n_b. The mobile ions in chamber (p) have number densities n_p^+, n_p^- and those in chamber (s) n_s^+, n_s^-. At thermal equilibrium, charge neutrality is established (on some mesoscopic length scale),

$$n_p^+ + n_b = n_p^-, \quad n_s^+ = n_s^- \doteq n_s,$$

as well as an electric potential difference and an osmotic pressure between the chambers:

$$\Delta\psi \doteq \psi_p - \psi_s, \quad \Delta\pi \doteq k_B T[n_p^+ + n_p^- - 2n_s].$$

The condition of chemical equilibrium for the mobile ions can then be stated as follows:

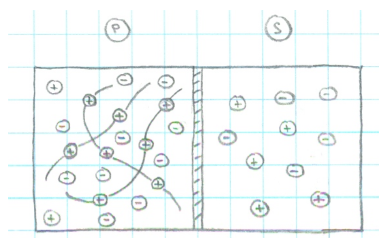
$$\mu_0 + k_\mathrm{B}T \ln n_\mathrm{p}^\pm \pm e_0\psi_\mathrm{p} = \mu_0 + k_\mathrm{B}T \ln n_\mathrm{s}^\pm \pm e_0\psi_\mathrm{s},$$

where we assume monovalency and equal reference values in both chambers.
(a) Convert this relation into

$$n_p^\pm = n_s \exp\big(\mp \beta e_0 \Delta\psi\big),$$

where e_0 is the elementary charge and $\beta \doteq 1/k_B T$.
(b) Use these ingredients to derive expressions for the densities $n_\mathrm{p}^\pm$, the Donnan potential $\Delta\psi$, and the osmotic pressure $\Delta\pi$, all as functions of n_b and n_s (see [pln62]).
(c) Simplify all results for the cases $n_s \ll n_b$ and $n_s \gg n_b$ of low and high salt concentrations, respectively.

[adapted from Doi 2013]



Solution: