Problem 12-05 Membrane equilibria, Donnan potential

A membrane permeable for ions Ca^{2+} and Cl^-, but not for high-molecular ions R^+, separates the inner compartment of the dialysis cell at the beginning containing the polyelectrolyte RCl in concentration c_1 and $CaCl_2$ in concentration $(c_2)_0$ = 200 mmol dm^{-3}, from the outer compartment containing only calcium chloride solution in concentration $(c_3)_0$ = 300 mmol dm^{-3}. In equilibrium, established at the temperature of 27 °C, the concentration of Ca^{2+} in the inner compartment was found to be 230 mmol dm^{-3}. (a) What is the concentration of RCl in the inner compartment? (b) Calculate the equilibrium Donnan potential.

[(a) c_1 = 125 mmol dm^{-3} ; (b) E = 2.07 mV]

Solution:

$c(\mathrm{RCl})_{\mathrm{in},\,0} = c_1$ $\qquad$ $\mathrm{RCl} = \mathrm{R}^+ + \mathrm{Cl}^-$

$c(\mathrm{CaCl_2})_{\mathrm{in},\,0} = c_2 = 200\ \mathrm{mmol\ dm^{-3}}$ $\qquad$ $\mathrm{CaCl_2} = \mathrm{Ca}^{2+} + 2\,\mathrm{Cl}^-$

$c(\mathrm{CaCl_2})_{\mathrm{out},\,0} = c_3 = 300\ \mathrm{mmol\ dm^{-3}}$

$c(\mathrm{CaCl_2})_{\mathrm{in,\,equil}} = c_4 = 230\ \mathrm{mmol\ dm^{-3}}$

$c(\mathrm{CaCl_2}) = c(\mathrm{Ca}^{2+})$

Balance:	at the beginning		in equilibrium	
	in	out	in	out
R^+	c_1	0	c_1	0
Ca^{2+}	c_2	c_3	$c_2 + x$	$c_3 - x$
Cl^-	$2\,c_2 + c_1$	$2\,c_3$	$2\,c_2 + c_1 + 2\,x$	$2\,c_3 - 2\,x$

$c_4 = 230\ \mathrm{mmol\ dm^{-3}} = c_2 + x \quad \Rightarrow \quad x = c_4 - c_2 = 230 - 200 = 30\ \mathrm{mmol\ dm^{-3}}$

Donnan equilibrium condition for $CaCl_2$:

$$(c_{\mathrm{Ca}^{2+}})_{\mathrm{in}} \cdot (c_{\mathrm{Cl}^-})^2_{\mathrm{in}} = (c_{\mathrm{Ca}^{2+}})_{\mathrm{out}} \cdot (c_{\mathrm{Cl}^-})^2_{\mathrm{out}}$$

$$(c_2 + x)\cdot(2\,c_2 + c_1 + 2\,x)^2 = (c_3 - x)\cdot(2\,c_3 - 2\,x)^2$$

$$(200 + 30)\cdot(400 + c_1 + 60)^2 = (300 - 30)\cdot(600 - 60)^2$$

$$c_1 = 125\ \mathrm{mmol\ dm^{-3}}$$

(b) Ions Ca^{2+} and Cl^- pass through the membrane from the outer to the inner compartment (T = 300.15 K)

$$(\mathrm{Ca}^{2+})_{\mathrm{out}} \rightarrow (\mathrm{Ca}^{2+})_{\mathrm{in}} \qquad z_{\mathrm{Ca}^{2+}} = 2$$

$$\mu^{\ominus}_{\mathrm{Ca}^{2+}}(p_{\mathrm{out}}) + \boldsymbol{R}T \ln(a_{\mathrm{Ca}^{2+}})_{\mathrm{out}} + z_{\mathrm{Ca}^{2+}} \cdot \boldsymbol{F} \cdot \varphi_{\mathrm{out}} = \mu^{\ominus}_{\mathrm{Ca}^{2+}}(p_{\mathrm{in}}) + \boldsymbol{R}T \ln(a_{\mathrm{Ca}^{2+}})_{\mathrm{in}} + z_{\mathrm{Ca}^{2+}} \cdot \boldsymbol{F} \cdot \varphi_{\mathrm{in}}$$

$$\mu^{\ominus}_{\mathrm{Ca}^{2+}}(p_{\mathrm{out}}) \doteq \mu^{\ominus}_{\mathrm{Ca}^{2+}}(p_{\mathrm{in}})$$

$$E = \varphi_{\mathrm{in}} - \varphi_{\mathrm{out}} = \frac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln \frac{(a_{\mathrm{Ca}^{2+}})_{\mathrm{out}}}{(a_{\mathrm{Ca}^{2+}})_{\mathrm{in}}} = \frac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln \frac{c_3 - x}{c_2 + x}$$

$$E = \frac{8.314 \cdot 300.15}{2 \cdot 96485.3} \cdot \ln \frac{300 - 30}{200 + 30} = 0.00207\ \mathrm{V}$$

or

$$(\mathrm{Cl}^-)_{\mathrm{out}} \rightarrow (\mathrm{Cl}^-)_{\mathrm{in}} \qquad z_{\mathrm{Cl}^-} = 1$$

$$\mu^{\ominus}_{\mathrm{Cl}^-}(p_{\mathrm{out}}) + \boldsymbol{R}T \ln(a_{\mathrm{Cl}^-})_{\mathrm{out}} - z_{\mathrm{Cl}^-} \cdot \boldsymbol{F} \cdot \varphi_{\mathrm{out}} = \mu^{\ominus}_{\mathrm{Cl}^-}(p_{\mathrm{in}}) + \boldsymbol{R}T \ln(a_{\mathrm{Cl}^-})_{\mathrm{in}} - z_{\mathrm{Cl}^-} \cdot \boldsymbol{F} \cdot \varphi_{\mathrm{in}}$$

$$\mu^{\ominus}_{\mathrm{Cl}^-}(p_{\mathrm{out}}) \doteq \mu^{\ominus}_{\mathrm{Cl}^-}(p_{\mathrm{in}})$$

$$E = \varphi_{\mathrm{in}} - \varphi_{\mathrm{out}} = -\frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{(a_{\mathrm{Cl}^-})_{\mathrm{out}}}{(a_{\mathrm{Cl}^-})_{\mathrm{in}}} = -\frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{2c_3 - 2x}{2c_2 + c_1 + 2x}$$

$$E = -\frac{8.314 \cdot 300.15}{96485.3} \cdot \ln \frac{600 - 60}{400 + 125 + 60} = 0.00207\ \mathrm{V}$$