Problem 12-04 Membrane equilibria, Donnan potential

Aqueous solution of a polyelectrolyte NaP (c_1 = 0.015 mol dm^{-3}) and low-molecular electrolyte NaBr (c_2 = 0.005 mol dm^{-3}) is separated from the compartment of the same volume filled with pure water by a semipermeable membrane. Both electrolytes are completely dissociated. At the temperature of 28 °C

(a) Calculate how many per cent of NaBr passes from the solution into water.

(b) Calculate how many per cent of NaBr would pass from the compartment containing NaBr and NaP, in case that the initial concentration is ten-times greater than in case (a).

(c) Calculate the value of Donnan potential for both cases.

[(a) 80 % (x_a = 0.004 mol dm^{-3}) , (b) 96.875 % (x_b = 4.84375·10^{-3} mol dm^{-3});
(c) $E_{(a)}$ = 0.036 V, $E_{(b)}$ = 0.089 V]

Solution:

NaP = Na^+ + P^- $\qquad c_1$ = 0.015 mol dm^{-3}
NaBr = Na^+ + Br^- $\qquad c_2$ = 0.005 mol dm^{-3}

Balance:	at the beginning		in equilibrium	
	Left	Right	Left	Right
P^+	c_1	0	c_1	0
Na^+	$c_1 + c_2$	0	$c_1 + c_2 - x$	x
Br^-	c_2	0	$c_2 - x$	x

Donnan equilibrium condition for NaBr:

$$(c_{Na^+})_{Left} \cdot (c_{Br^-})_{Left} = (c_{Na^+})_{Right} \cdot (c_{Br^-})_{Right}$$

$$(c_1 + c_2 - x) \cdot (c_2 - x) = x \cdot x$$

(a)

$$(0.015 + 0.005 - x_a) \cdot (0.005 - x_a) = x_a^2$$

$$0.0001 - 0.025\, x_a + x_a^2 = x_a^2$$

$$x_a = \frac{0.0001}{0.025} = 0.004 \text{ mol dm}^{-3}$$

x_a mol dm^{-3} passed from the left compartment to the right one, i.e.

$$100 \cdot \frac{x_a}{c_2} = 100 \cdot \frac{0.004}{0.005} = 80\ \%$$

(b) $c_{1b} = 10\, c_{1a}$ = 0.15 mol dm^{-3}

$$(0.15 + 0.005 - x_b) \cdot (0.005 - x_b) = x_b^2$$

$$0.000775 - 0.16\, x_b + x_b^2 = x_b^2$$

$$x_b = \frac{0.000775}{0.16} = 4.84375 \cdot 10^{-3} \text{ mol dm}^{-3}$$

From the left to the right compartment passed x_b mol dm^{-3}, i.e.

$$100 \cdot \frac{x_b}{c_2} = 100 \cdot \frac{4.84375 \cdot 10^{-3}}{0.005} = 96.875\ \%$$

(c) Ions Na^+ and Cl^- pass from the **L**eft to the **R**ight compartment, T = 301.15 K

z_{Cation} = 1, z_{Anion} = 1,

$$\mu^{\ominus}_{Na^+}(p_L) + \boldsymbol{R}T \ln (a_{Na^+})_L + z_{Na^+} \cdot \boldsymbol{F} \cdot \varphi_L = \mu^{\ominus}_{Na^+}(p_P) + \boldsymbol{R}T \ln (a_{Na^+})_P + z_{Na^+} \cdot \boldsymbol{F} \cdot \varphi_P$$

$$\mu^{\ominus}_{Na^+}(p_L) \doteq \mu^{\ominus}_{Na^+}(p_P)$$

$$E = \varphi_P - \varphi_L = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{(a_{Na^+})_L}{(a_{Na^+})_P} = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{c_1 + c_2 - x}{x}$$

$$E_{(a)} = \frac{8.314 \cdot 301.15}{96485.3} \cdot \ln \frac{0.015 + 0.005 - 0.004}{0.004} = 0.036 \text{ V}$$

$$E_{(b)} = \frac{8.314 \cdot 301.15}{96485.3} \cdot \ln \frac{0.15 + 0.005 - 4.84375 \cdot 10^{-3}}{4.84375 \cdot 10^{-3}} = 0.089 \text{ V}$$

or

$$\mu^{\ominus}_{Br^-}(p_L) + \boldsymbol{R}T \ln (a_{Br^-})_L - z_{Br^-} \cdot \boldsymbol{F} \cdot \varphi_L = \mu^{\ominus}_{Br^-}(p_P) + \boldsymbol{R}T \ln (a_{Br^-})_P - z_{Br^-} \cdot \boldsymbol{F} \cdot \varphi_P$$

$$\mu^{\ominus}_{Br^-}(p_L) \doteq \mu^{\ominus}_{Br^-}(p_P)$$

$$E = \varphi_P - \varphi_L = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{(a_{Br^-})_P}{(a_{Br^-})_L} = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{x}{c_2 - x}$$

$$E_{(a)} = \frac{8.314 \cdot 301.15}{96485.3} \cdot \ln \frac{0.004}{0.005 - 0.004} = 0.036 \text{ V}$$

$$E_{(b)} = \frac{8.314 \cdot 301.15}{96485.3} \cdot \ln \frac{4.84375 \cdot 10^{-3}}{0.005 - 4.84375 \cdot 10^{-3}} = 0.089 \text{ V}$$