Problem 12-09 Membrane hydrolysis, Donnan potential

Aqueous solution of a polyelectrolyte M_zR (M^+ is univalent low-molecular cation, R^{z-} a high-molecular anion) of concentration 0.0065 mol dm^{-3} was separated by a semipermeable membrane from the same volume of pure water. The membrane is permeable for M^+, non-permeable for R^{z-}. In equilibrium established at the temperature of 39.8 °C the pH in the right compartment containing initially pure water was 8.5. In the aqueous solution the polyelectrolyte is completely dissociated. Calculate
(a) the charge z of the high-molecular anion,
(b) pH of the polyelectrolyte solution in equilibrium,
(c) the membrane potential in equilibrium.
The ionic product of water at given temperature is $K_w = 3.795 \cdot 10^{-14}$ (standard state $c^{st} = 1$ mol dm^{-3}).

[a) z = 7; (b) pH = 4.92; E = 222.2 mV]

Solution:

$M_zR = z\,M^+ + R^{z-}$ $\qquad$ $c_0 = 0.0065$ mol dm^{-3}

$H_2O = H^+ + OH^-$

$c_0 = 0.0065$ mol dm^{-3}

Balance:	at the beginning		in equilibrium	
	Left	Right	Left	Right
R^{z-}	c_0	0	c_0	0
M^+	$z\,c_0$	0	$z\,c_0 - x$	x
OH^-			K_w/x	x
H^+			x	K_w/x

Donnan equilibrium condition (passing ions are M^+ and OH^-):

$$c(M^+)_{Left} \cdot c(OH^-)_{Left} = c(M^+)_{Right} \cdot c(OH^-)_{Right}$$

$$(z\,c_0 - x)\cdot\frac{K_w}{x} = x^2 \quad , \quad c_{OH^-} = \frac{K_w}{c_{H^+}} = \frac{K_w}{x}$$

(a) $(pH)_{Right} = -\log\dfrac{K_w}{x} = 8.5$

$$\frac{K_w}{x} = 10^{-8.5} \qquad \Rightarrow \qquad x = \frac{3.795\cdot 10^{-14}}{10^{-8.5}} = 1.2\cdot 10^{-5} \text{ mol dm}^{-3}$$

$$z = \frac{1}{c_0}\cdot\left(x + \frac{x^3}{K_w}\right) = \frac{1}{0.0065}\left(1.2\cdot 10^{-5} + \frac{(1.2\cdot 10^{-5})^3}{3.795\cdot 10^{-14}}\right) = 7.0015 \doteq 7$$

(b) $(pH)_{Left} = -\log x = -\log 1.2\cdot 10^{-5} = 4.92$

(c) Ions M^+ and OH^- pass from the Left into the Right compartment,

$z_{Cation} = 1$, $z_{Anion} = 1$, $T = 312.95$ K

$$\mu^{\ominus}_{M^+}(p_{Left}) + \boldsymbol{R}T\ln(a_{M^+})_{Left} + z_{M^+}\cdot\boldsymbol{F}\cdot\varphi_{Left} = \mu^{\ominus}_{M^+}(p_{Right}) + \boldsymbol{R}T\ln(a_{M^+})_{Right} + z_{M^+}\cdot\boldsymbol{F}\cdot\varphi_{Right}$$

$$\mu^{\ominus}_{M^+}(p_{Left}) \doteq \mu^{\ominus}_{M^+}(p_{Right})$$

$$E = \varphi_{Right} - \varphi_{Left} = \frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\frac{(a_{M^+})_{Left}}{(a_{M^+})_{Right}} = \frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\frac{z\,c_0 - x}{x}$$

$$E = \frac{8.314\cdot 312.95}{96485.3}\cdot\ln\frac{7\cdot 0.0065 - 1.2\cdot 10^{-5}}{1.2\cdot 10^{-5}} = 0.2222 \text{ V}$$