Problem 10-10 Conductivity, molar conductivity, dissociation constant

Calculate the conductivity of the $2\cdot10^{-5}$ molar solution of propionic acid, the dissociation constant of which has the value of $1.32\cdot10^{-5}$ (standard state infinite dilution, c^{st} = 1 mol dm^{-3}, activity coefficients for all substances can be taken as equal to one). The conductivity of water used for the measurement was $6.6\cdot10^{-5}$ S m^{-1} and the limiting molar conductivities of ions have the following values:

$$\lambda^{\infty}(H^+) = 0.03497 \text{ S m}^2 \text{ mol}^{-1}\ ,\ \lambda^{\infty}(C_3H_7COO^-) = 0.00358 \text{ S m}^2 \text{ mol}^{-1}$$

[$\kappa_{solution} = 4.88\cdot10^{-4}$ S m^{-1}]

Solution:

$$C_3H_7COOH = C_3H_7COO^- + H^+$$
$$PH \qquad P^-$$

$c_0 = 2\cdot10^{-5}$ mol dm^{-3}

Balance: the conversion degree $\alpha = \dfrac{c_0 - c_{PH}}{c_0} \Rightarrow c_{PH} = c_0(1-\alpha)$

$c_{P^-} = c_{H^+} = c_0\,\alpha$

$$K = 1.32\cdot10^{-5} = \frac{a_{P^-}\cdot a_{H^+}}{a_{PH}} = \frac{\gamma_-\cdot c_{P^-}\cdot\gamma_+\cdot c_{H^+}}{\gamma_{PH}\cdot c_{PH}}\cdot\frac{1}{c^{st}} = \frac{\gamma_\pm^2\cdot c_0\cdot\alpha^2}{1-\alpha} \qquad (\gamma_{PH}=1\ ,\ \gamma_\pm = 1\ ,\ c^{st} = 1 \text{ mol dm}^{-3})$$

$$\alpha^2 + \frac{1.32\cdot10^{-5}}{2\cdot10^{-5}}\,\alpha - \frac{1.32\cdot10^{-5}}{2\cdot10^{-5}} = 0$$

$\alpha^2 + 0.66\,\alpha - 0.66 = 0$

$\alpha = -0.33 \pm (0.1089 + 0.66)^{1/2} = 0.54687$

$$\alpha = \frac{\lambda}{\lambda^{\infty}}$$

$\lambda^{\infty}(H^+) = 0.03497$ S m^2 mol^{-1} , $\lambda^{\infty}(C_3H_7COO^-) = 0.00358$ S m^2 mol^{-1}

$\lambda^{\infty} = \lambda^{\infty}(H^+) + \lambda^{\infty}(C_3H_7COO^-) = 0.03497 + 0.00358 = 0.03855$ S m^2 mol^{-1}

$\lambda = \alpha\cdot\lambda^{\infty} = 0.54687\cdot0.03855 = 0.021082$

$$\lambda = \frac{\kappa}{c_0} = \frac{\kappa_{solution} - \kappa_{water}}{c_0}\ ;\ c_0 = 2\cdot10^{-5} \text{ mol dm}^{-3} = 2\cdot10^{-2} \text{ mol m}^{-3}\ (c_0 \text{ in mol m}^{-3}!!)$$

$$\left[\frac{\text{S m}^{-1}}{\text{mol m}^{-3}} = \text{S m}^2 \text{ mol}^{-1}\right]$$

$\kappa_{solution} = \kappa_{water} + \lambda\cdot c_0 = 6.6\cdot10^{-5} + 0.021082\cdot2\cdot10^{-2} =$

$\kappa_{solution} = 4.8764\cdot10^{-4}$ S m^{-1}