Problem 10-09 Conductivity, molar conductivity, dissociation constant

The conductivity of aqueous solution of benzoic acid with concentration 0.01 mol dm^{-3} at 21 °C was determined to be $3.004 \cdot 10^{-2}$ S m^{-1} and the conductivity of water used for the measurement was $2.4 \cdot 10^{-4}$ S m^{-1}. Assume that the activity coefficient of undissociated acid as well as the mean activity coefficient may be taken as unity. Calculate the dissociation constant of benzoic acid for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3}. Limiting molar conductivities of ions:

$$\lambda^{\infty}(H^+) = 0.03497, \quad \lambda^{\infty}(C_6H_5COO^-) = 0.00323 \ \text{S m}^2 \text{ mol}^{-1}.$$

[$K = 6.6 \cdot 10^{-5}$ ($\alpha = 0.078$)]

Solution:

$$\underset{BH}{C_6H_5COOH} = \underset{B^-}{C_6H_5COO^-} + H^+$$

Balance: $c_0 = 0.01$ mol dm^{-3}

$c_{BH} = c_0 (1 - \alpha)$

$c_{B-} = c_{H+} = c_0 \ \alpha$

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

The conversion degree: $\alpha = \dfrac{\lambda}{\lambda^{\infty}}$

$\lambda^{\infty}(H^+) = 0.03497$, $\quad \lambda^{\infty}(C_6H_5COO^-) = 0.00323$ S m^2 mol^{-1}

$\lambda^{\infty} = \lambda^{\infty}(H^+) + \lambda^{\infty}(C_6H_5COO^-) = 0.03497 + 0.00323 = 0.0382$ S m^2 mol^{-1}

$$\lambda = \frac{\kappa}{c_0} = \frac{\kappa_{solution} - \kappa_{water}}{c_0} = \frac{3.004 \cdot 10^{-2} - 2.4 \cdot 10^{-4}}{0.01 \cdot 10^3} = 0.00298$$

$$\alpha = \frac{0.00298}{0.0382} = 0.07801$$

$$K = \frac{0,01 \cdot 0,078^2}{1 - 0,078}$$

$K = 6.6 \cdot 10^{-5}$