Elektrochemie HS 2019

Solution 2 "Electrolyte Conductivity and Cell Constant" September 2019

Assistent: Adrian Mularczyk
Tel.: (0)56-310-5726
Email: adrian.mularczyk@psi.ch

Answers can be given in German or English. Antworten können in Deutsch oder Englisch gegeben warden.

Task 1:

15% (wt.) NaOH solution (Density 1.210 $g \cdot cm^{-3}$) is filled in a reservoir between two electrodes with a surface area of A = 20 cm^2 and standing at the distance l = 4 cm. The electrical conductance of this solution at 18°C is L= 1.815 S. Calculate the molar electrical conductivity of this solution (Λ_m).

Solution:

Calculate the molar concentration of the solution (c) using its density (d), the weight fraction of NaOH (w) and molar mass of NaOH (M):

$$w = \frac{m(NaOH)}{m(solution)} = \frac{n(NaOH) \cdot M(NaOH)}{V(solution) \cdot d(solution)} = c \cdot \frac{M(NaOH)}{d(solution)}$$

$$c = w\frac{d(solution)}{M(NaOH)} = 4.53 * 10^{-3}\,\frac{mol}{cm^3}$$ 2 PTS

Then we can find the conductivity (κ) and the molar electrical conductivity (Λ_m) of the solution:

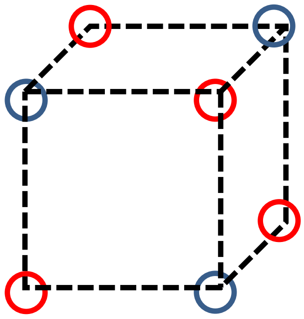
$$\kappa = L * \frac{l}{A} = 0.363\,\frac{S}{cm}$$

$$\Lambda_m = \frac{\kappa}{1_c} = \frac{\kappa}{c} = 80\,\frac{Scm^2}{mol}$$ 2+1 PTS

Answer: Λ_m = 80 $S \cdot cm^2 \cdot mol^{-1}$

Task 2:

Two equal portions of NaOH are given into two flasks. One is to be mixed with pure ethanol the other with pure water. What is the ratio between the volumes of water and ethanol needed to obtain the same electrostatic force between dissolved charges in both solutions? Use Coulombs Law and assume full dissociation with a distribution of charges in solution as indicated in the image below. The dielectric constants of water (78.3) and ethanol (25.8).



$$\vec{K}=\frac{q_1 \cdot q_2}{4\pi\varepsilon_0\varepsilon_r \cdot r^2}$$

Solution(2 +2 +1 Points):

$$K_{Ethanol} = K_{Water}$$

$$\frac{q_1 * q_2}{4\,\pi\,\varepsilon_0\,\varepsilon_{Ethanol} * r_{Ethanol}^2} = \frac{q_1 * q_2}{4\,\pi\,\varepsilon_0\,\varepsilon_{Water} * r_{Water}^2}$$

$$\varepsilon_{Ethanol} * r_{Ethanol}^2 = \varepsilon_{Water} * r_{Water}^2$$

$$\frac{\varepsilon_{Ethanol}}{\varepsilon_{Water}} = \frac{r_{Water}^2}{r_{Ethanol}^2}$$

Relation between r and number of NaOH molecules:

$$\frac{V_{Water}}{N_{NaOH,Water}} = r_{Water}^3$$

$$N_{NaOH,Water} = \frac{V_{water}}{r_{Water}^3}$$

$$N_{NaOH,Ethanol} = \frac{V_{Ethanol}}{r_{Ethanol}^3}$$

$$\frac{N_{NaOH,Ethanol}}{N_{NaOH,Water}} = \frac{V_{Ethanol}}{V_{water}}\frac{r_{Water}^3}{r_{Ethanol}^3}$$

From this we obtain:

$$\frac{V_{Ethanol}}{V_{water}} = \frac{N_{NaOH,Ethanol}}{N_{NaOH,Water}}\left(\frac{\varepsilon_{Ethanol}}{\varepsilon_{Water}}\right)^{-\frac{3}{2}} = 5.29$$

Task 3 (5 Points):

The resistance (R) of $La_{1.7}Bi_{0.3}Mo_2O_{9-\delta}$ solid electrolyte was measured as a function of temperature (T):

T, [°C]	1223	1173	1123	1073
R, [Ohm]	62.8	76.1	96.3	128.1

Calculate the activation energy (E_a, kJ·mol^{-1}) of conductivity (k) assuming the following Arrhenius-like dependency:

$$\kappa = \frac{const}{T}\exp\left(-\frac{E_a}{\bar{R}T}\right)$$

Solution:

$$\kappa = \frac{const}{T}\exp\left(-\frac{E_a}{\bar{R}T}\right)$$

$$\kappa = \frac{1}{R} * \frac{l}{A} = \frac{const}{T}\exp\left(-\frac{E_a}{\bar{R}T}\right)$$

$$\frac{T}{R} = const' * \exp\left(-\frac{E_a}{\bar{R}T}\right)$$

$$\ln\left(\frac{T}{R}\right) = const'' * -\frac{E_a}{\bar{R}T}$$ 2PTS

Thus, we need to calculate $\ln\left(\frac{T}{R}\right)$ and fit it linearly vs. 1/RT.

T, °C	R, Ohm	$\ln\left(\frac{T}{R}\right)$	$\frac{1000}{\bar{R}T}$
1223	62.8	3.171	0.08
1173	76.1	2.945	0.083
1123	96.3	2.674	0.086
1073	128.1	2.352	0.089

2PTS

E_a can be calculated from the slope of the line: E_a = 91.45 kJ/mol

Answer: E_a = 91.45 kJ/mol 1PT

Task 4 (5 Points):
The conductivity of a 0.135M solution of propionic acid κ_{acid} = 4.79×10^{-4} S×cm^{-1} and the conductivity of 0.001M solution of sodium propionate κ_{salt} = 7.54×10^{-5} S×cm^{-1}. The mobilities of Na^+ and H^+ are the following: $\Lambda_{0_{Na^+}}$ = 44.4 S×cm^2×mol^{-1}, $\Lambda_{0_{H^+}}$ = 349.8 S×cm^2×mol^{-1}. Assuming that at the given concentration the salt is fully dissociated and ions don't interact with each other, calculate the dissociation constant of propionic acid.

Solution:

The equivalent conductivities (Λ) of the acid and its salt can be calculated from their conductivities (κ) and concentrations (c):

$$\Lambda_{acid} = \frac{\kappa_{acid}}{1c_{acid}} = \frac{\kappa_{acid}}{c_{acid}} = 3.548\ \frac{Scm^2}{mol}$$

$$\Lambda_{salt} = \frac{\kappa_{salt}}{1c_{salt}} = \frac{\kappa_{salt}}{c_{salt}} = 75.4\ \frac{Scm^2}{mol}$$ 2PTS

At the given concentration (0.001M) the salt is fully dissociated and ions don't interact with each other, which means that we can assign the above found value of the equivalent conductivity to the infinitely diluted solution, i.e. $\Lambda_{0_{salt}} = \Lambda_{salt} = 75.4\frac{Scm^2}{mol}$
Then we can calculate the equivalent conductivity at infinite dilution (Λ_0) of the acid:
$\Lambda_{0_{acid}} = \Lambda_{0_{salt}} + \Lambda_{0_{H^+}} - \Lambda_{0_{Na^+}} = 380.8\frac{Scm}{mol}$. The dissociation degree of propionic acid (α) in the solution can be estimated as a ratio of the actual equivalent conductivity to the equivalent conductivity at infinite dilution:

$$\alpha = \frac{\Lambda_{acid}}{\Lambda_{0_{acid}}} = 9.318 * 10^{-3}$$

Then the dissociation constant of the acid (K_a) can be found:

$$K_a = \frac{[C_2H_5COO^-][H^+]}{[C_2H_5COOH]} = \frac{\left(\alpha\frac{c}{c_0}\right)^2}{(1-\alpha)\frac{c}{c_0}} = 1.18 * 10^{-5}$$

Answer: K_a = 1.18×10^{-5} 2+1 PTS