A 20 Direct determination of the migration velocity of an ion

Task:

To determine the Migration Velocity of an MnO_4^--ion using the Moving Boundary method.

Basics:

The mobility of a coloured ion can be immediately determined by observing the displacement of the boundary layer between coloured and non-coloured electrolyte solutions of equal conductivity in an electrical field.

$$u = \frac{v \cdot l}{V} \quad [\mathrm{m}^2/(Vs)] \tag{1}$$

v: Migration Velocity in m/s that the boundary layer displaces

l: Electrode spacing in m

V: Potential difference in Volts between the electrodes.

The relationship between the mobility $u^{\pm}$ and the molar conductivity $\Lambda^{\pm}$ of each ion is as follows:

$$\Lambda^{\pm} = u^{\pm} z^{\pm} F \quad [\mathrm{cm}^2/\Omega\cdot\mathrm{mol}] \tag{2}$$

F: Faraday constant = 96,485 C/mol

$z^{\pm}$: Charge number

If the Migration Velocity of the anion (u^-) as well as the cation (u^+) is known, it is possible to calculate the transport number t of the cation and the anion respectively.

$$t^+ = u^+/(u^+ + u^-) \qquad (3a)$$

$$t^- = u^-/(u^+ + u^-) \qquad (3b)$$

From (2) and (3) respectively, we can further determine the molar conductivity of the analysed electrolyte at a given temperature and concentration:

$$\Lambda = F(u^+ + u^-) = \Lambda^+ + \Lambda^- \qquad (4)$$

Experimental Procedure:

Fill 50 ml $KMnO_4$-solution into a beaker and dissolve enough boric acid in it to produce a saturated solution. Pour an amount into the funnel of the graduated vessel then open the tap until the capillary is entirely full with $KMnO_4$-solution. Close the tap, and rinse the u-pipe several times with distilled water and finally with a small amount of KNO_3-solution. Now fill the funnel with $KMnO_4$-solution, and the u-pipe (to approx. the +25 mark) with KNO_3-solution. Attach the electrodes (but do not attach the power source). By carefully opening the tap the KNO_3-solution becomes underlayered by the $KMnO_4$-solution whose specific weight has been increased through the addition of boric acid. Make certain that there is a clear, horizontal dividing line between the two solutions. A rate of ascent of 1 cm/min is advisable. Close the tap when the electrodes are completely submerged in the KNO_3-solution.

Connect the electrodes to the power source. From this point on, the displacement of the boundary layer in relation to time should be recorded every 3 minutes. In the analysis, the upward moving layer should be taken into account, as this layer generally stays clear during the whole experiment. The experiment is finished after 30 minutes. Record the distance between the electrodes and the room temperature, and then rinse the apparatus with distilled water.

Data Analysis:

1. Plot the displacement *s* of the boundary layer against time *t*, and determine the velocity *v* from the inclination of the curve obtained. (What type of curve is obtained?). Conduct an error analysis for velocity *v*.
2. Calculate the mobility of the MnO_4^- ion.
3. How large is the transport number of the MnO_4^- ion and the K^+ ion when the mobility of the K^+ ion at 18 °C is $u_o^+ = 6.47 \cdot 10^{-8}\ \mathrm{m^2/Vs}$, and the temperature dependency is $u^+(\theta) = u^+(18°)(1 + 0.0217 \cdot (\theta - 18))$? ($\theta$ = Temperature in °C)
4. How large is the molar conductivity Λ of the solution, and the ion conductivities Λ_{K_+} and $\Lambda_{MnO_4^-}$?
5. From the mobility calculate the radius of the MnO_4^- ion using Stokes' Law.
6. Perform an error propagation for tasks 2 to 5.
7. Compare your results to the literature.

What you should know:

Migration velocity, mobility, specific conductance, transport number, molar or equivalent conductivity, solvation shell, ion cloud (basics of Debye-Hückel-theory), Stokes' law for friction force.

Extra Question:

1. How does the mobility of the H^+ and the OH^- ions differ from other monovalent ions in water?
2. How do you determine transport numbers of non-coloured electrolytes (Hittorf method)?

Literature:

G. Wedler und H.-J. Freund, Lehrbuch der Physikalischen Chemie, 6. Aufl., Wiley-VCH.

C. H. Hamann und W. Vielstich, Elektrochemie, 2005, Wiley-VCH.