**EXERCISE 4**

**CONDUCTOMETRY**

**Theoretical topics**

ionic conductivity, electronic conductivity, equivalent conductivity, specific conductivity, limiting conductivity, conductometric titration endpoint, cell constant, conductometric solubility product measurement, conductometric probe standardization, titration curves, units of molar conductivity, units of equivalent conductivity and limiting conductivity, law of independent ion migration

**Experimental Part – 4.1.**

**Topic:**  
Solubility product of sparingly soluble salts.

**Objective:**  
Use conductometry to determine the solubility product of salts based on the measurement of the conductivity of their saturated solutions.

**Apparatus:**  
conductometer, magnetic stirrer, beakers

**Reagents:**  
four saturated salt solutions: HgCl₂, CaSO₄, MnSO₄, Na₂CO₃

**Procedure:**

1. Fill a beaker with a saturated solution of HgCl₂, pouring the entire content of the volumetric flask with the salt solution into it, and place the electrode inside.
2. Wait for the conductivity of the solution to stabilize, read the value, and record it in Table 1.
3. Lift the conductometric electrode from the solution, wait 15 seconds, and immerse it again. Wait for the conductivity to stabilize, read it, and record it as the second measurement.
4. Conduct a total of 6 measurements.
5. After the measurements are completed, transfer the HgCl₂ solution back to the appropriate volumetric flask, and place the electrode in distilled water.
6. Similarly (steps 1–5), measure the conductivity of the remaining saturated salt solutions in the following order: CaSO₄, MnSO₄, Na₂CO₃.
7. Use the average values from six measurements for the calculations.

**Report:**

1. Present the measurement results in Table 1.
2. Calculate the following:
   * Average specific conductivity κ with standard deviation [S/cm]
   * Limiting equivalent conductivity (based on Kohlrausch's law) [S∙cm²/equiv]
   * Salt concentration [mol/dm³]
   * Solubility product L

The obtained values should be compiled in Table 2.

1. Provide conclusions from the exercise.

**Experimental Part – 4.2.**

**Topic:**  
Determining dissociation constants of weak electrolytes from conductivity measurements

**Objective:**  
Use electrochemical methods to determine the dissociation constants of weak electrolytes

**Apparatus:**  
conductometer, magnetic stirrer, beakers

**Reagents:**  
0.1 M CH₃COOH

**Procedure:**

1. In 100 ml volumetric flasks, there are solutions of weak electrolytes (CH₃COOH) with the following concentrations: 1/64 M, 1/128 M, 1/256 M, 1/512 M, 1/1024 M. If any flask lacks solution or is insufficient, prepare the solution by diluting the stock acetic acid solution of 0.1 M. Consult the instructor on how to prepare the solution and show the necessary calculations.
2. Fill a beaker with the acetic acid solution of the lowest concentration by transferring the entire content of the volumetric flask, and place the electrode in the beaker.
3. Wait for the conductivity to stabilize, read the value, and record it in Table 3.
4. Lift the conductometric electrode, wait 15 seconds, and immerse it again. Wait for the conductivity to stabilize, read the value, and record it as the second measurement.
5. Conduct a total of 6 measurements.
6. Similarly (steps 2–5), measure the conductivity of the remaining acetic acid solutions in increasing concentration order.
7. Use the average values from six measurements for the calculations.

**Report:**

1. Present the measurement results in Table 3.
2. Perform the following calculations:
   * Obtain the correct concentrations of the studied CH₃COOH solutions (1/64 M, 1/128 M, 1/256 M, 1/512 M, 1/1024 M) from the stock solution.
   * Average specific conductivity κ with standard deviation [S/cm]
   * Molar conductivity Λ [S∙cm²/mol]
   * Degree of dissociation α
   * Dissociation constant

The obtained values should be compiled in Table 4.

1. Provide conclusions from the exercise.

**Experimental Part – 4.3.**

**Topic:**  
Conductometric titration

**Objective:**  
Conductometric determination of hydrochloric acid and acetic acid separately and in a mixture via titration with sodium hydroxide.

**Apparatus:**  
conductometer, magnetic stirrer, beakers, automatic pipette

**Reagents:**  
0.5 M NaOH, 0.1 M HCl, 0.1 M CH₃COOH

**Procedure:**

1. Take 10 ml of 0.1 M hydrochloric acid in a beaker, add 100 ml of distilled water using a cylinder, and place a cylindrical magnetic stirrer inside the beaker.
2. Set the beaker on the magnetic stirrer and place the electrode inside.
3. Wait for the conductivity to stabilize, read the value, and record it in Table 5 as NaOH volume v=0.
4. Titrate the acid with 0.5 M NaOH solution by adding successive portions of 0.2 ml each. In each case, record the total added titrant volume and the conductivity value after stabilization. After reaching the equivalence point, continue titration until the initial conductivity of the solution is reached.
5. After the measurements, place the electrode in distilled water.
6. Perform titration of 0.1 M acetic acid in the same way as hydrochloric acid (steps 1–5), except that each added volume of 0.5 M NaOH solution should be 0.1 ml. After reaching the equivalence point, continue titration until the total volume of NaOH used reaches 3 ml.
7. Titrate a mixture of hydrochloric and acetic acids by adding 5 ml of their 0.1 M solutions and 100 ml of distilled water to the beaker. Conduct titration similarly to the previous two acids by adding 0.2 ml of 0.5 M NaOH solution. Record enough points to obtain results for both equivalence points of HCl and CH₃COOH, titrating until the initial conductivity of the solution is restored.

**Report:**

1. Present the measurement results in Table 5.
2. Draw three graphs of the dependence of the solution’s conductivity on the added NaOH volume for hydrochloric acid, acetic acid, and their mixture, and determine the equivalence points.
3. Calculate the concentration of hydrochloric and acetic acids titrated separately and in the mixture.
4. Provide conclusions from the exercise.

**Appendix to Exercise 4:**

Equivalent limiting conductivities of ions:  
SO₄²⁻: 79.8 S∙cm²/equiv  
CO₃²⁻: 72.0 S∙cm²/equiv  
Cl⁻: 76.4 S∙cm²/equiv  
Ca²⁺: 59.5 S∙cm²/equiv  
Hg²⁺: 65.9 S∙cm²/equiv  
Na⁺: 50.1 S∙cm²/equiv  
Mn²⁺: 57.8 S∙cm²/equiv

Specific conductivities of acetic acid:  
1/64 M: 0.00012 S/cm  
1/128 M: 0.00007 S/cm  
1/256 M: 0.00005 S/cm  
1/512 M: 0.000036 S/cm  
1/1024 M: 0.000028 S/cm

Limiting molar conductivity of acetic acid:  
Λ₀ = 390.7 S∙cm²/mol