**EXERCISE 3**

**POTENTIOMETRIC METHODS**

**Theoretical topics**

galvanic cells, half-cells, SEM cells, redox potential, standard potential, electrodes (types and storage), cell voltage, Nernst equation, equilibrium constant for electrochemical reactions, half-cell potential, voltage series, pH, buffer solutions, buffer capacity, types of potentiometric titration

**Experimental Part – 3.1.**

**Topic:**  
Potentiometric titration of glycine

**Objective:**  
Determination of pK1, pK2, and pI for glycine.

**Apparatus:**  
pH meter, combination electrode, beakers, automatic pipette

**Reagents:**  
0.05 M glycine, 0.1 M HCl, 0.1 M NaOH

**Procedure:**

1. Measure 25 ml of 0.05 M glycine solution into a beaker and place a cylindrical magnetic stirrer in it.
2. Place the test solution on the magnetic stirrer.
3. Immerse the pH meter electrode in the test solution, ensuring it does not touch the rotating stirrer. Turn on the magnetic stirrer and measure the initial pH of the solution, recording it in the table.
4. Add 0.25 ml of 0.1 M HCl to the solution, wait for the pH value to stabilize, and record it in the table along with the amount of titrant added.
5. Continue adding 0.1 M HCl in increments, each time noting the total volume of titrant added and the corresponding pH value in the table. Stop the titration when the pH reaches 2.5 and record the final pH and titrant volume.
6. After the last measurement, place the electrode in distilled water.
7. Repeat the titration with 0.1 M HCl two more times (according to steps 1-6), using a new portion of glycine each time.
8. Measure 25 ml of 0.05 M glycine solution into another beaker and place a cylindrical magnetic stirrer in it.
9. Place the test solution on the magnetic stirrer.
10. Immerse the pH meter electrode in the test solution, ensuring it does not touch the rotating stirrer. Turn on the magnetic stirrer and measure the initial pH of the solution, recording it in the table.
11. Add 0.25 ml of 0.1 M NaOH to the solution, wait for the pH value to stabilize, and record it in the table along with the amount of titrant added.
12. Continue adding 0.1 M NaOH in increments, each time noting the total volume of titrant added and the corresponding pH value in the table. Stop the titration when the pH reaches 11.
13. After the last measurement, place the electrode in distilled water.
14. Repeat the titration with 0.1 M NaOH two more times (according to steps 8-13), using a new portion of glycine each time.
15. Use the average values from the three measurements for calculations.

**Report:**

1. Compile the measurement results in Table 1.
2. Create a graph showing the pH dependence on the volume of added NaOH and HCl,
3. Calculate the pK1, pK2, and pI values for glycine.
4. Provide conclusions for the experiment.

**Experimental Part – 3.2.**

**Topic:**  
Determination of pH and pKa of salicylic acid.

**Objective:**  
Determination of the pH and pKa values of salicylic acid in water-organic mixtures.

**Apparatus:**  
pH meter, combination electrode, beakers

**Reagents:**  
salicylic acid, organic solvents: methanol, ethanol, propanol, acetonitrile, 0.05 M NaOH

**Procedure:**

NOTE: The instructor will indicate which water-organic mixtures (according to Table A) to study.

* 1. Prepare a 0.01 M salicylic acid solution in a water-organic mixture. To do this, weigh 0.0138 g of salicylic acid on an analytical balance using a weighing paper, then transfer the weighed acid into a beaker using the specified amount of organic solvent from Table A, and then add the specified amount of water.
  2. Place a magnetic stirrer in the beaker.
  3. Place the test solution on the magnetic stirrer and immerse the electrode in it.
  4. Measure the initial pH of the solution and record the value.
  5. Add 0.1 ml of 0.05 M NaOH in increments (until the pH reaches 12). After each addition, wait for the pH value to stabilize and record it in the table.
  6. After the titration is complete, place the electrode in distilled water, and empty and rinse the beaker containing the sample.
  7. Repeat the titration procedure (steps 1-5) for subsequent salicylic acid samples in the indicated water-organic mixtures.
  8. Repeat the titration procedure for pure organic solvents (10 ml of solvent, without added water) as indicated by the instructor.

**Table A. Volumes [ml] of organic solvent and water required to prepare water-organic mixtures.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **solvent** | **mole fraction of the solvent in the mixture** | | | | |
| **methanol** | **0.1** | **0.3** | **0.5** | **0.7** | **0.9** |
| solvent volume | 1.9 | 5.0 | 7.1 | 8.5 | 9.5 |
| water volume | 8.0 | 5.0 | 2.9 | 1.5 | 0.5 |
| **ethanol** | **0.1** | **0.3** | **0.5** | **0.7** | **0.9** |
| solvent volume | 2.7 | 5.8 | 7.7 | 8.8 | 9.7 |
| water volume | 7.3 | 4.2 | 2.3 | 1.2 | 0.3 |
| **propanol** | **0.1** | **0.3** | **0.5** | **0.7** | **0.9** |
| solvent volume | 3.2 | 6.5 | 8.1 | 9.0 | 9.8 |
| water volume | 6.8 | 3.5 | 1.9 | 1.0 | 0.2 |
| **acetonitrile** | **0.1** | **0.3** | **0.5** | **0.7** | **0.9** |
| solvent volume | 2.5 | 5.5 | 7.5 | 8.7 | 9.7 |
| water volume | 7.5 | 4.5 | 2.5 | 1.3 | 0.3 |

**Report:**

* 1. Compile the measurement results in Table 2.
  2. Create graphs showing pH dependence on the volume of added NaOH for all systems.
  3. Calculate corresponding pKa values.
  4. Provide conclusions for the experiment.