

A 25 Conductometric Titration

Task:

Determine the Normality, with 0.1 n NaOH, of a HCl- and a CH₃COOH-Solution using Conductometric Titration. The solutions should be titrated singularly, as well as simultaneously.

Basics:

The Specific Conductivity

$$\chi = \frac{C}{R} \quad [\Omega^{-1}cm^{-1}]$$

(R = Resistance in Ω

C = Cell constant in cm^{-1})

of an Electrolyte is, first and foremost, dependant on the number and migration velocity on the existing ions in the solution. Electrolytes that contain many, and highly mobile, ions have a higher Specific Conductivity χ , and vice versa. A change in the conductivity can be initiated by the substitution of one ion type with an ion type of faster or slower migration velocity.

This is what the process of Conductometric Titration is based on, whereby the concentration, or the number of present ions, of an electrolyte can be determined. To do this, a titrant – an electrolyte of known concentration (number of ions) - is added step by step to the solution to be analysed. The added ion type A can substitute a corresponding lower or higher mobile ion type X in the solution to be analysed. By observing the changes in the Specific Conductivity χ the

point where practically all X ions have been substituted by A ions can be observed (are **all** X ions really substituted at this point?) This point is known as the Equivalence Point. The concentration of a strong acid, e.g. a watery HCl-solution, and a strong base, e.g. a watery NaOH-solution, can be particularly well conductometrically determined.

In this case, the highly mobile H_3O^+ -ion gets substituted by the lower mobile base cation (e.g. Na^+), where the H_3O^+ and OH^- ions react to produce water molecules. The conductivity χ initially sinks proportionately to the total amount of added titrant, that is to the number of added Na^+ -ions. When practically all of the H_3O^+ -ions have been substituted by the base-cations, χ will have reached its lowest value: this is the Equivalence Point. With further addition of titrant, χ rises again due to the increased electrolyte concentration. This increase is distinctive due to the equally fast moving OH^- ions. From the amount of titrant needed to reach the minimum χ , the original number of ions in the analysed acid can be determined.

Before beginning, the qualitative progression of the Specific Conductivity of all three titrations should be known!

Experimental Procedure:

The solutions to be tested will be handed out by the technical assistants in the lab.

The graduated flasks with the supplied substances should be filled to 100ml with distilled water.

The following solutions should be titrated:

- a) 50 ml HCl-Solution
- b) 50 ml CH_3COOH -Solution

c) 20 ml HCl + 20 ml CH₃COOH-Solution

An exact amount of solution should be pipetted into a beaker (250 ml) which has been cleaned with distilled water. Place a magnetic stirrer and an immersion cell into the beaker. The solution must be a minimum of 1cm over the electrodes, if necessary add distilled water.

The digital measuring instrument will immediately show the conductivity χ (what scale is being measured?)

Small amounts (ca. 0.5 ml) of 0.1 n NaOH should be added dropwise to the solution.

After each addition the solution should be stirred well, and the Specific Conductivity χ subject to the amount of titrant added measured until the equivalence point has been significantly exceeded.

Data Analysis:

- 1) The Specific Conductivity χ should be plotted against the volume of added NaOH (in ml). The respective Normality of the original solutions should be calculated from the equivalence points. Conduct an error analysis for the HCl titration. Reasonably estimate the possible error for each measured value, from these calculate the error for each straight line, and determine the error of Normality for HCl.
- 2) Explain the progression of the titration curve for each system.
- 3) Calculate the titration curve $1/R = f(V(\text{NaOH}))$ for the titration of 50ml of a 0.01 n HCl-solution with a 1 n NaOH-solution (the dilution effect can be ignored). Sketch the result!

$$1/R = 1/C \cdot 10^{-3} \cdot \sum_i c_i \lambda_i; \quad i = H^+, Na^+, Cl^-, OH^-$$

$$10^{-3} = \text{Conversion factor cm}^3 \text{ in l}$$

R = Resistance in Ω

C = Cell constant, assuming $C = 1\text{ cm}^{-1}$

c_i = Concentration of ion I in mol/l

λ_i = Equivalent conductivity of the ion i

Use the following values for the Equivalence Ability:

H^+ : $307\text{ cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$

Na^+ : $41\text{ cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$

Cl^- : $62\text{ cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$

OH^- : $167\text{ cm}^2\ \Omega^{-1}\ \text{mol}^{-1}$

(The intrinsic resistance of H_2O can be ignored)

What you should know:

Kohlrausch's square root law, Ostwald's law of dilution, conductivity of ions, migration velocity, ion mobility, extraconductivity, Grotthuß mechanism, transport numbers, salt bridge diffusion potential, basics of the Debye-Hückel theory, Nernst-Einstein relation