

Lab session 1

Conductometric determination of the ionization constant of a weak electrolyte (acetic acid)

Material	1 glass rod/ 1 funnel/ 1 weighting boat / 1 Pasteur pipette
2 volumetric flasks of 250 mL	1 dropping pipette and 1 washing bottle
1 volumetric flask of 100 mL	1 burette of 50 mL
2 Erlenmeyer flasks of 250 mL with cap	1 conductivity instrument with its conductivity cell
1 high beaker of 250 mL	
3 beakers of 100 mL	Products
1 high beaker of 50 mL	Sodium hydroxide
6 Erlenmeyer flasks of 100 ml with cap	Phenolphthalein
1 graduated pipette of 10 mL	KCl standard solution 0.01M
1 graduated pipette of 2 mL	Acetic acid
1 graduated pipette of 20 mL	Potassium Phthalate acid

Objectives

1. Relate the ionization constant of the acetic acid with the dissociation degree and the activity coefficients.
2. Determine the specific conductivity and the molar conductivity of the acetic acid solutions.
3. Determine the ionization degree as function of the concentration and the molar conductivity.
4. Determine the ionic strength and the average ionic activity coefficient.
5. Determine the ionization/dissociation constant for the acetic acid.

Theoretical background

1. Acid-base equilibrium of the acetic acid

The measurement of a chemical magnitude of the relevance of the dissociation constant of a weak acid has been the objective of many studies, for that reason it is easy to understand that a large of number of methods had been developed for obtaining a precise measurement of this magnitude. In this lab session a procedure based on the measurement of the conductivity of electrolyte dilute solutions will be shown.

For weak electrolytes type 1:1 the equilibrium between the ionized and non-ionized forms of the solute can be written as:



and the acidity constant as function of the activities is:

$$K_a = \frac{a_{\text{Ac}^-} a_{\text{H}^+}}{a_{\text{HAc}}} \quad (2)$$

where the activity is defined as: $a_i = \gamma_i [C]_i$ (3)

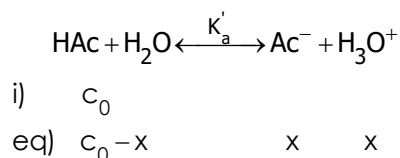
substituting (3) in (2) and reorganizing, the equilibrium constant K_a can be written as:

$$K_a = \frac{\gamma_- \gamma_+}{\gamma_{\text{HAc}}} \frac{[\text{Ac}^-][\text{H}^+]}{[\text{HAc}]} \quad (4a)$$

$$\text{or: } K_a = \gamma_{\pm}^2 K'_a \quad (4b)$$

where γ_{\pm} is the ionic average activity coefficient ($\gamma_{\pm}^2 = \gamma_+ \gamma_-$) and K'_a is the equilibrium apparent constant in function of the concentrations. (Remind that $\gamma_{\text{HAc}} = 1$ has been considered). Then, for the determination of K_a , K'_a and γ_{\pm} should be known.

On the other hand, as HAc is a weak electrolyte it will be partially dissociated according to:



if the dissociation degree, α , is defined as:

$$\alpha = \frac{x}{c_0} \quad (5)$$

the apparent equilibrium constant will be:

$$K'_a = \frac{[\text{Ac}^-][\text{H}^+]}{[\text{HAc}]} = \frac{c_0 \alpha^2}{1 - \alpha} \quad (6)$$

2. Degree of dissociation and conductivity: determination of K'_a .

The conductivity is the capacity that the ions of an electrolytic solution have for carrying or moving the electricity (electrons or charges) through itself. In addition to the electrolytic conducting there is matter transport. The conductivity depends on different factors, among them: size and charge of the electrolyte (chemical nature of the electrolyte), ions speed, ions number (concentration), solution viscosity and temperature.

The specific conductivity (the one that is measured in conductivity meter instruments) is defined:

$$\kappa = k L \quad (7)$$

where k is the cell constant and L the conductance. The units of κ in the International System (S.I.) are S.m^{-1} (although usually is expressed in S.cm^{-1}). It is an additive magnitude, then the total solution conductivity will be the addition of the one for the dissolvent plus the corresponding of solute.

The molar conductivity, Λ , is defined:

$$\Lambda = 1000 \frac{\kappa}{c_0} \quad (8)$$

where c_0 is the molar concentration and 1000 is a conversion (between L and cm^3).

The relationship between molar conductivity, concentration and dissociation degree, is given by the Kohlrausch's Equation (obtained for dilute solutions of strong electrolytes):

$$\Lambda_e = \Lambda^0 - B \sqrt{c_0 \alpha} \quad (9)$$

where Λ_e is the equivalent molar conductivity that a weak electrolyte will had if it will be fully dissociated, Λ^0 is the molar conductivity at infinite dilution (when the solute concentration goes to zero) and B is the Osanger's limit coefficient, with the value:

$$B = a + b \Lambda^0 \quad (10)$$

For diluted water solutions of 1:1 electrolyte and at 25 °C, the coefficients are: $a = 60.2 \text{ S cm}^2 \text{ mol}^{-1} \text{ M}^{-1/2}$, $b = 0.229 \text{ M}^{-1/2}$ and the value of Λ^0 for HAc is: $\Lambda^0 = \lambda_+^0 + \lambda_-^0 = 390.51 \text{ Scm}^2\text{mol}^{-1}$. Substituting these values in equations (9) and (10), the Kohlrausch's equation for HAc can be written:

$$\Lambda_e = 390.51 - 149.63\sqrt{c_0\alpha} \quad (11)$$

For calculating the dissociation degree from conductivity measurements, we will use in a first step the Arrhenius' Equation for the molar conductivity (although this equation is not fully adequate):

$$\alpha = \frac{\Lambda}{\Lambda^0} \quad (12)$$

Furthermore, it was proposed an improvement for this equation, given for:

$$\alpha = \frac{\Lambda}{\Lambda_e} \quad (13)$$

Finally, substituting the equation (11) in (13) we will obtain the expression for calculating α :

$$\alpha = \frac{\Lambda}{\Lambda^0 - 149.63\sqrt{c_0\alpha}} \quad (14)$$

this is an irrational equation requiring an iterative process for their resolution. Using the α value for each concentration and the equation (6) the equilibrium apparent constants K'_a can be obtained.

3. Debye-Hückel's limit law: determination of γ_{\pm}

In order to complete the objective, the γ_{\pm} coefficient should be calculated for each concentration through the Debye-Hückel's limit law:

$$\log \gamma_{\pm} = A z_+ z_- \sqrt{I} \quad (15)$$

Where I is the ionic strength of the medium: $I = \frac{1}{2} \sum_i m_i |z_i|^2$ and $z_+ = 1$ $z_- = -1$, the charge of H_3O^+ y Ac^- ions. The relationship between the molality and molarity is: $c_i = \rho_1 m_i$ and the water density, $\rho_1 = 1 \text{ g/mL}$.

As $c_i = c_0 \alpha$, then $I = \frac{1}{2} (c_0 \alpha + c_0 \alpha) = c_0 \alpha$ and finally the equation (15) can be expressed as:

$$\log \gamma_{\pm} = -A \sqrt{c_0 \alpha} \quad (16)$$

where "A" is the Debye-Hückel's constant, which theoretical value can be calculated from:

$$A = \frac{\sqrt{2\pi N_A \rho_1}}{2.303} \sqrt{\left(\frac{e^2}{4\pi \epsilon k_B T} \right)^3} \quad (17)$$

being N_A Avogadro's number, e electron charge, ε medium dielectric permittivity ($\varepsilon = \varepsilon_r \cdot \varepsilon_0$), k_B Boltzman's constant and T the absolute temperature.

Finally, for each concentration, α will be calculated with the (14), K'_a with equation (6), γ_{\pm} with equation (16) and the acidity constant K_a will be calculated with equation (4b).

Solutions

1. 250 mL of acetic acid approximately 0.1 M from the commercial one (in the glass cabinet).
2. 250 mL of sodium hydroxide approximately 0.1 M from the solid form.

Experimental procedure

1. Connect the conductivity meter.
2. Prepare the acetic acid and sodium hydroxide solutions.
3. Titrate the NaOH solution with potassium phthalate acid and phenolphthalein as indicator (at least three times). Calculate the necessary amount of potassium phthalate acid to spent approximately 20 mL of the NaOH solution.
4. Titrate the acetic acid solution using 20 mL of the NaOH and Phenolphthalein as indicator (at least three times).
5. Calibrate the conductivity meter using a standard solution of KCl 0.01M (following the instructions on the manual, specific conductivity $\kappa_{KCl} = 1.41 \text{ mS/cm}$ at 25 C). Write down the cell constant.
6. Titrate by conductivity 20 mL of the acetic acid dissolution 0.1 M by adding to 40 mL of NaOH.
7. From the 0.1M solution of acetic acid, prepare by dilution, 100 mL of any of the following HAc solutions: 0.001, 0.005, 0.008, 0.01, 0.02 and 0.05 M.
8. Measure the solvent conductivity, κ_{H_2O} , and write down it.
9. Transfer the different prepared AcH solutions to an Erlenmeyer flask of 100 mL with cap and do the measurement of the conductivities and write down them.

Conductivity measurements: previous to the measurement of any solution, the cell must be cleaned with deionized water and afterward with problem solution. All the conductivity measurements must be done at constant temperature of 25 C adjusting the temperature sounding line of the conductivity meter. It is suggested to do the measurements in increasing order of concentration (for that, the cell will be cleaned with deionized water and afterward with problem solution the first time and after only with problem solution).

Note: Remind that there are containers for discarding the residues at the end of each experience.

Experimental results: data presentation

1. Tabulate the data (mass and volume) needed for preparing the solutions 1 and 2 calculated as real.
2. Gather in tables the results of the titration of sodium hydroxide with Potassium Phthalate acid and the acetic acid with NaOH. For the conductometry, the conductivity as function of NaOH volume must be shown in the table.
3. Tabulate the different volume of the mother acetic acid solution to be taken for preparing the 5 solutions.
4. Show in a table, the specific conductivities measure for the solvent and the 5 acetic acid solutions.

Processing and Discussion of results

1. Calculate the NaOH real concentration with their accidental error.
2. Calculate the HAc real concentration with their accidental error.
3. Recalculate the concentrations of all the HAc solutions, with their significant figures.
4. Build up a new table gathering:
 - the real concentrations of the acid solutions
 - the specific conductivity of each solution ($\kappa_{\text{HAc}} = \kappa_i - \kappa_{\text{H}_2\text{O}}$)
 - the molar conductivity, calculated for each concentration
 - the ionization degree** (check point 5 for their calculation)
 - the K'_a
 - the γ_{\pm}
 - the $c_0\alpha$ product
5. ** For calculating the ionization degree it is necessary to do the following process: for each c_0 , obtain the testing value of α using equation (12), which will be successively used in equation (14) doing an iterative process up to reach a constant value (usually in three iterations can be obtained).

$$\alpha_0 = \frac{\Lambda}{\Lambda^0} \rightarrow \alpha_1 = \frac{\Lambda}{\Lambda^0 - B\sqrt{c_0\alpha_0}} \rightarrow \alpha_2 = \frac{\Lambda}{\Lambda^0 - B\sqrt{c_0\alpha_1}} \rightarrow \alpha_3 = \frac{\Lambda}{\Lambda^0 - B\sqrt{c_0\alpha_2}}$$

In order to make easy the iterative process build up a new table in which the concentration and different values of α obtained are gathered. Move the definitive value α to the general table of point 4. This calculation can also be done with "solver", initially using the test value.

6. Calculate the A Debye-Huckel's constant using equation (17), all the magnitudes should be expressed in S.I. units. For that, it is recommendable to search in a data base (<http://chemnetbase.com>) the values of e , k_B , ϵ_0 , ϵ_r , ρ_1 (at 25 C).

7. Determine the acidity constant K_a by using equation (4b) showing their average value with their accidental error. Search the literature value of $K_{a(\text{HAc})}$ at 25 C and compare it with the experimental one.
8. Represent in a figure the variation of κ_{solution} , of Λ_m , of α and of γ_{\pm} with the concentration and discuss the corresponding dependences.
9. Determine the concentration of acetic acid from the conductometric titration. For that, the solution specific conductivity as function of the added NaOH volume must be represented, do the linear adjustment of the points and obtain the NaOH volume of the equivalence point in the intersection point of both straight lines. Compare the result with the one obtained in the point 2.