Determine the rate constant of the saponification of Ethylacetate by NaOH conductometrically.

A) Requirements:

Ethylacetate solution (N/25), NaOH (N/25), Acetic acid (N/10), Oxalic acid, Conductometer and Conductivity cell, Burette, Pipette, Conical flask, beakers.

B) Theory:

In the presence of base, NaOH, the hydrolysis of CH_3COOEt ester takes place to produce $H_3CCOO^-Na^+$ and EtOH as follows:

$$H_3CCOOEt + NaOH \rightarrow H_3CCOO^-Na^+ + EtOH$$

The reaction follows the 2nd order kinetics. The rate of the reaction can given by:

$$\text{Rate} = -\frac{d}{dt}[Ester] = k\,[ester][OH-]$$

where k = Second order rate constant in unit of $mol^{-1}LS^{-1}$.

The integrated expression of 2nd order rate equation can be given as

$$k = \frac{1}{t}\frac{x}{a\,(a-x)} \ldots..(1)$$

where, a = initial concentration of reactant, x= concentration of product at time, t. (a-x) = concentration of the remaining reactant at time t.

In the above reaction hydroxide ion progressively consumed by acetate ion. Since the ionic mobility of OH^- (λ_0 = 198.5 $Ohm^{-1}cm^2mol^{-1}$) is much higher than CH_3COO^- ion (λ_0 = 40.9 $Ohm^{-1}cm^2mol^{-1}$); the conductance of the reaction mixture progressively decreased with the time t. The conductance measurement of the reaction mixture thus provides a means of estimation of the amounts of these ions present and hence allow us to monitor the progress of reaction with time.

If the conductance of the reaction mixture are C_o, C_t & C_∞ at the beginning (t = 0), any intermediate time (t = t) and at completion of reaction (t = ∞) respectively (where, $C_o > C_t > C_\infty$), then,

$$a \propto (C_0 - C_\infty),$$
$$x \propto (C_0 - C_t)$$
$$\text{hence, } (a-x) \propto (C_t - C_\infty).$$

Thus, the equation (1) can be rewritten as:

$$\frac{(c_0 - c_t)}{(c_t - c_\infty)} = k\,a\,t$$

Plot of (C_o - C_t)/ (C_t - C_∞) vs. t (time) gives a straight line passing through origin with positive slope of 'k x a'. Since, the initial concentration of the ester is known, k can be obtained from the slope. While, C_t is determined from the measurements of conductance at different time interval, C_∞ can be determined indirectly by measuring the conductance of a mixture of solution having same concentration of NaOH and acetic acid. For, determination of C_0 only NaOH solution of same concentration need to be measured.

C) Procedure:

1. Preparation of exact N/10 Oxalic acid standard solution.
2. Standardization of ~N/10 NaOH (given) with prepared oxalic acid solution.
3. Preparation of 100 mL N/25 NaOH (exact).
4. 50 ml (N/25) exact ethyl acetate was prepared.
5. Measure the conductance of 50 mL N/25 NaOH which is considered as C_0.
6. Prepare the reaction mixture by adding 50mL of N/25 NaOH in 50 mL of N/25 ethyl acetate.
7. Start taking conductance reading using conductivity cell connected to conductivity meter. The conductivity meter should be calibrated before start of the experiment.
8. The conductance reading of the reaction mixture in different time should be noted in **Table 2**. This reading is denoted as C_t value.
9. After about one hour (when the variation of conductance will be very small), reaction mixture is heated (~80 °C for ~30 mints), then cooled and conductance reading is taken in a same way. This reading is marked as C_α. [Note: Alternatively, the conductance of solution containing 50 ml N/25 NaOH and 50 ml N/25 AcOH can be treated as C_∞].

D) Observation and Calculation:

Laboratory temperature: 30.5 °C
Weight of Oxalic acid taken = 0.635 g
Strength of the prepared 100 mL oxalic acid solution=

(0.635/63.5)x (1000/100)= 0.1N

1. Table 1: Standardization of NaOH solution by titrating against standard oxalic acid solution.

S.No.	Volume of oxalic acid taken / ml	Volume of NaOH required / ml	Concordant value/ ml
1.	10		
2.			
3.			

Calculation
$V_1N_1 = V_2N_2$; N_2 =

2. Preparation of exact 100 ml (N/25) NaOH solution: Add mL of distilled water in of 0.101 N NaOH.

3. Preparation of exact (N/25) ethyl acetate (50 ml) solution.

4. **Table 2:** Observation table for conductance measurement:

C_0= mS
C_α = ms

a= C_0 - C_α = mS

S.No.	Time /min	Conductance / mS, (C_t)	(C_o-C_t) / mS	(C_t-C_∞) / mS	(C_o-C_t) /(C_t-C_∞)	$k = \frac{C_o - C_t}{at(C_t - C_\infty)}$
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						
11.						
12.						

[No need of reporting k_{avg} from Table 4]

Determine the slope of the straight line in Graph 1:

Slope = 0 = k a

k = slope/a= mol^{-1}Lmin^{-1}.

E) Result: The rate constant (k) for base (NaOH) catalysed hydrolysis of ethyl acetate at laboratory temperature (30.5 °C) was found to be mol^{-1}Lmin^{-1}.

Graph 1: The variation of conductance with time during the progress of reaction of ethylacetate hydrolysis in base medium:

For Example, a plot (Origin programme is used to plot).