Experiment 5

DETERMINATION OF THE RATE CONSTANT FOR THE ACID-CATALYZED HYDROLYSIS OF METHYL ACETATE

AIM

To determine the rate constant for the acid-catalyzed hydrolysis of methyl acetate.

THEORY

Methyl acetate undergoes hydrolysis, in the presence of an acid (HCl, for example), to give acetic acid and methyl alcohol.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

In the presence of an acid, this reaction should be of second order, since two molecules are reacting. But, it is found to be first order. This may be explained in the following way :

The rate of the reaction is given by

$$dx / dt = k [CH_3COOCH_3] [H_2O]$$

where k is the rate constant (or specific rate constant).

Since water is present in large excess, its active mass (molar concentration) virtually remains constant during the course of the reaction. Therefore, its active mass gets included in the constant, and the above equation reduces to :

$$dx / dt = k [CH_3COOCH_3]$$

Thus, the rate of the reaction is determined by one concentration term only (that is, by a single power of the concentration term only).

Hence, the reaction is first order. Such reactions are also referred to as pseudo first order reactions.

The progress of the reaction (hydrolysis of ester) is followed by removing a definite volume of the reaction mixture, at definite intervals of time, cooling it in ice, and titrating the acetic acid formed against alkali, which has already been standardized. The amount of alkali used is equivalent to the total amount of hydrochloric acid present originally and the amount of acetic acid formed in the reaction.

The amount of acetic acid formed (x), at definite intervals of time (t), can be obtained.

The amount of acetic acid formed, at the end of the reaction, is equivalent to the initial concentration (a) of the ester. Suppose the volumes of the sodium hydroxide solution (titre value) required for neutralization of 5 ml of the reaction mixture are:

(i) at the commencement of the reaction is Vo

(ii) after time (t) is Vt

(iii) at the end of the reaction is V∞

Then :

x (amount of acetic acid formed after time) is proportional to (Vt -Vo).

a (initial concentration of ester) is proportional to (V∞ -Vo).

[a – x] (concentration of ester present after time t) is proportional to

(V∞ -Vo) - (Vt -Vo) = (V∞ -Vt)

The first order rate expression given by :

$$\log(a-x) = -Kt / 2.303 + \log a$$

Hence, the rate constant (k) could be calculated.

MATERIALS REQUIRED

Methyl acetate, HCl, NaOH, 0.1N standard Oxalic acid, phenolphthalein, thermostat, reagent bottles, conical flask, burette, pipette (10 ml, 5 ml,), ice.

PROCEDURE

Step I: Standardization of NaOH using standard Oxalic acid(0.1N)

1.10ml of given 0.1N standard Oxalic acid is pipetted out into a 100ml conical flask.

2.This solution is titrated against the given unknown concentration of NaOH using phenolphthalein indicator until the end point is colorless to pale pink.

3.Tabulate the values and repeat the titration for concurrent readings and determine the unknown concentration of supplied NaOH solution.

OBSERVATIONS AND CALCULATIONS

$(HCOO)_2$ $N_1 V_1 = N_2 V_2$ (NaOH)

Concentration of NaOH, N_2 = _______________

Step II: Standardization of HCl using NaOH solution.

1. 2 ml of given HCl is pipetted out into a 100ml conical flask.

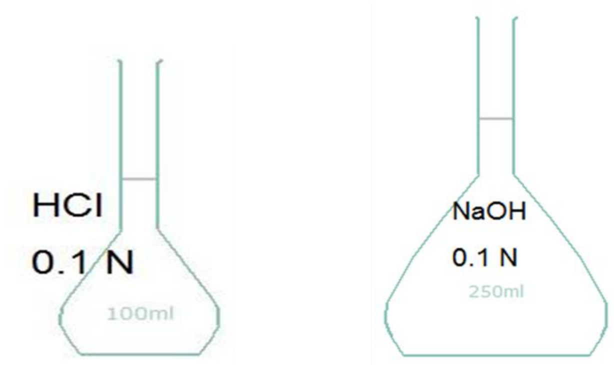
2. This solution is titrated against the NaOH using phenolphthalein indicator until the end point is colorless to pale pink.

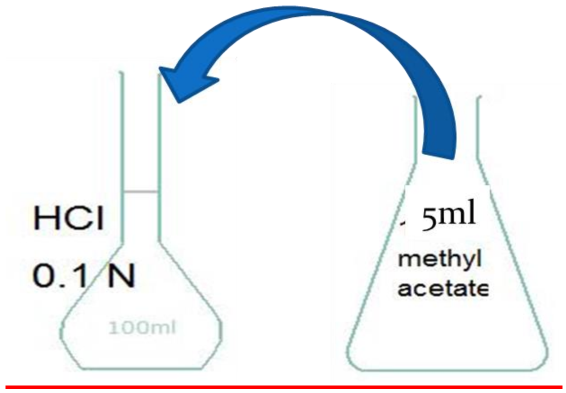
3. Tabulate the values and repeat the titration for concurrent readings and determine the unknown concentration of supplied HCl solution.

(NaOH) $N_2 V_2 = N_3 V_3$ (HCl)

Concentration of HCl, N_3 = ______________

Step III: Determination of rate constant (k1) for the acid-catalyzed hydrolysis of methyl acetate.





1. 100 ml of given HCl (whose strength is determined in step II) solution is taken in a stoppered reagent bottle.

2. 5 ml of methyl acetate solution is added to the HCl solution. Note the time when half of the methyl acetate solution is added. The mixture is shaken well.

3. Pipette out 5 ml of the reaction mixture and discharge it into 50 ml of ice cold water kept in a conical flask.

4. Titrate the reaction mixture against NaOH solution using phenolphthalein as indicator. This titre value corresponds to **Vo**.

5. Steps 3 and 4 are repeated at intervals of 5, 10, 15, 20, 30, 45, 60 minutes. Each titre value corresponds to **V_t.**

6. Take 10 ml only of the remaining solution and leave it for 24 hours and repeat step 3&4 and record **V_{NaOH} = [a]**

7. The remaining solution is taken in a stoppered conical flask and heated to 60^{o}C, and kept at this temperature for 5 minutes.

7. The solution is allowed to cool to room temperature.

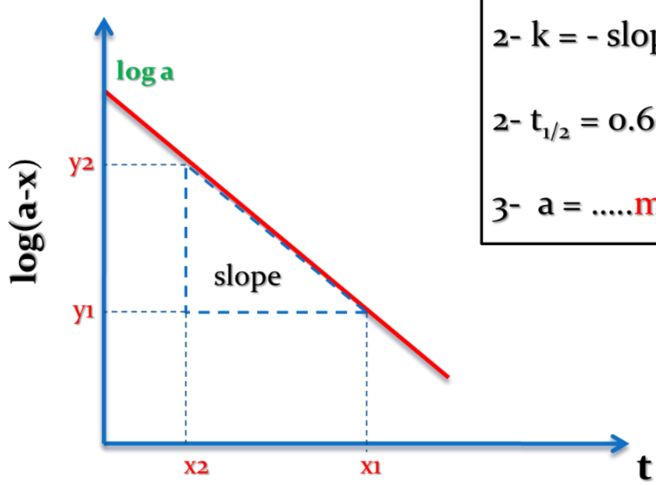
8. Repeat Steps 3 and 4. This titre value corresponds to **V**∞ till concurrent values are obtained.

9. Plot a graph of **log (V**∞ **-Vt)** versus time **(t)** and determine the slope.

10. <u>Report the theoretical and graphical value of rate constant</u> (k).

Table

S.No	Time (min)	Volume of solution taken (ml)	Volume of NaOH consumed (ml)	(V∞ -Vt) ml **=(a-x)**	Log (V∞ -Vt) ml	(V∞ -V_0) ml **= (a)**
1	**0(Vo)**					
2	**5(Vt1)**					
3	**10(Vt2)**					
4	**15(Vt3)**					
5	**20(Vt4)**					
6	**30(Vt5)**					
7	**45(Vt6)**					
8	**60(Vt7)**					
9	V∞					



1- slope =(y2-y1)/(x2-x1)

2- k = - slope × 2.303 (min^{-1})

2- $t_{1/2}$ = 0.69327/k (min)

3- a = ...mol/l

OBSERVATIONS AND CALCULATIONS

Room Temperature = …….…... °C ; V∞ = …….. ml ; Vo = …….. ml ; (V∞-Vo) = …….. ml ; log(V∞-Vo) = ...

Mean Value of Rate Constant (k1) = ______________________

RESULTS

1. Strength of NaOH Solution = ____________________

1. Strength of HCl Solution = ____________________

2. Rate Constant (k1) for the acid-catalyzed hydrolysis of methyl acetate

(CH3COOCH3)

= ______________________ (theoretical).

= ______________________ (graphical).

3. Comment on the nature of the graph.