



Kinetic study of the hydrolysis of ester with mineral acid by spectrophotometer at different temperature

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Abstract

To determine the kinetic parameters and activation energy of the hydrolysis of ethyl acetate with hydrochloric acid monitored by spectrophotometry. The first order fits were automatically drawn and the values of the first order rate constants (k) were calculated using standard equations as part of the program. Acidic hydrolysis of ethyl acetate is essentially an irreversible and first order reaction whereas alkaline hydrolysis is an irreversible and second order reaction. Rate of reaction is the change in the number of molecules of reacting species per unit volume per unit time. In this hydrolysis of ethyl acetate with hydrochloric acid to accelerate the reaction mixture. A simple and sensitive kinetic spectrophotometric method presented for the determination of rate constant, order of reaction and activation energy. This method based on a kinetic investigation of ethyl acetate and hydrochloric acid at 35°C and 45°C temperature. The reaction followed spectrophotometrically by measuring the absorbance at 500 nm as a function of time. The initial rate and fixed time methods utilized for construction of calibration graphs successfully for the determination of rate constant, order of reaction and activation energy. The rate constant after calculation from the graphs was approximately $k_1 \approx 0.00260 \text{ Sec}^{-1}$ $k_2 \approx 0.00322 \text{ Sec}^{-1}$ by titration and spectrophotometric method respectively, order of reaction found to be first order and the activation energy for this reaction is 17.44 kJ/mol. One factor that influences the absorbance of a sample is the concentration (c). As the concentration increases, more radiation is absorbed and the absorbance increase. Therefore, the absorbance is directly proportional to the concentration.

Keywords: Spectrophotometer; Activation energy; Rate constant; Ethyl acetate; First order reaction; Hydrolysis

1. Introduction

Spectrophotometers measure light intensity as a function of wavelength and are commonly used to measure the concentration of a compound in an aqueous solution. Depending on the type of spectrophotometer, different wavelengths of light can be analyzed. UV-Vis spectrophotometers (ultraviolet visible) measure in the UV and visible regions of the electromagnetic spectrum (190 to 380 nm and 380 to 760 nm, respectively). UV-Vis near-infrared spectrophotometers (UV VIS NIR) are also available and typically measure up to 2600 to 3300 nm.

Spectrophotometers come in both single beam and double beam configurations. A single beam spectrophotometer uses a reference standard to standardize or blank the instrument before taking measurements. A double beam spectrophotometer splits the beam of light into two different paths, one of which passes through the sample while the other passes through a reference standard. Double beam spectrophotometers measure the ratio of light intensities and, therefore, are not as sensitive to fluctuations in the light source or detector. However, single beam spectrophotometers are usually more compact and have a higher dynamic range shown in Figure 1. It is used in many different fields, especially to check for the quality of product, identification and quantifying microscopic samples such as kinetics, matching colors, qualifying gems and minerals, determining the color of paint or ink, and so on [1- 6]. Spectrophotometry considered the most convenient analytical technique, because of its inherent simplicity, low cost, and wide availability in most quality control laboratories [7- 10].

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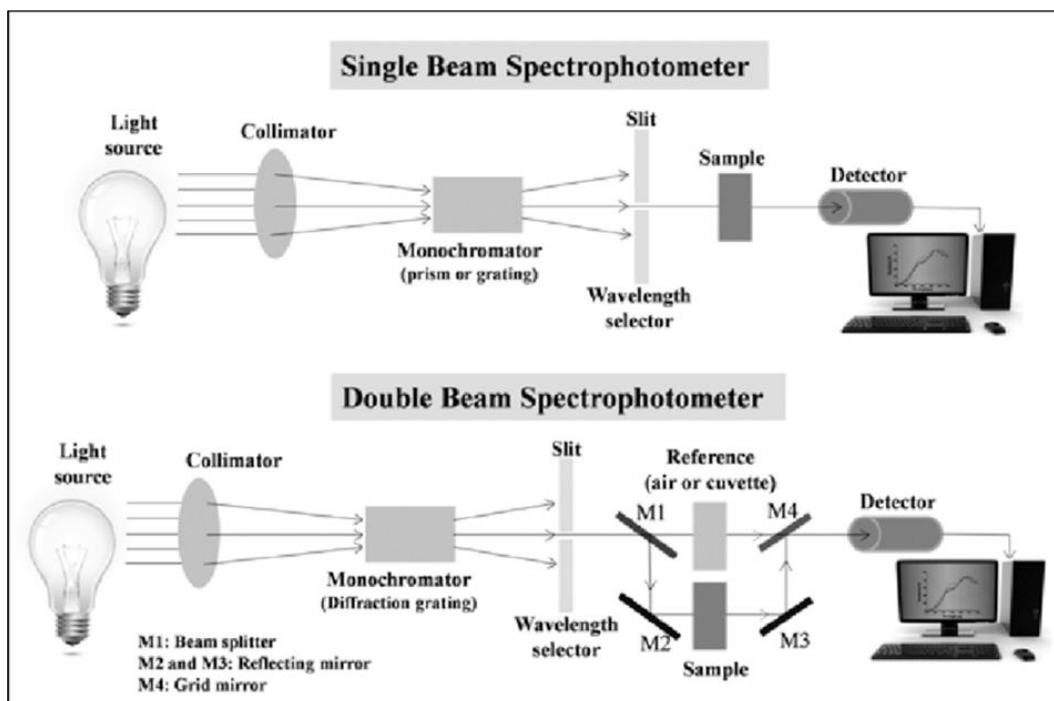


Figure 1 Representative diagram of a simple UV-Visible Spectrophotometer

In spectrophotometry, electromagnetic radiation absorbed by the sample. Electromagnetic (EM) radiation exists in many forms, one of which is the visible light used in this experiment whereas; others include ultraviolet light (UV), infrared (heat), x-rays, and radio waves.

1.1. Absorbance (A) and Transmittance (T)

The underlying principle in spectrophotometry is the absorption of light energy by a sample. When a beam of photons (light) passes through a solution, some of the photons are absorbed. The remainder of the photons transmitted through the solution to the detector. When no sample is present (nothing in front of the beam), no photons are absorbed, and all of light is transmitted (100% transmission, 0% absorption). When a sample is present, and some of the photons are absorbed, the % T is smaller and the absorption increases.

$$A = -\log T$$

$$A = \log (1/T)$$

$$A = -\log (\%T / 100)$$

$$A = \log (100 / \%T)$$

1.2. Beer-Lambert law

The Beer-Lambert law relates the absorbance (A) to the concentration (c) of a solution. The absorbance is equal to a molar absorptivity constant (ϵ) multiplied by the path length (l) and the concentration (c).

$$A = \epsilon.l.c$$

The molar absorptivity constant (ϵ) is unique for each substance at a given wavelength (or frequency). The path length (l) is the width of the interior of the sample holder (cuvette), and is equal to 1.00 cm for most analyses. Beer-Lambert Law used to determine the concentration of an unknown solution shown in Figure 2. A plot of Absorbance (A) vs concentration (c) will give a linear plot with a slope equal to the molar absorptivity constant (ϵ). If the absorbance of the unknown is knowing the concentration can be determined from the equation for the best fit line.

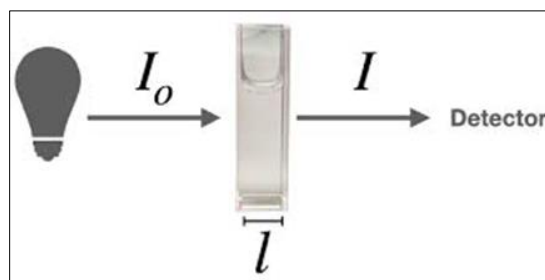


Figure 2 Beer-Lambert law

The kinetic spectrophotometric method offers an easy, less time consuming, sensitive analysis, by using simple and available reagents, which can be used for routine determinations of substances. Therefore, kinetic spectrophotometric analysis is one of the major interests of analytical laboratories. This work represents the determination of kinetic parameters and activation energy by spectrophotometer. The reaction followed up spectrophotometrically and the rate of change of absorbance at 500 nm is measured. The fixed time method is adopted after full investigation and understanding of the kinetics of the reaction. The proposed method is simple, accurate and sensitive [11, 12].

1.3. Chemical kinetics

Chemical kinetics is the quantitative determination of rate of chemical reactions and of the factors upon which the rates depend. Chemical reaction takes place when a certain number of molecules of one or more than one species has lost their identity and assumed a new form by a change in the kind or number of atoms in the compound and by a change in structure or configuration of these atoms. In this classical approach to chemical reaction, it assumed that the total mass neither created nor destroyed when a chemical reaction occurs. Chemical kinetic is the part of physical chemistry that studies rate of reaction, order of reaction and rate constant. The rate of reaction for a reactant or product in a particular reaction defined as how fast a reaction takes place, which is critical for discovering the mechanism of many reactions. For example, oxidation of iron under the atmosphere is a slow reaction that can take years, but the combustion of butane in a fire is a reaction that takes place in seconds [13-15]. In the past years, different methods used to demonstrate chemical kinetics in the lab, such as stopped-flow methods, chemical relaxation methods and spectrophotometry methods [16-18]. Among these methods, detecting chemical reaction kinetics in diluted aqueous solution using spectrophotometry most commonly used due to its simplicity and safety. This study presents the design and practice of the laboratory exercise using UV-VIS spectroscopy to monitor the concentration changes of the reactants. The hydrolysis of ester was chosen as example to study the chemical reaction kinetics.

1.4. Rate of reaction

The rate or velocity of a reaction expressed in terms of any one of the reactants or any one of the products of the reaction. The rate of reaction defined as the change in the number of molecules of reacting species per unit volume per unit time. It also defined to be proportional to the concentration of reacting species raised to a power called the order of reaction. It is usually taken as the rate at which the reactant disappears or the rate at which the product is formed. The rate at which the reactant 'a' is disappearing is proportional to its concentration at any instance,

$$\text{Rate} \propto (a - x)$$

$$\text{Rate} = k (a - x)$$

Where k = rate constant

The concept of rate of reaction is very important to determining chemical reacting systems. It is the core factor in the development of performance models to stimulate reactor functional parameters. In place of concentration of reactant or product any physical property that is directly related with concentration, such as viscosity, surface tension, refractive index, absorbance etc. can be measured for the determination of the rate of reaction [19].

1.5. Factors determining the rate of reaction

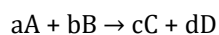
- Surface area of the reactants: greater the surface area of a solid, greater the rate of reaction.
- Concentration: increase in concentration increase the rate of reaction.
- Pressure: increase in pressure results in an increase in the rate of reaction, if the reactants and products are

gaseous.

- Catalyst: presence of a catalyst increases the rate of reaction. There are however, negative catalysts that lower the rate of reactions.
- Temperature: increase in temperature increase rate of reaction.

1.6. Rate Expression

The rate expression for a chemical reaction can be obtained from experimental data. From the experimental rate expression, a detailed mechanism for the reaction can be developed. In general, consider the rate of a general chemical reaction:



The rates of appearance of the products or the disappearance of the reactants are related to the overall reaction rate by:

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Where the brackets refer to concentrations generally in mol L⁻¹. The rate expression often has the form

$$\text{Rate} = k [A]^a [B]^b$$

where k is the rate constant and a and b are the reaction order with respect to each reactant. The concentrations of products and catalysts can also occur in the rate law. There is no relationship between the values of the reaction orders, a and b, and the stoichiometric coefficients, because the reaction may occur in more than one mechanistic step. When the reactants are present at their unit concentrations,

$$\text{Rate} = k$$

Thus, the rate constant is the rate of reaction when concentrations of the reactants are unity. The rate constant under these conditions is known as the specific rate or the rate coefficient. The rate constant for any reaction can be determined

- By measuring the rate of the reaction at unit concentrations of the reactants.
- By knowing the rate at any concentration of reactant using the relation

$$\text{Rate constant} = \text{Rate} / [A]^a [B]^b$$

The case where the reaction is slow enough, the thermal equilibrium will be maintained due to constant collisions between the molecules and k remains constant at a given temperature. However, if the reaction is very fast the tail part of the Maxwell-Boltzmann distribution will deplete so rapidly that the thermal equilibrium will not be re-established. In such cases rate constant will not truly be constant and it should be a rate coefficient [20 - 24].

Therefore, the kinetics of the reaction can be determined by taking a known quantity of ethyl acetate and mixing it with a relatively large quantity of hydrochloric acid. An aliquot of the reaction mixture withdrawn at different intervals of time and titrated against sodium hydroxide. Obviously, as the reaction proceeds, the value of alkali required to neutralize the acid progressively increases.

The fact that this is a first order reaction established by substituting the results in the first order rate expression;

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \dots\dots\dots (1)$$

As the reaction proceeds, each hydroxide ion (OH⁻) removed in the formation of ethanol removes one molecule of ethyl acetate, being the number of moles of either hydroxide ion or ethyl acetate so removed the concentration of the reactants decreases. If we start with equal concentrations of the reactants, the concentration of sodium hydroxide can be conveniently followed at different time intervals by withdrawing an aliquot from the reaction mixture and determining the sodium hydroxide measure the rate of reaction, so the greater the value of the rate constant, the faster the reaction. Each reaction has a certain value of the rate constant at a particular temperature and the value of the rate

constant for the same reaction changes with temperature and the values do not depend upon the concentration of reaction but depend upon order of reaction.

1.7. Activation Energy

Activation energy defined as the minimum amount of extra energy required by a reacting molecule to convert into a product or the minimum amount of energy needed to activate or energize molecules or atoms so that they can undergo a chemical reaction or transformation. Activation energy is denoted by E_a and measured in joules (J) and or kilojoules per mole (kJ/mol) or kilocalories per mole (kcal/mol). Activation energy is inversely proportional to the rate of reaction. As the activation energy increases, the rate of reaction decreases. Molecules can only complete the reaction once they have reached the top of the activation energy barrier. Activation energy is the energy required for a reaction to occur, and determines its rate.

1.7.1. Factors Affecting Activation Energy

Activation energy depends on two factors:

- Nature of Reactants

In the case of ionic reactant, the value of (E_a) will be low because there is an attraction between reacting species. While in the case of covalent reactant, the value of E_a will be high because energy is required to break the older bonds.

- Effect of Catalyst

Positive catalyst provides such an alternate path in which the value of E_a will be low, while the negative catalyst provides such an alternate path in which the value of E_a will be high.

Activation Energy Formula

The formula used to find the value of Activation Energy; E_a is:

$$k = Ae^{-E_a/RT}$$

Where

k = Rate Constant

A = Arrhenius Constant

E_a = Activation Energy

R = Gas constant = 8.314J/K/mol

$$k = Ae^{-E_a/RT}$$

Taking log on both sides

$$\ln k = \ln A - (E_a/RT) \ln e$$

$$2.303 \log k = 2.303 \log A - E_a/RT$$

$$\log k = \log A - E_a/2.303RT$$

2. Chemistry of Ethyl Acetate

Ethyl Acetate is the ester of ethyl alcohol and acetic acid. Its formula is $C_4H_8O_2$ and it has a molecular weight of 88.10 shown in Figure 3.

2.1. Structure and formula for Ethyl Acetate

The formula of Ethyl Acetate easily memorized because as the name suggests it contains ethyl group (CH_2-CH_3 or C_2H_5) and acetate group (CH_3COO).

- Chemical formula of Ethyl Acetate $C_4H_8O_2$
- Extended formula for Ethyl Acetate $CH_3COOCH_2CH_3$

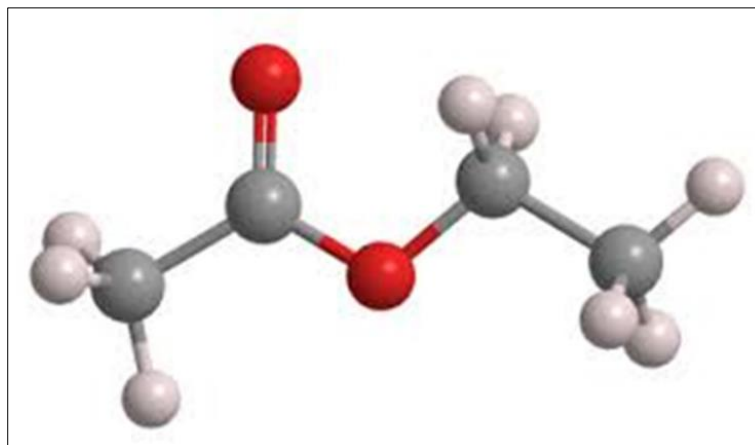


Figure 3 Structure of Ethyl Acetate

2.2. Physical and Chemical Properties

Ethyl Acetate is a clear volatile, flammable liquid with a characteristic fruity odor and a pleasant taste when diluted. It slowly decomposed by moisture and then acquires an acid reaction due to the acetic acid formed. It absorbs water up to 3.3% w/w. Ethyl Acetate is miscible with water, alcohols, acetone, chloroform, and ether.

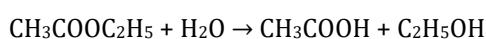
2.2.1. Physical properties of Ethyl acetate

Table 1 Physical properties of Ethyl acetate

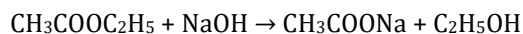
Chemical Formula	CH ₃ COOC ₂ H ₅
Condensed Formula	C ₄ H ₈ O ₂
IUPAC name	Ethyl Ethanoate
Molar Mass or Molecular weight	88.106gmol ⁻¹
Odor	Fruity smell
Density	0.902gcm ⁻³
Boiling Point	77.1°C
Volatility	Highly volatile liquid
Flammability	Highly flammable
Freezing point	-83.6°C
Physical state	1 atm
Heat of combustion	-10,110
Heat of decomposition	Not pertinent

2.2.2. Chemical properties of Ethyl acetate

Hydrolysis: Ethyl acetate gives acetic acid and ethanol on reaction with water.



Reaction with Sodium Hydroxide: When ethyl acetate reacts with sodium hydroxide then it gives sodium acetate and ethanol.



Ethyl acetate hydrolyzed in an acidic solution, following a law of speed of the first order in equal amounts of ethanol and acetic acid. Based on the calculation of the acetic acid formed, one can draw conclusions on the concentration of the ester in time. The reaction speed for this reaction calculated at different temperatures and the activation energy is calculated.

The rate of a chemical reaction measured analytically and experimentally and thereafter treated as a mathematical analysis or model. Likewise, the specific reaction rate constants calculated at two different temperatures and thereafter, the activation energy is determined.

It is highly flammable and generally found in alcoholic drinks like wines and used as an organic solvent in paints, cellulose, rubber, etc.

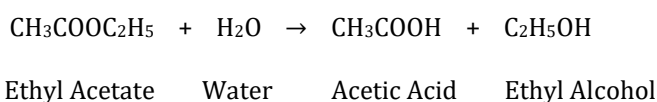
2.3. Method of Manufacture

Ethyl Acetate obtained by the slow distillation of ethanol and acetic acid in the presence of sulfuric acid. Reaction are acid-catalyzed nucleophilic additions of the respective alcohol to the acetic acid.

2.4. Hydrolysis of ethyl acetate with hydrochloric acid

Hydrolysis is a chemical decomposition involving breaking of a bond and the addition of water molecule. The use of an acid catalyst accelerates the hydrolysis. The reaction rate expressed in terms of chemical composition of the reacting species.

2.4.1. *The hydrolysis of ethyl acetate with hydrochloric acid gives acetic acid and ethyl alcohol.*



And verifying the constancy of the value of rate constant, k or in this case, $(a-x) \propto (V_\infty - V_0)$ and $a \propto (V_t - V_0)$

$$k = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_t - V_0)} \dots \dots \dots (2)$$

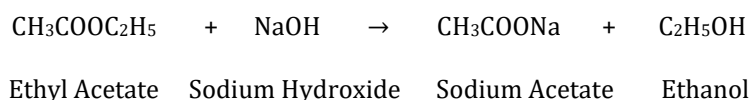
Where, V_0 = initial titre value

V_∞ = final titre value at the end of the experiment and

V_t = titre value at the various time intervals chosen

As the hydrolysis proceeds, there will be proportional increase in the concentration of acetic acid formed.

2.4.2. *The hydrolysis of ethyl acetate with sodium hydroxide that gives sodium acetate and ethanol as product from which second order rate constant can be calculated. The saponification of ethyl acetate under alkaline conditions represented by the following reaction equation [15].*



The hydrolysis of ethyl acetate with sodium hydroxide is second order being first order with respect to both ethyl acetate and sodium hydroxide. The second order reaction established by the consistency of the values of rate constant (k) determined by substituting the titration results at different time intervals in the second order rate equation as follows:

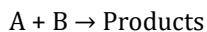
$$k = \frac{1}{t} \times \frac{(V_0 - V_t)}{V_0 \cdot V_t} \dots \dots \dots (3)$$

Where V_0 = volume of the acid equivalent to the alkali present at initial stage of experiment
 V_t = volume of the acid equivalent to the alkali present at any selected time interval

Obviously, V_t is proportional to $(a - x)$ and V_0 is proportional to 'a' in the original rate equation for the second order reaction of type I.

$$k = \frac{1}{t} \times \frac{x}{a(a-x)} \dots \dots \dots (4)$$

If we start with different concentrations of the reactants, the second order rate type II used for establishing the reaction to be of second order.



$$k = \frac{2.303}{t(a-b)} \times \log \frac{b(a-x)}{a(b-x)} \dots \dots \dots (5)$$

If 'b' moles of ethyl acetate and 'a' moles of sodium hydroxide are taken initially, then

$a' \propto V_0$ (Volume of acid equivalent to the amount of NaOH present initially)

$(a - x) \propto V_t$ (Volume of acid equivalent to the amount of NaOH present at time, t)

$(a - b) \propto V_\infty$ (Volume of acid equivalent to the amount of NaOH present at the end of the reaction)

$$x = a - (a - x) = V_0 - V_t$$

$$b = a - (a - b) = V_0 - V_\infty$$

Therefore

$$\begin{aligned} (b - x) &= a - (a - b) - [a - (a - x)] \\ &= a - (a - b) - a + (a - x) \\ &= (a - x) - (a - b) = V_t - V_\infty \end{aligned}$$

by substitution equation 5 become

$$k = \frac{2.303}{t.V_\infty} \times \log \frac{(V_0 - V_\infty)V_t}{(V_t - V_\infty)V_0} \dots \dots \dots (6)$$

$$k = \frac{2.303}{t.V_\infty} \left[\log \frac{(V_0 - V_\infty)}{(V_t - V_\infty)} - \log \frac{V_0}{V_t} \right] \dots \dots \dots (7)$$

$$\log \frac{V_0 - V_\infty}{V_t - V_\infty} = \frac{k.V_\infty.t}{2.303} + \log \frac{V_0}{V_t} \dots \dots \dots (8)$$

Since this equation is of the form: $y = mx + c$, this represents an equation for a straight line.

Therefore, a plot of $\log (V_0 - V_\infty)/(V_t - V_\infty)$ vs. time gives a straight line with a slope equal to $(k.V_\infty)/2.303$. From the value of the slope, the value of the rate constant, k can be calculated.

3. Experimental Section

3.1. Equipment and Chemicals

Double – beam Spectrophotometer model 6800, Thermostat, Thermometer, pipettes, burette, stand, volumetric flasks, titrimetric flasks, stop-clock, ethyl acetate, sodium hydroxide, hydrochloric acid, and phenolphthalein

3.2. Experimental Procedure

10 ml of 0.1 N hydrochloric acid measured accurately with a pipette into each of six numbered 250 ml conical flasks. 500 ml of 0.1 N sodium hydroxide solution placed in a thermostatic water bath set at 35°C and 45°C temperature. At time zero, 5ml of ethyl acetate measured with a syringe into the reaction vessel and the mixture thoroughly shaken for ten to fifteen seconds. 10 ml of the sample was withdrawn and discharged as rapidly as possible into the respective 250 ml conical flask containing the 10 ml 0.1 N hydrochloric acid already and titrated against 0.1 N of sodium hydroxide solution using two or three drops phenolphthalein as an indicator [25]. The experiment repeated with ethyl acetate at different temperature. All reagents used in this experiment are of analytical grade. In this experiment, we will find the order of a reaction with respect to the reactants and calculate the value of the rate constant and activation energy.

4. Results and discussions

All the absorbance spectral measurements were using UV/Vis spectrophotometer with a wavelength 500 nm with 1cm matched quartz cells. A thermostat used to control the heating temperature for color development. The mixture in each flask mixed well and record the absorbance at 500 nm as a function of time. The initial rate of the reaction at different concentrations obtained from the slope of the tangent to absorbance time curves. The initial rate, rate constant, fixed absorbance, and fixed time methods were tested and the most suitable analytical methods chosen regarding the applicability, sensitivity, and the values of the intercept and correlation coefficient. The initial rate and fixed time methods utilized for construction of calibration graphs successfully for the determination of rate constant, order of reaction and activation energy. The rate constant after calculation from the graphs was approximately $k_1 \approx 0.00260 \text{ Sec}^{-1}$ $k_2 \approx 0.00322 \text{ Sec}^{-1}$ by titration and spectrophotometric method respectively, order of reaction found to be first order and the activation energy for this reaction is 17.44 kJ/mol. There is a direct relationship between absorbance and concentration. As we increase the concentration of solution, absorbance will increase shown in the plot. For a first order reaction, as shown in the following plot, the plot of the logarithm of [A] versus time is a straight line with $k = -$ slope of the line. Other graphs are curved for a first order reaction.

Table 2 Volume of 5 ml of ethyl acetate at 35°C temperature

Time (min)	Volume of NaOH (ml)	$V_0 - V_\infty$	$V_t - V_\infty$	$\frac{(V_0 - V_\infty)}{(V_t - V_\infty)}$	$\text{Log} \frac{(V_0 - V_\infty)}{(V_t - V_\infty)}$
0	6.20	-19.0	-19.0	1.00	0.00
10	17.0	-19.0	-8.20	2.32	0.37
20	21.0	-19.0	-4.17	4.56	0.66
30	23.0	-19.0	-2.20	8.64	0.94
40	24.1	-19.0	-1.10	17.3	1.24
90	25.2	-19.0	0.0	-	-

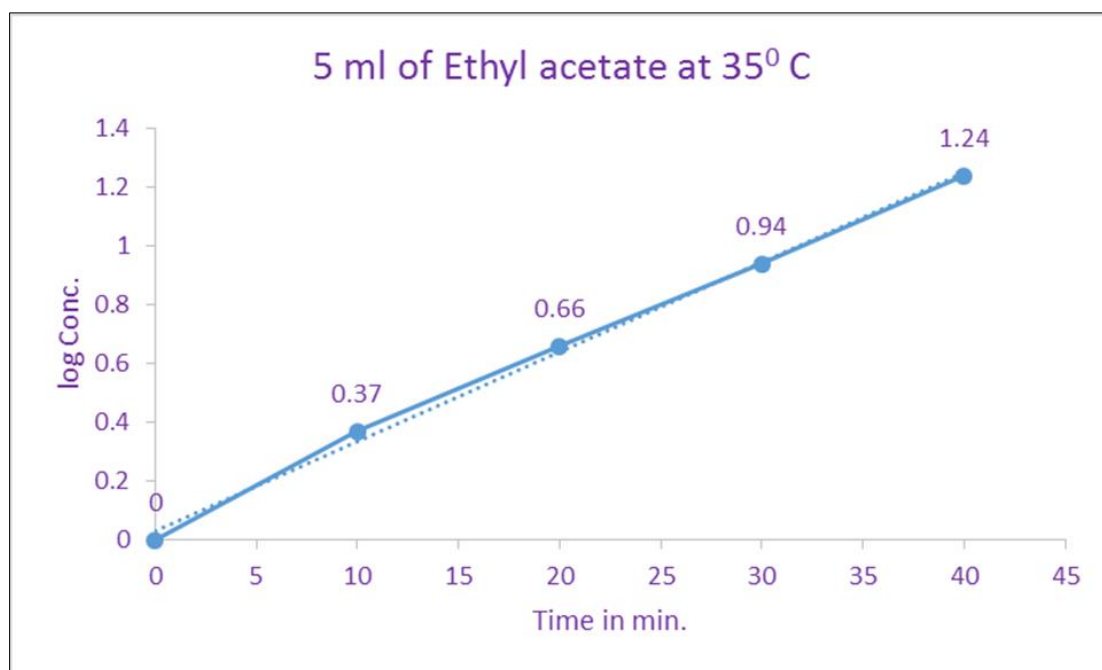


Figure 4 Plot (log conc. vs. time) for volume of 5 ml of ethyl acetate at 35°C temperature

For the 5 ml of ethyl acetate at 35°C temperature:

From equation 7,

$\log \frac{V_0 - V_\infty}{V_t - V_\infty} = \frac{k \cdot V_\infty \cdot t}{2.303} + \log \frac{V_0}{V_t}$ using table 2, a plot of $\log \frac{(V_0 - V_\infty)}{(V_t - V_\infty)}$ against time in figure 4, gives a slope that is equal to $\frac{k \cdot V_\infty}{2.303}$ from which k evaluated.

$$\text{Slope} = \frac{k \cdot V_\infty}{2.303} = 0.0285 \text{ Sec}^{-1}$$

$$\text{Therefore, } 0.0285 = \frac{k \times 25.2}{2.303}$$

$$k = \frac{0.0285 \times 2.303}{25.2} = 0.00260458 \text{ Sec}^{-1}, k \approx 0.00260 \text{ Sec}^{-1}$$

Table 3 Volume of 5 ml of ethyl acetate at 45°C temperature

Time (min)	Volume of NaOH (ml)	$V_0 - V_\infty$	$V_t - V_\infty$	$\frac{(V_0 - V_\infty)}{(V_t - V_\infty)}$	$\text{Log} \frac{(V_0 - V_\infty)}{(V_t - V_\infty)}$
0	7.00	-21.6	-21.6	1.00	0.00
10	19.1	-21.6	-9.50	2.27	0.36
20	24.2	-21.6	-4.40	4.91	0.69
30	27.1	-21.6	-1.50	14.4	1.16
40	28.0	-21.6	-0.60	36.0	1.56
90	28.6	-21.6	0.0	-	-

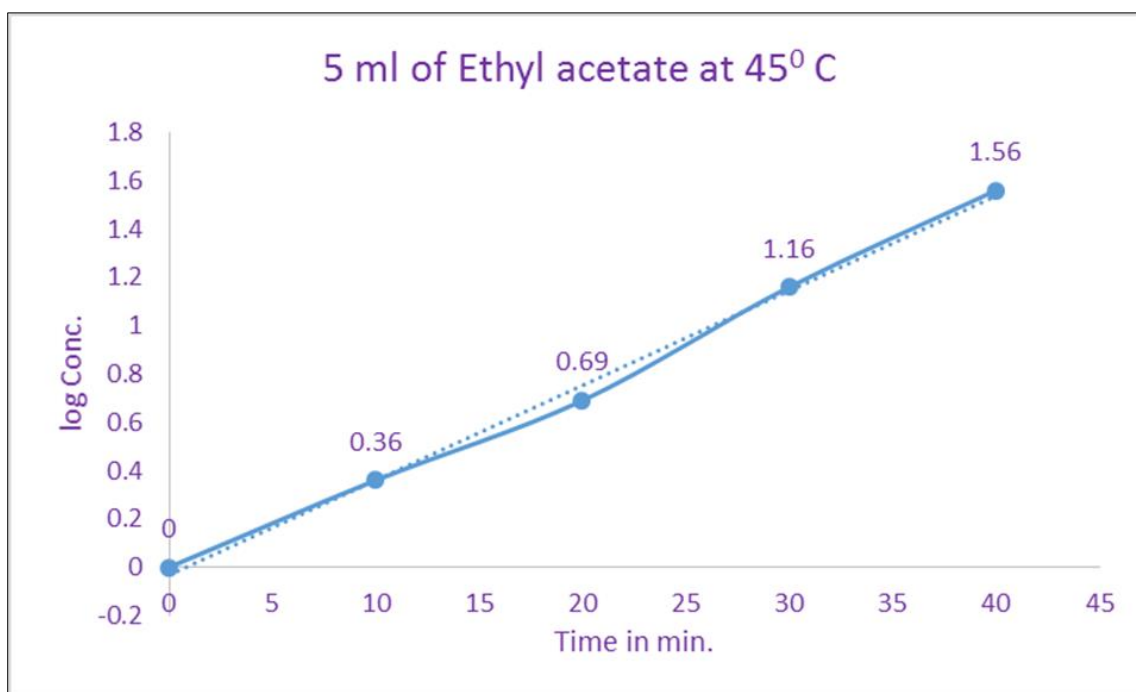


Figure 5 Plot (log conc. vs. time) for volume of 5 ml of ethyl acetate at 45°C temperature

For the 5 ml of ethyl acetate at 45°C temperature:

From equation 7,

$\log \frac{V_0 - V_\infty}{V_t - V_\infty} = \frac{k \cdot V_\infty \cdot t}{2.303} + \log \frac{V_0}{V_t}$ using table 3, a plot of $\log \frac{(V_0 - V_\infty)}{(V_t - V_\infty)}$ against time in figure 5, gives a slope that is equal to $\frac{k \cdot V_\infty}{2.303}$ from which k evaluated.

$$\text{Slope} = \frac{k \cdot V_\infty}{2.303} = 0.04 \text{ Sec}^{-1}$$

$$\text{Therefore, } 0.04 = \frac{k \times 28.6}{2.303}$$

$$k = \frac{0.04 \times 2.303}{28.6} = 0.00322097 \text{ Sec}^{-1}, \quad k \approx 0.00322 \text{ Sec}^{-1}$$

Calculation of Activation Energy

The activation energy can be determined using the equation:

$$\ln (k_2/k_1) = E_a / R \times (1/T_1 - 1/T_2)$$

where

E_a = the activation energy of the reaction in J/mol

R = the ideal gas constant = 8.3145 J/K·mol

T_1 and T_2 = absolute temperatures (in Kelvin)

k_1 and k_2 = the reaction rate constants at T_1 and T_2

Step 1: Convert temperatures from degrees Celsius to Kelvin

$$T = \text{degrees Celsius} + 273.15$$

$$T_1 = 35 + 273.15$$

$$T_1 = 308.15 \text{ Kelvin}$$

$$T_2 = 45 + 273.15$$

$$T_2 = 318.15 \text{ Kelvin}$$

Step 2: Find E_a

$$\ln (k_2/k_1) = E_a / R \times (1/T_1 - 1/T_2)$$

$$\ln (0.00322/0.00260) = E_a / 8.3145 \text{ J/K}\cdot\text{mol} \times (1/308.15 \text{ K} - 1/318.15 \text{ K})$$

$$\ln (1.2385) = E_a / 8.3145 \text{ J/K}\cdot\text{mol} \times 0.000102 \text{ K}^{-1}$$

$$0.2139 = E_a / 8.3145 \text{ J/K}\cdot\text{mol} \times 0.000102 \text{ K}^{-1}$$

$$E_a = 17435.99 \text{ J/mol}$$

or in kJ/mol, (divide by 1000)

$$E_a = 17.44 \text{ kJ/mol}$$

The activation energy for this reaction is 17.44 kJ/mol.

There is a direct relationship between absorbance and concentration. All the absorbance spectral measurements were using UV/Vis spectrophotometer with a wavelength 500 nm with 1cm matched quartz cells at different concentration. As the concentration increases absorbance increases and transmittance decreases.

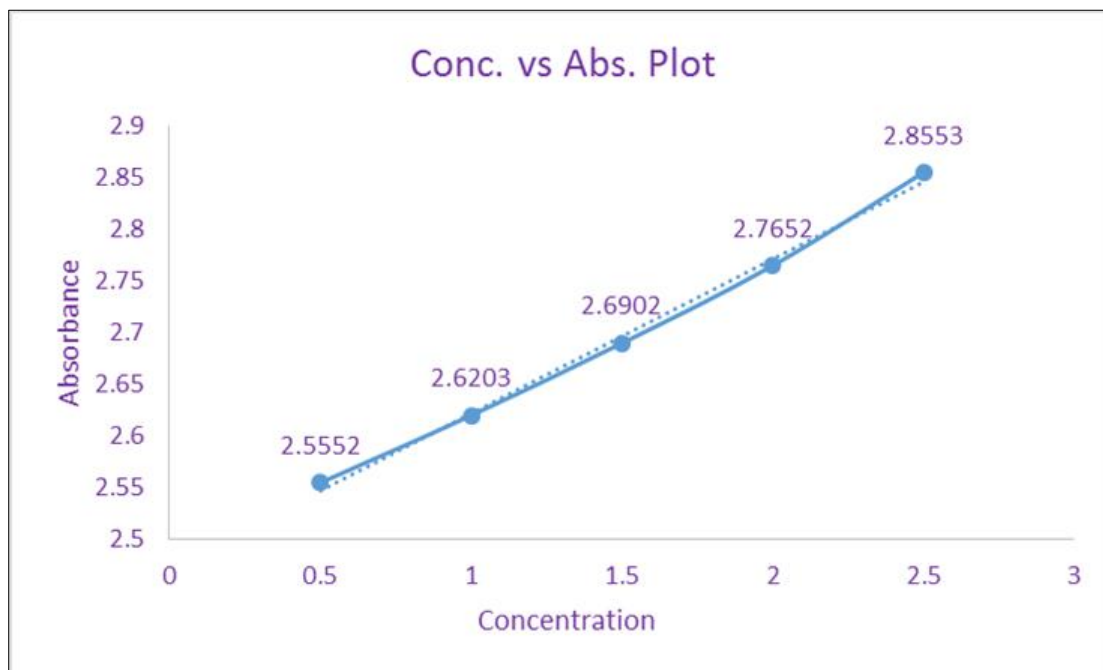


Figure 6 Plot for concentration vs. absorbance of ethyl acetate

The plot of $\ln[A]$ vs. time is linear because first-order processes see the concentration of $[A]$ undergo exponential decay; therefore, a graph of $\ln[A]$ for a first-order process would theoretically be linear with a slope = $-k$.

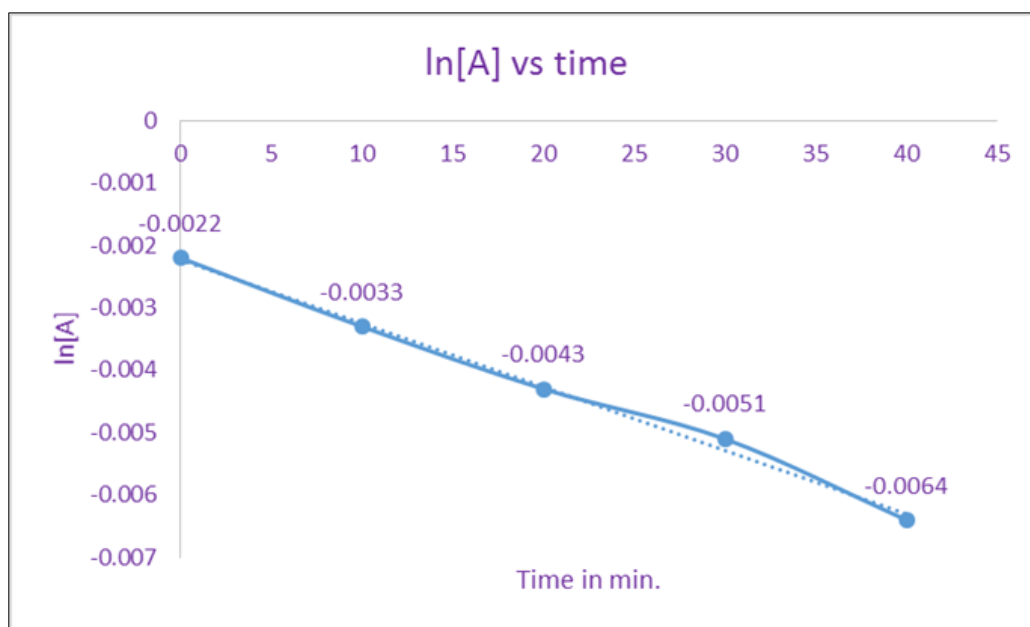


Figure 7 Plot for $\ln [A]$ vs. time of ethyl acetate

5. Practical Applications

- Chemical kinetics is the measurement of how quickly reactions occur.
- The speed of a chemical reaction is important in determining the efficiency of many industrial chemical reactions.
- If changes in conditions affect the speed of reaction, we can learn something about how the reaction happens.
- In organic reactions particularly, where there is the possibility of several reactions going on simultaneously, reaction that is fastest is the one that predominates.
- The rate of hydrolysis of ethyl acetate is useful in calculating the activity of hydrogen ions in solutions.
- Kinetic studies are important in understanding reactions, and they have practical implications, too. For example, in industry, reactions conducted in reactors in which compounds mixed together, possibly heated and stirred for a while, and then moved to the next phase of the process. It is important to know how long to hold the reaction at one stage before moving on, to make sure that reaction has finished before starting the next one.
- By understanding how a reaction takes place, many processes can improve. For example, if we know that a particular intermediate is involved in a reaction, we might avoid the use of conditions (such as certain solvents) that are incompatible with that intermediate. We might also be able to think of reagents to add that would make certain steps in the reaction happen more easily.
- Not only are kinetic studies important in industry, but they are also used to understand biological processes, especially enzyme-catalyzed reactions. They also play a role in environmental and atmospheric chemistry, as part of an effort to understand a variety of issues ranging from the fate of prescription pharmaceuticals in wastewater to the cascade of reactions involved in the ozone cycle.

6. Conclusion

The developed kinetic spectrophotometric method for the determination of rate constant, order of reaction and activation energy of hydrolysis of ethyl acetate with hydrochloric acid formulations was sensitive, accurate, and precise at temperature 35°C and 45°C. The reaction followed spectrophotometrically by measuring the absorbance at 500 nm as a function of time. The initial rate and fixed time methods utilized for construction of calibration graphs successfully for the determination of rate constant, order of reaction and activation energy. The rate constant after calculation from the graphs was approximately $k_1 \approx 0.00260 \text{ Sec}^{-1}$ $k_2 \approx 0.00322 \text{ Sec}^{-1}$ by titration and spectrophotometric method respectively, the order of reaction found to be first order and the activation energy for this reaction is 17.44 kJ/mol. The developed method has more speed and higher sensitivity as compared to reported spectrophotometric methods and has a wider range of linearity. Moreover, all the analytical reagents are inexpensive, have good shelf life, and are available in any analytical laboratory along with the lower reagent's consumption leading to an environmentally friendly spectrophotometric procedure, which makes it especially suitable for routine quality control analysis work.

The results obtained compared statistically with those obtained by the titration method and spectrophotometric method showed no significant differences regarding accuracy and precision.

Compliance with ethical standards

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Author's contribution

The manuscript was written through the contributions of both authors.

Disclosure of conflict of interest

There is no conflict of interest to declare.

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Data availability statement

All data generated or analyzed during this study are included in this article.

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