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(RESEARCH ARTICLE)

Estimation of kinetic parameters and activation energy of ester by spectrophotometric method

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Abstract

To estimate the kinetic parameters, activation energy and half life time of the hydrolysis of ester with hydrochloric acid monitored by spectrophotometric method. 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. Rate of reaction is the change in the number of molecules of reacting species per unit volume per unit time. A simple sensitive kinetic spectrophotometric method presented for the determination of rate constant, order of reaction, activation energy and half life time. This method based on a kinetic investigation of methyl 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, activation energy and half life time. The rate constant after calculation from the graphs was approximately $k_1 \approx 0.242$ min^{-1} $k_2 \approx 0.253$min^{-1} by titration and spectrophotometric method respectively, order of reaction found to be first order, activation energy for this reaction is 3.86995×10^{-8} kJ/mol and half life time $t_1 \approx 2.864$ min $t_2 \approx 2.736$ min. One factor that influences the absorbance of a sample is the concentration. As the concentration increases, more radiation is absorbed by the sample and the absorbance increase. Therefore, the absorbance is directly proportional to the concentration.

Keywords: Spectrophotometer; Methyl acetate; Activation energy; Half life time; Order of reaction; Rate constant

1. Introduction

Kinetic parameters relating with the rates of chemical reactions, order of reaction, molecularity, rate constant, activation energy and the factors upon which the rates depend. It is contrast by thermodynamics, that give the direction in which a process occurs but nothing deals about its rate. When chemical reaction takes place a definite number of atoms/molecules of one or more than one reactant has lost their specification and a new specification form by a change in the number of atoms/molecules in the compound and by a change in structure, specification and configuration of these atoms/molecules in the products. By the formation of new product, it is to be assumed that by the law of conservation of mass the total mass neither created nor destroyed when a chemical reaction occurs. The rate of chemical reaction for a reactant or product in a specific reaction defined as how fast or slow a reaction takes place, which is critical view for the mechanism of many reactions. For example, the combustion of butane in a fire is a reaction that takes place in seconds, but oxidation of iron around environmental condition is a slow reaction that can take years [1]. In the past decade, different methodologies used to determine chemical kinetics parameters in the laboratory, such as chemical kinetic methods, stopped-flow methods, radiochemical methods, chemical relaxation methods and spectrophotometry methods [2-5]. Chemical kinetic methods use the rate of a chemical reaction and either its integrated or differential rate law. Rate of reaction are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time can be written as M/sec, M/min and M/hour. In term of rate of reaction, chemical reaction can be fast, moderate and slow reaction. The importance of kinetics is that it provides the mechanisms of chemical processes, knowledge of reaction mechanisms is of practical use in deciding what is the most effective way of causing a reaction to occur. Among these methodologies,

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analysis of chemical kinetics parameters in diluted aqueous solution using spectrophotometry method is most commonly used due to its simplicity, safety, easy and less time-consuming process. This study based on the reaction between methyl acetate and hydrochloric acid by titration method using UV-VIS spectroscopy to monitor the concentration changes of the reactants. The hydrolysis of ester in presence of acid catalyst was chosen as an experiment to study the chemical kinetics reaction. This method is easy, safe, low cost and no special facilities and protective equipment is needed to complete the reaction kinetics [5].

1.1. Rates of chemical reactions

Chemical reactions need different amount of time for completion, depending upon the characteristics of the reactants, products and the conditions under which the reaction is going on. The rate of a reaction deals with any one of the reactants or any one of the products of the reaction. Rate of reaction expressed as the change in the number of atoms/molecules of reacting species present in reactant per unit volume per unit time. It also to be proportional to the concentration of reacting atoms/molecules raised to a power called the order of reaction. It is also expressed as the rate at which the reactant disappears (decrease in concentration) or the rate at which the product is formed (increase in concentration). Rate of reaction or reaction rate is the speed at which reactants are converted into products by a chemical reaction. Some chemical reactions are nearly instantaneous, while others usually take some time to reach the final equilibrium [6 - 10]. The rate at which the reactant 'a' is disappearing is proportional to its concentration at any instance,

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

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

where k = rate constant

Rate of reaction is very important to determining chemical reacting systems that is the core factor in the development of performance models to stimulate reaction 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 calculation of the rate of reaction [11].

1.2. Rate expression of chemical reactions

Rate expression for chemical reaction can obtained from experimental data observation and mechanism for the reaction can be developed by the experiment. The rate law for a chemical reaction is an expression that gives a relationship between the rate of the reaction and the concentrations of the reactants participating in it. if reaction is not a simple stoichiometry but involves different number of moles of reactants or products, the rate should be divided by corresponding stoichiometric coefficient in the balanced chemical equation for normalizing it and making it comparable [12]. The rate expression can be given in 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 reactant A and reactant B. The concentrations of products and catalysts can also present in the rate law. There is no relationship between the order of reaction and the stoichiometric coefficients, because the reaction may proceed in different mechanistic pathway. When the reactants are present at their unit concentrations or unity, the rate should be equal to rate constant. Rate constant under these conditions is known as the specific rate or rate coefficient. The rate constant for any reaction can be determined by measuring the rate of the reaction at unit concentrations of the reactants and knowing the rate at any concentration of reactant using the relation

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

If the reaction is slow, the thermal equilibrium is maintained due to constant collisions between the molecules and rate constant 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 [13, 14].

1.3. Factors determining the rate of reaction

- Reactant surface area: if surface area of reactant is greater, rate of reaction is more.

- Concentration of reactant: if concentration of reactant is more, rate of reaction is more.
- Pressure: if the reactants and products are gaseous, pressure is more results in an increase in the rate of reaction,
- Catalyst: if catalyst is present, increases the rate of reaction. whereas, negative catalysts that lower the rate of reactions.
- Temperature: increase in temperature increase the rate of reaction.

1.4. Activation energy of chemical reactions

Activation energy is the minimum amount of energy required by a reacting species to convert into a product undergo a chemical reaction. It is denoted by E_a and measured in joules (J) and or kilojoules per mole (kJ/mol) or kilocalories per mole (kcal/mol). It is a key factor in determining kinetic parameters and transport properties of chemical reactions. It is inversely proportional to the rate of chemical reaction. As the activation energy increases, the rate of reaction decreases. Reactants can only complete the reaction once they have reached the top of the activation energy barrier. The energy required for a reaction to occur, and determines its rate. The reaction that released and absorbed energy in term of activation energy [15-17] is exothermic and endothermic reaction.

1.5. Factors Affecting Activation Energy

Activation energy depends on two factors:

1.5.1. Nature of Reactants

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

1.5.2. Effect of Catalyst

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

1.5.3. Calculation of Activation Energy

The activation energy can be calculated 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

1.6. Chemistry of Methyl Acetate

Methyl acetate is a carboxylate ester with a molecular formula of $C_3H_6O_2$ shown in Figure 1. A clear, colorless flammable liquid has a typical ester odor similar to glues and nail polish removers. It is an acetate ester, which results from the condensation of acetic acid and methanol. It is commonly found in apple and various other fruits such as bananas, grapes, etc. As it is an ester it can be synthesized in an esterification reaction by reacting acetic acid with methanol in the presence of sulfuric acid.

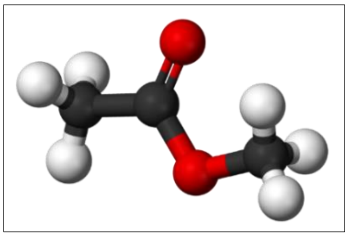

Figure 1 Structure of Methyl Acetate

- Hydrolysis of Methyl acetate: Methyl acetate gives methanol and acetic acid on reaction with water.

$$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$$

- Reaction with Sodium Hydroxide: Methyl acetate reacts with sodium hydroxide then it gives sodium acetate and methanol.

$$CH_3COOCH_3 + NaOH \rightarrow CH_3COONa + CH_3OH$$

Hydrolysis of methyl 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 reaction mixture. The reaction rate expressed in terms of chemical composition of the reacting species in a reaction mixture.

The hydrolysis of methyl acetate with hydrochloric acid gives acetic acid and methyl alcohol.

$$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$$

Methyl Acetate Water Acetic Acid Methyl Alcohol

That verifying the constancy of the value of rate constant, k or in this case, $(a - x) \propto (V\infty - V0)$ and $a \propto (Vt - V0)$

$$k = \frac{2.303}{t} \log \frac{(V\infty - V0)}{(Vt - V0)}$$

Where, Vo = initial titre value, $V\infty$ = final titre value at the end of the experiment and Vt = titre value at the various time intervals chosen. As the reaction proceeds, there will be proportional increase in the concentration of acetic acid formed. Since this equation is of the form: y = mx + c, this represents an equation for a straight line.

2. Experimental Procedure

10 ml of 0.1 N hydrochloric acid measured accurately with a pipette and put 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 methyl 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. The experiment repeated with methyl acetate at different temperature and measure absorbance by spectrophotometer. All reagents used in this experiment are of analytical grade.

3. Results and discussion

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 volume of sodium hydroxide increased with the time at different temperature when it is added in the mixture of methyl acetate and hydrochloric acid, the reaction produces water and a salt of methyl acetate hydrochloride. This reaction is an example of neutralization, in which an acid and a base react to form a neutral solution. As the reaction proceeds, the concentration of the hydrochloric acid decreases and the concentration of the sodium hydroxide increases. Therefore, the volume of sodium hydroxide added will increase with time as it is needed to neutralize the remaining acid in the mixture shown in the Figure 2.

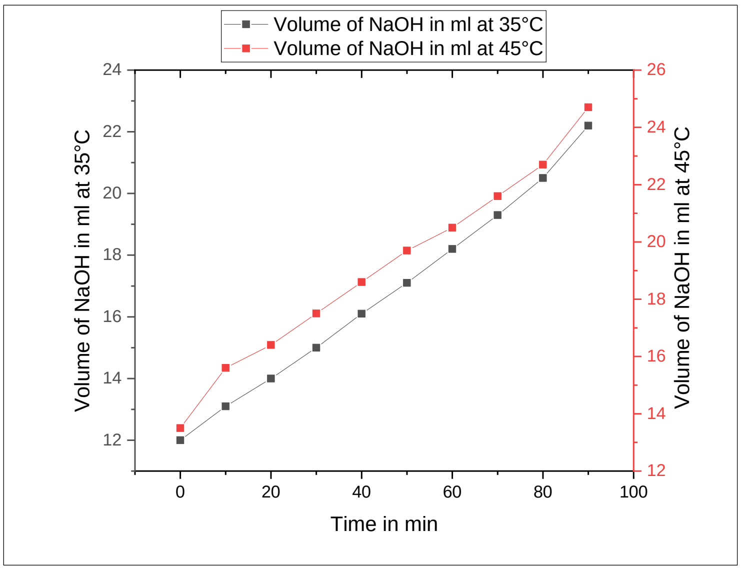

Figure 2 Volume of NaOH consumed with regular time interval at different temperature

In our experiment, the consumed time and volume of sodium hydroxide used are directly proportional to each other at both temperatures. As the reaction is proceed in the water bath at 35°C and 45°C, the acetic acid produced in the reaction increases and more amount of sodium hydroxide is used to reach the equivalence point to neutralizing the acetic acid. As the increase in temperature from 35°C to 45°C the rate of reaction increased, which complete the hydrolysis of methyl acetate and sodium hydroxide used to neutralize the acetic acid. In our experiment, the consequences obtained from the figure shows that the reaction of methyl acetate acid hydrolysis is a first order reaction with respect to the concentration of methyl acetate. The graph decreases as time increases has a negative gradient, which compared with the integrated rate law, log $(V_\infty - V_t)$ shows the rate constant for the reaction of acid hydrolysis of methyl acetate which is $k_1 \approx 0.242\ \text{min}^{-1}$ $k_2 \approx 0.253\ \text{min}^{-1}$ at different temperatures shown in Figure 3.

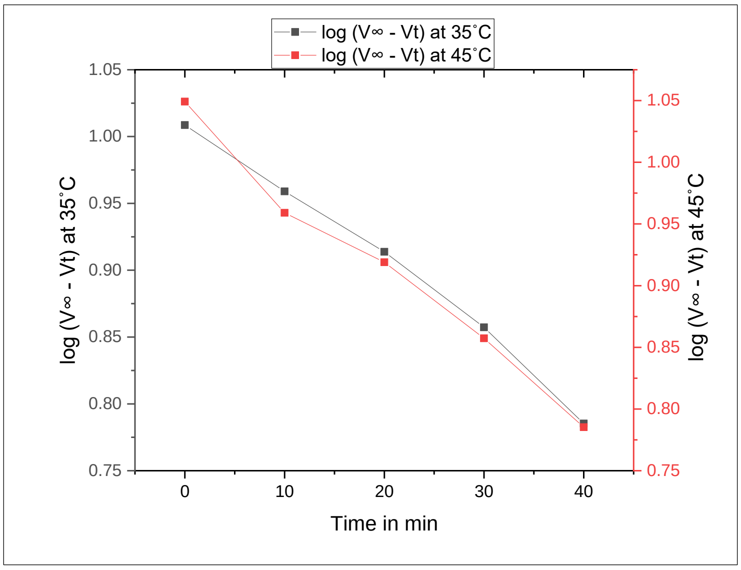

Figure 3 Plot of log $(V_\infty - V_t)$ with regular time interval at different temperature

When hydrochloric acid is used as catalyst at different temperature the rate constant of hydrolysis of methyl acetate is accurate, other than concentration of methyl acetate must be held constant shown in Figure 4. Temperature is one of the variables that influences the rate of a reaction to accurately determine the rate constant from experiment, the reaction is stopped using ice. The precaution taking in this experiment are using distilled water to clean pipette and burette, then rinsed them again with the solution that will avoid contamination. To maintain the accuracy of reading and preventing parallax error, confirm that the eye level is the same as the level of meniscus and titrate slowly to prevent overshooting.

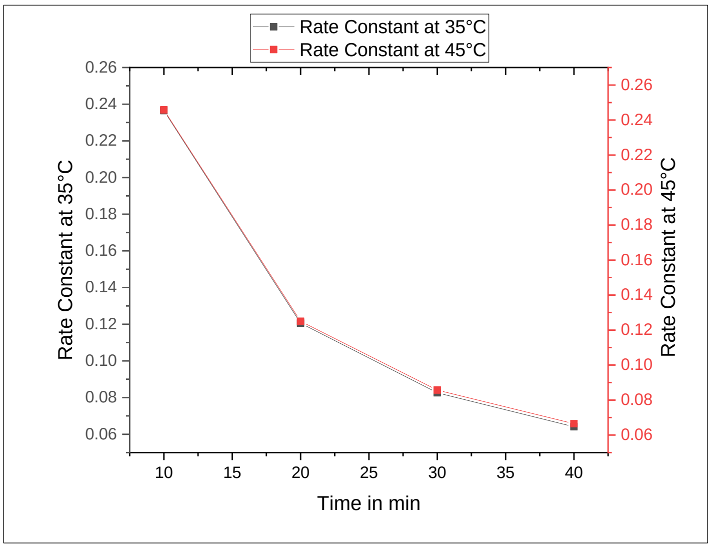

Figure 4 Plot of rate constant with regular time interval at different temperature

The mixture in each flask mixed well and record the absorbance at 500 nm as a function of time by spectrophotometer. The initial rate of the reaction at different concentrations obtained from the slope of the tangent to absorbance time curves. There is a direct relationship between absorbance and concentration. As the concentration increases absorbance increases and transmittance decreases shown in Figure 5.

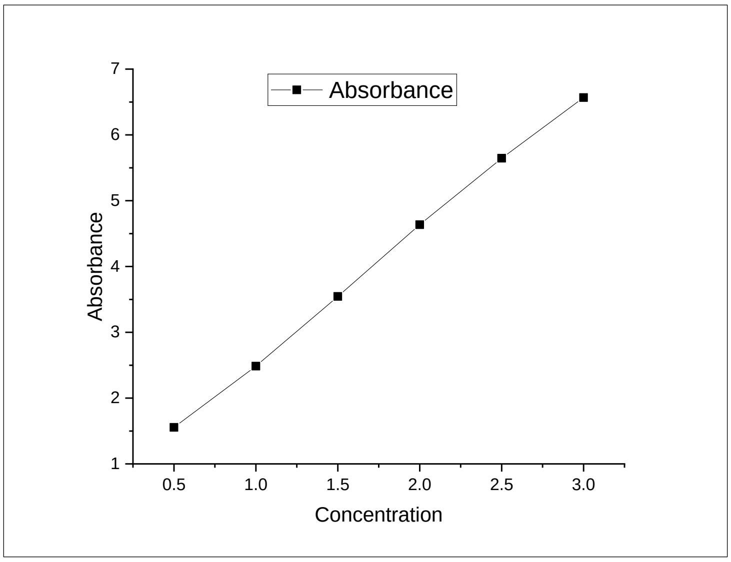

Figure 5 Plot of concentration vs absorbance at 500 nm wavelength

There is a direct relationship between absorbance and concentration. As the concentration increases, absorbance will increase for a first order reaction, as shown in Figure 6, 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. 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.

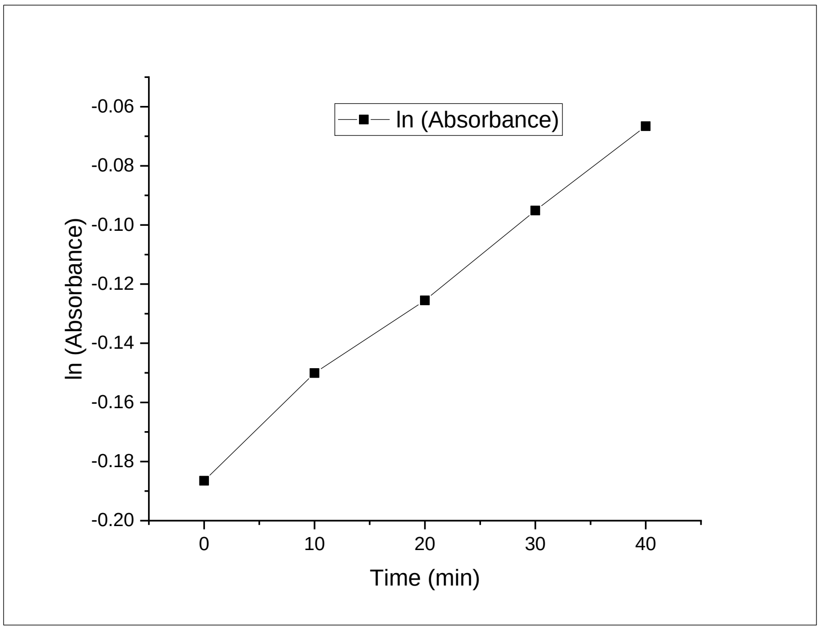

Figure 6 Plot of ln (Absorbance) vs time at 500 nm wavelength

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, activation energy and half life time. The rate constant after calculation found to be approximately $k_1 \approx 0.242$ min^{-1} $k_2 \approx 0.253$ min^{-1} by titration and spectrophotometric method respectively, order of reaction found to be first order, the activation energy for this reaction is 3.86995×10^{-8} kJ/mol and half life time $t_1 \approx 2.864$ min $t_2 \approx 2.736$ min.

3.1. 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 methyl acetate is useful in calculating the activity of hydrogen ions in solutions.

4. Conclusion

The developed kinetic spectrophotometric method for the determination of rate constant, order of reaction, activation energy and half life time of hydrolysis of methyl 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, activation energy and half life time. The rate constant after calculation from the graphs was approximately $k_1 \approx 0.242$ min^{-1} $k_2 \approx 0.253$ min^{-1} by titration and spectrophotometric method respectively, the order of reaction found to be first order, activation energy for this reaction is 3.86995×10^{-8} kJ/mol and half life time $t_1 \approx 2.864$ min $t_2 \approx 2.736$ min. 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 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.

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Disclosure of conflict of interest

The authors declare no conflict of interest.

Data availability statement

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

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