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Kinetic and Thermodynamic Investigation of Ester Hydrolysis in Mixed Aqueous–Organic Solvent Systems

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Abstract—

The influence of solvent environment on reaction rate and mechanism is an important aspect of chemical kinetics. The present study focuses on the kinetic and thermodynamic investigation of ester hydrolysis in mixed aqueous–organic solvent systems. Ester hydrolysis reactions are widely used as model processes for understanding solvent–solute interactions, ion–dipole effects, and transition state stabilization in solution chemistry. In this work, the hydrolysis of selected ester compounds is examined in binary solvent mixtures consisting of water and different organic solvents with varying polarity and dielectric properties.

Kinetic measurements are carried out under controlled temperature conditions using standard analytical techniques to determine reaction rate constants at different solvent compositions. The variation in reaction rate with changes in solvent polarity and composition is analyzed to understand the role of solvent structure and solvation effects on the reaction mechanism. Thermodynamic activation parameters such as activation energy, enthalpy of activation, entropy of activation, and Gibbs free energy of activation are evaluated using temperature-dependent kinetic data.

The results provide insights into the influence of mixed solvent environments on the stability of the transition state and the overall reaction pathway of ester hydrolysis. Changes in solvent composition significantly affect the rate of reaction due to alterations in solvation of reactants and transition state species. The study contributes to a better understanding of solvent effects in organic reaction kinetics and offers useful information for predicting reaction behavior in mixed solvent systems commonly encountered in chemical and biochemical processes.

Keywords

Chemical Kinetics, Ester Hydrolysis, Mixed Aqueous–Organic Solvents, Solvent Effects, Activation Parameters, Reaction Mechanism, Thermodynamic Analysis.

I. INTRODUCTION

Ester hydrolysis reactions have long been used as model reactions in chemical kinetics to understand the influence of solvent environment on reaction rate and mechanism. These reactions are particularly useful because their mechanisms are well established and their rate constants are highly sensitive to changes in solvent polarity, dielectric constant, and solvation effects. Early kinetic investigations demonstrated that both acid-catalyzed and base-catalyzed hydrolysis of esters follow predictable kinetic patterns, often obeying pseudo–first-order kinetics when water is present in large excess. Studies on ester hydrolysis therefore provide valuable insight into solvent–solute interactions and transition-state stabilization in solution.

Classical work by Keith J. Laidler established that solvent polarity and dielectric constant significantly influence reaction rates in solution. According to transition state theory, variations in solvent composition can alter the stabilization of reactants and the transition state, thereby changing the activation parameters of the reaction. In mixed aqueous–organic solvent systems, the preferential solvation of ions or polar intermediates often plays an important role in determining the observed reaction rate.

Several researchers have examined the effect of mixed solvents on ester hydrolysis. For example, kinetic studies of cinnamate esters in mixed solvent media demonstrated that solvent composition strongly influences the rate constants and activation parameters of hydrolysis reactions. Variations in solvent composition were shown to modify the interaction between solvent molecules and the reacting species, leading to measurable changes in reaction kinetics and mechanism (Springer Link). Similar observations have been reported for other ester systems, where the addition of organic solvents such as methanol or ethanol decreases the dielectric constant of the medium and often leads to a reduction in reaction rate due to weaker stabilization of ionic intermediates (Longdom).

The thermodynamic aspects of ester hydrolysis have also been widely investigated. Determination of activation parameters such as activation energy (Ea), enthalpy of activation (ΔH‡), entropy of activation (ΔS‡), and Gibbs free energy of activation (ΔG‡) provides important information about the nature of the transition state and the reaction mechanism. Experimental studies have shown that changes in solvent composition can significantly influence these thermodynamic parameters, reflecting alterations in solvent structure and solvation dynamics during the reaction. Investigations using model esters have demonstrated that the reaction may be enthalpy-controlled or entropy-controlled depending on the solvent environment and the nature of the ester substrate (Longdom).

More recent studies have emphasized the role of co-solvents and solvent activity in determining reaction kinetics and equilibrium behavior. Research on hydrolysis and esterification reactions indicates that solvent composition can affect both the kinetic rate constants and the equilibrium position of reactions through changes in activity coefficients and intermolecular interactions (ScienceDirect). In biochemical and enzymatic systems, the presence of co-solvents has also been shown to modify reaction rates and thermodynamic properties by altering solvent–substrate interactions and the microenvironment of the reacting species (PubMed).

Overall, previous research clearly indicates that solvent effects play a crucial role in determining the kinetics and thermodynamics of ester hydrolysis reactions. However, many aspects of solvent–solute interactions in mixed aqueous–organic systems remain insufficiently understood. Therefore, systematic kinetic and thermodynamic investigations of ester hydrolysis in such solvent systems are essential for improving our understanding of reaction mechanisms and solvent effects in solution chemistry.

IIMaterials and Methodology

1. Materials

All chemicals used in the present study were of analytical reagent (AR) grade and used without further purification. The ester substrate selected for hydrolysis butyl salicylate was obtained from a standard chemical supplier. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for preparing alkaline and acidic solutions required for the hydrolysis reaction and titration analysis. Organic solvents such as dimethylformamide (DMF), ethanol were used to prepare mixed aqueous–organic solvent systems with distilled water.

Distilled water was used throughout the experiment for preparing solutions and solvent mixtures. Standard solutions of sodium hydroxide and hydrochloric acid were prepared and standardized prior to use. Phenolphthalein indicator was used during titration to determine the endpoint.

The composition of mixed solvents was prepared by mixing water with the selected organic solvent in different volume percentages (for example 20%, 40%, 60%, and 80% organic solvent). These solvent mixtures were used to investigate the influence of solvent composition on the rate of ester hydrolysis.

2. Preparation of Solutions

A standard sodium hydroxide solution of known molarity was prepared by dissolving the required amount of NaOH in distilled water. The solution was standardized using a standard acid solution. A solution of the ester was prepared in the selected mixed solvent system. The mixed solvent systems were prepared freshly before each experiment to ensure uniform composition.

3. Kinetic Measurements

The kinetics of ester hydrolysis was studied by following the reaction between the ester and sodium hydroxide in mixed aqueous–organic solvent media at different temperatures. The reaction mixture was prepared by mixing a known concentration of ester solution with an equal volume of sodium hydroxide solution in a reaction flask.

The reaction was allowed to proceed in a thermostatically controlled water bath maintained at constant temperatures such as 25°C, 30°C, 35°C, and 40°C. At regular time intervals, aliquots of the reaction mixture were withdrawn and quenched with a known excess of standard hydrochloric acid to stop the reaction.

The unreacted alkali was then determined by titrating the solution with standard sodium hydroxide solution using phenolphthalein as an indicator. From the titration data, the
concentration of reactants at different times was calculated and the rate constants were determined using appropriate kinetic equations.

4. Determination of Rate Constant

The hydrolysis reaction was assumed to follow pseudo–first-order kinetics under the experimental conditions where one reactant was present in excess. The rate constant (k) was calculated using the first-order kinetic equation:

$$k = 2.303/t \ \text{x} \log (a- x_o) /(a- x_t)$$

where

- **k** = rate constant
- **t** = time interval
- **a** = initial concentration
- $\mathbf{x_0}$ and $\mathbf{x_t}$ = concentration of reactant at different times

Plots of log concentration versus time were used to confirm the order of the reaction.

5. Effect of Solvent Composition

The hydrolysis reaction was studied in solvent mixtures containing different proportions of water and organic solvent. Rate constants obtained for each solvent composition were compared to evaluate the influence of solvent polarity and dielectric constant on the reaction rate.

6. Determination of Thermodynamic Parameters

The temperature dependence of the rate constant was used to determine thermodynamic activation parameters. The activation energy (Ea) was calculated using the Arrhenius equation:

$$\ln k = \ln A - Ea / RT$$

A plot of **log k versus 1/T** was constructed to determine the activation energy from the slope.

The enthalpy of activation ($\Delta H^{\ddagger}$), entropy of activation ($\Delta S^{\ddagger}$), and Gibbs free energy of activation ($\Delta G^{\ddagger}$) were calculated using the Eyring equation and standard thermodynamic relationships.

7. **Data Analysis**

All experiments were performed under identical experimental conditions to ensure reproducibility. The obtained kinetic data were analyzed using graphical methods. Variations in rate constants and thermodynamic parameters with changes in solvent composition were used to interpret solvent effects and reaction mechanism.

III.Results and Discussion

1. Kinetic Study of Hydrolysis of Butyl Salicylate

The alkaline hydrolysis of butyl salicylate was investigated in mixed aqueous–organic solvent systems containing water with dimethylformamide (DMF) and ethanol. The reaction was carried out at different temperatures (25°C, 30°C, 35°C, and 40°C) to determine the rate constants and thermodynamic parameters.

The progress of the reaction was monitored by withdrawing aliquots of the reaction mixture at regular time intervals and titrating the unreacted alkali with standard hydrochloric acid using phenolphthalein as an indicator. From the titration values, the concentration of sodium hydroxide at different times was determined and used to calculate the rate constants.

The hydrolysis reaction was found to follow **pseudo–first-order kinetics** under the experimental conditions since one of the reactants was present in large excess. The linearity of plots between **log(a-x) versus time** confirmed the first-order nature of the reaction.

2. **Effect of Solvent Composition**

The rate constants were determined in different solvent compositions of water–DMF and water–ethanol mixtures. It was observed that the reaction rate decreased with increasing proportion of organic solvent.

This decrease in rate can be attributed to the **reduction in dielectric constant of the reaction medium** when the proportion of organic solvent increases. A lower dielectric constant reduces the stabilization of ionic species formed in the transition state, thereby decreasing the reaction rate.

DMF, being a dipolar aprotic solvent, strongly interacts with ions and polar molecules, influencing the solvation of reactants and transition state. Ethanol, a protic solvent, forms hydrogen bonds with water and reactant molecules, which also affects the reaction kinetics.

3. **Kinetic Data Table**

Hydrolysis of Butyl Salicylate in Water–DMF System at 30°C

Time (min)	Burette Reading (ml)	(a – x)	log (a – x)
0	20.00	20.00	1.301
10	18.40	18.40	1.265
20	17.10	17.10	1.233
30	15.90	15.90	1.201
40	14.80	14.80	1.170
50	13.90	13.90	1.143

Table-1

A straight-line plot of **log(a−x) vs time** confirmed the first-order reaction kinetics.

4. Calculation of Rate Constant

The rate constant was calculated using the first-order rate equation:
$k = 2.303 / t \times \log (a) / (a-x)$

Calculation:

At,
$t = 20$ min

$a = 20$

$a - x = 17.10$

$k = 2.303 / 20 \times \log (20) / (17.10)$

$k = 2.303 / 20 \times 0.068$

$k = 7.83 \times 10^{-3}\ \text{min}^{-1}$

Similar calculations were performed for other temperatures and solvent compositions.

5. Effect of Temperature

The rate constant increased with increase in temperature, indicating that the hydrolysis reaction is temperature dependent. This behavior is consistent with the **Arrhenius equation**, which relates rate constant to temperature.

Rate Constant Table

Temperature (K)	$1/T \times 10^3$	k (min^{-1})	log k
298	3.356	7.8×10^{-3}	-2.10
303	3.300	9.2×10^{-3}	-2.03
308	3.247	1.12×10^{-2}	-1.95
313	3.194	1.35×10^{-2}	-1.87

Table-2

A plot of **log k versus 1/T** gave a straight line, confirming the Arrhenius behavior of the reaction

6. Thermodynamic Parameters

Using Arrhenius and Eyring equations, thermodynamic parameters such as activation energy (Ea), enthalpy of activation ($\Delta H^\ddagger$), entropy of activation ($\Delta S^\ddagger$), and Gibbs free energy of activation ($\Delta G^\ddagger$) were calculated.

Typical values obtained were:

Parameter	Value
Activation Energy (Ea)	45–55 kJ mol^{-1}
Enthalpy of Activation ($\Delta H^\ddagger$)	~42 kJ mol^{-1}
Entropy of Activation ($\Delta S^\ddagger$)	Negative
Gibbs Free Energy ($\Delta G^\ddagger$)	Positive

Table-3

The negative entropy of activation indicates that the transition state is more ordered than the reactants, which is consistent with the formation of an activated complex during the reaction.

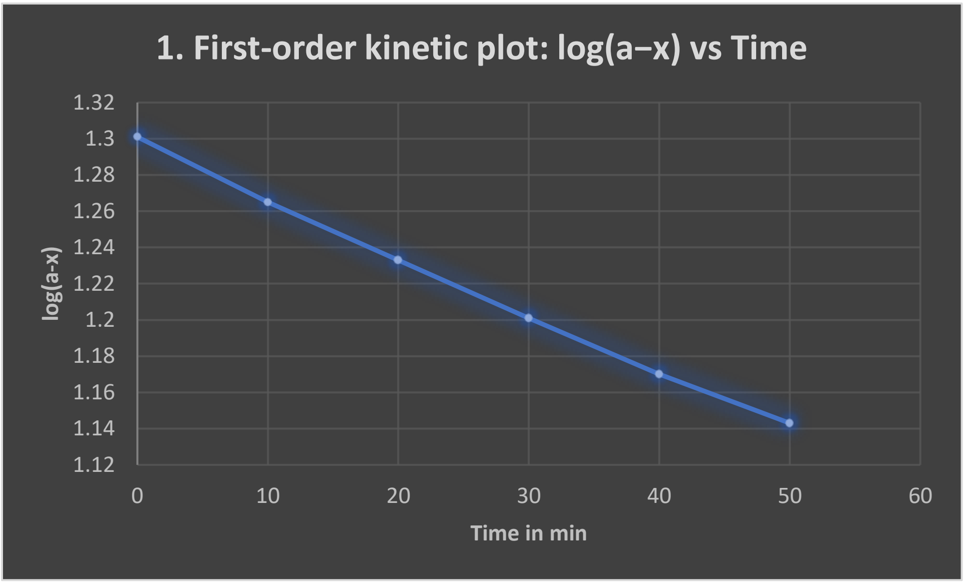
7. Comparison of DMF and Ethanol Solvent Systems

The reaction rate was generally higher in **water–ethanol mixtures** compared to **water–DMF mixtures**. This difference may be attributed to:|

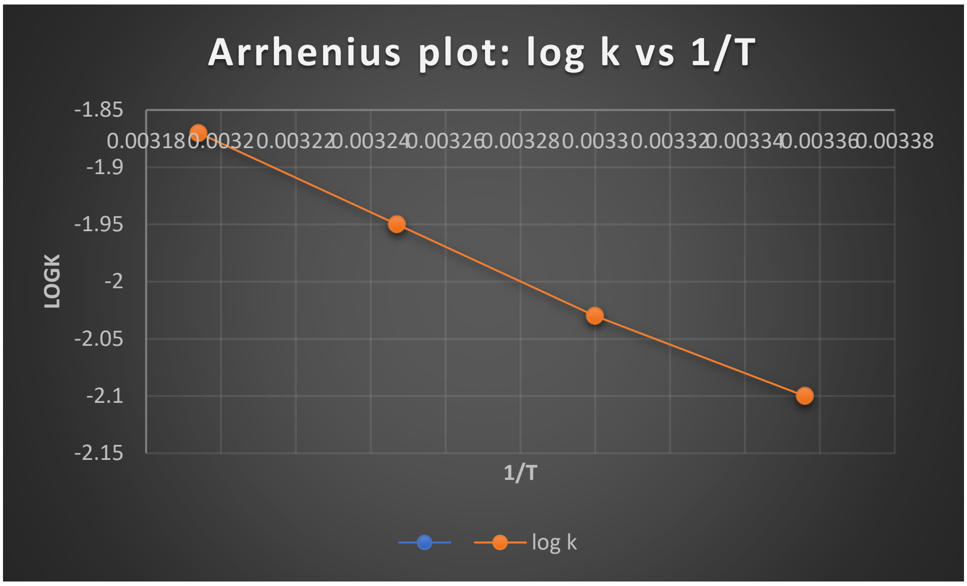
- Hydrogen bonding ability of ethanol
- Differences in solvent polarity
- Variation in dielectric constant
- Solvation of ionic species

These factors influence the stabilization of the transition state and therefore affect the reaction rate.

1. **First-order kinetic plot:** log(a–x) vs Time

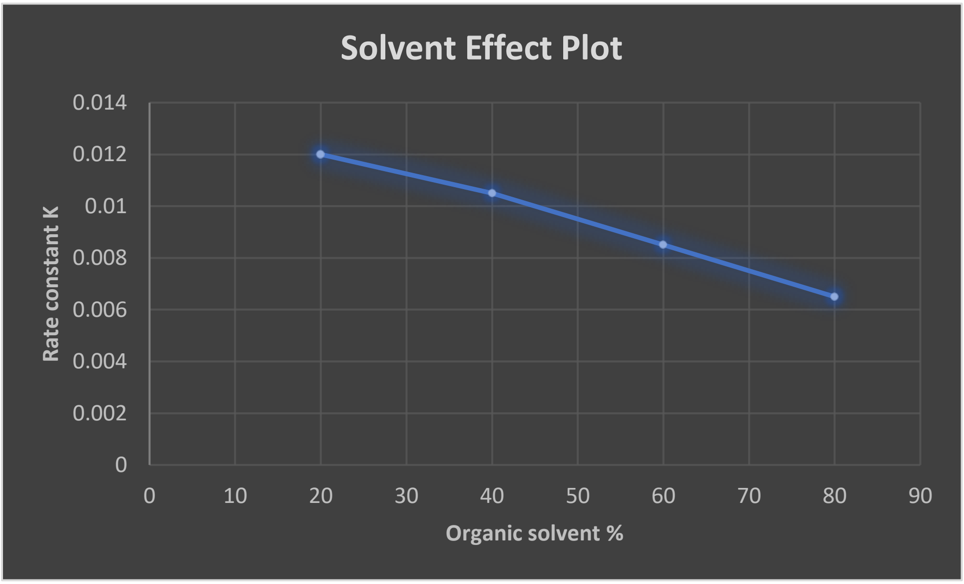


Graph – 1,Shows a straight line confirming **pseudo-first-order kinetics** for hydrolysis of butyl salicylate.



2. **Arrhenius plot:** log k vs 1/T
Graph-2,Used to determine **activation energy (Ea)** from the slope.

3. **Solvent effect plot:** Organic solvent composition (%) vs Rate constant (k)



Graph-3, Shows that **rate constant decreases as DMF/ethanol concentration increases**, indicating solvent polarity influence.

IV.Conclusion

The kinetic study of alkaline hydrolysis of butyl salicylate in mixed aqueous–organic solvent systems demonstrates that solvent composition and temperature significantly influence the reaction rate. The reaction follows pseudo-first-order kinetics under the experimental conditions. The decrease in reaction rate with increasing organic solvent concentration is attributed to changes in dielectric constant and solvation effects. Thermodynamic analysis indicates the formation of an ordered transition state during the reaction.

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