

Investigating the Effect of Aqueous Ethylene Glycol on the Kinetics and Mechanism of Alkaline Hydrolysis of Ethyl Pyruvate

Rachana Rani*, D.K Verma

Department of Chemistry, Patna University, Patna-800005 (India)

DOI: <https://doi.org/10.51583/IJLTEMAS.2026.150900133>

Received: 30 September 2026; Accepted: 05 October 2026; Published: 19 October 2026

ABSTRACT

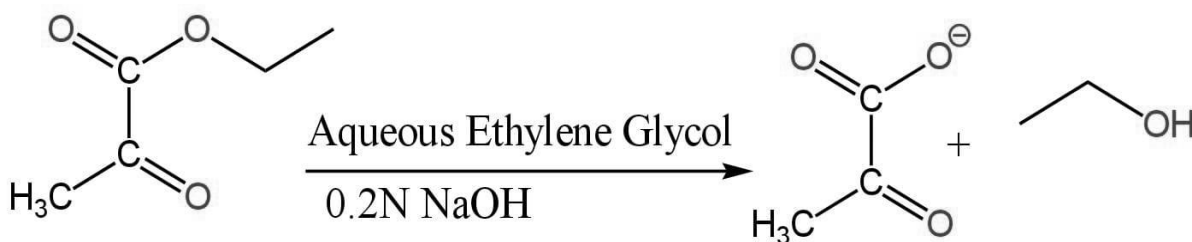
The alkaline hydrolysis of ethyl pyruvate, a biologically relevant α -keto ester, was investigated in aqueous ethylene glycol media over solvent composition from 10-50% (v/v) and temperatures 20-50°C. The reaction kinetics were followed by conductometric measurements, and the corresponding specific rate constants were evaluated from the conductivity data. A systematic decrease in the specific rate constant was observed with increasing ethylene glycol content in the reaction medium. This behaviour is attributed to changes in the solvent environment, including solvation, hydrogen-bonding interactions and solvent polarity. Thermodynamic activation parameters were subsequently evaluated to obtain information about the energetic changes associated with formation of the activated state. The iso-composition activation energy decreases from 46.50 kJmol⁻¹ to 34.73 kJmol⁻¹ with increasing ethylene glycol concentration from 10 to 50% (v/v). The variation of the kinetic and activation parameters with solvent composition provides insight into the influence of ethylene glycol–water interactions on hydroxide-ion reactivity and transition-state stabilization. The study demonstrates that changing the composition of an aqueous ethylene glycol medium can significantly modify the kinetic characteristics of alkaline ester hydrolysis.

Keywords: Ethyl pyruvate; alkaline hydrolysis; ethylene glycol; solvation; thermodynamic activation parameters.

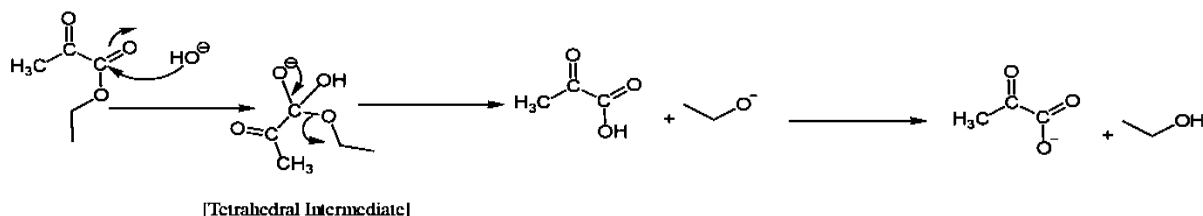
INTRODUCTION

The kinetics of chemical reactions in mixed aqueous solvents are strongly influenced by the physicochemical characteristics of the reaction medium. Solvent composition can modify molecular interactions, reactant solvation, ionic mobility, and the relative stability of the reactants and activated complex. Consequently, investigating chemical reactions in binary solvent systems provides valuable information about the relationship between solvent structure and reaction mechanism.

Ester hydrolysis is an important reaction in physical organic chemistry because its rate is sensitive to the characteristics of the ester, the nature of the attacking nucleophile, and the surrounding solvent environment. Under alkaline conditions, hydroxide ions attack the electrophilic carbonyl carbon of the ester, initiating nucleophilic acyl substitution^[1] The subsequent transformation produces the corresponding carboxylate ion and alcohol.



Ethyl pyruvate is an α -keto ester containing both ester and keto functional groups^[2]. Its structural characteristics make it an interesting substrate for investigating solvent-dependent reaction kinetics. The presence of the adjacent keto group may influence the electronic environment of the ester functionality and its interaction with the surrounding solvent molecules^[3]. The alkaline hydrolysis of ethyl pyruvate begins with nucleophilic attack of hydroxide ion on the ester carbonyl carbon. This produces a tetrahedral intermediate in which the carbonyl oxygen carries increased electron density. Subsequent collapse of this intermediate results in cleavage of the ester alkoxy group and formation of the carboxylate product^[4,5].



Ethylene glycol is a polar protic solvent containing two hydroxyl groups capable of participating in hydrogen-bonding interactions. When mixed with water, it produces a solvent environment with properties that differ from those of pure water. Changes in ethylene glycol concentration can influence solvent polarity, hydrogen-bonding structure, and the solvation behaviour of ionic species^[6].

In alkaline hydrolysis, the interaction of hydroxide ions with water and ethylene glycol molecules may affect their effective reactivity toward the ester substrate^[7]. Variations in solvent composition can also modify the relative solvation of the reactants and the activated complex, thereby influencing the observed reaction rate.

The objective of the present work is to investigate the kinetics of alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol mixtures and evaluate the effects of solvent composition and temperature on the rate constants, activation energy, and thermodynamic activation parameters.

EXPERIMENTAL

Materials

Ethyl pyruvate (ethyl 2-oxopropanoate), sodium hydroxide, ethylene glycol, potassium chloride and oxalic acid of analytical grade were used for the experiments. Freshly prepared double-distilled water was used for preparing the solutions and reaction mixtures.

Instrumentation

Conductometric measurements were carried out using a calibrated conductivity meter fitted with a suitable conductivity cell. A thermostatically controlled water bath was used to maintain the required reaction temperature during the kinetic measurements.

Kinetic Measurements

The conductivity meter was calibrated using standard 0.01 N KCl solution, and the conductivity cell was rinsed thoroughly with double-distilled water before each measurement to avoid contamination and ensure reliable readings. The alkaline hydrolysis of ethyl pyruvate was investigated conductometrically in aqueous ethylene glycol mixtures of composition from 10% to 50% (v/v) and temperature range 20°C to 50°C. Equimolar solutions of ethyl pyruvate and sodium hydroxide were employed for the kinetic studies. The required solvent mixtures were prepared by mixing appropriate volumes of ethylene glycol and double-distilled water while maintaining a constant final reaction volume. Before mixing, the reactant solutions were allowed to attain the desired temperature. The reaction was initiated by combining the reactants, and conductivity readings were recorded at regular time intervals until the reaction approached completion. The resulting conductivity data were used to calculate the corresponding second-order rate constants for each

ethylene glycol composition and temperature. Identical experimental conditions were maintained throughout the kinetic measurements to ensure consistency and facilitate comparison of the solvent-dependent reaction behaviour.

RESULTS AND DISCUSSION

Effect of ethylene glycol composition on the specific rate constant

The specific rate constants (k) obtained for the alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol at different solvent compositions and temperatures are presented in Table 1 and variation of $\log k$ with increasing mol% shown in Table-2 and Fig-1. The reaction rate shows a systematic dependence on the proportion of ethylene glycol in the reaction medium^[8].

At a given temperature, the specific rate constant decreases as the ethylene glycol content is increased^[9,10]. This indicates that modification of the solvent environment affects the interaction between hydroxide ion and ethyl pyruvate, and it also affects the stabilisation of transition state^[11].

TABLE 1 Specific rate constants, k , ($\text{Lmol}^{-1}\text{s}^{-1}$) for alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol at different solvent compositions and temperatures.

Temperature in °C	Specific rate constants k at different composition of ethylene glycol (v/v)%				
	10%	20%	30%	40%	50%
20°C	19.53	16.61	14.79	13.19	11.75
30°C	36.36	30.95	26.31	21.88	19.08
40°C	66.22	57.80	46.94	38.02	30.21
50°C	117.64	96.15	78.12	60.60	44.84

TABLE 2 The variation of $\log k$ with ethyl pyruvate with increasing mol% of ethylene glycol at different temperatures.

% of Ethylene glycol (v/v)	mol% of Ethylene glycol	log k at different Temperature			
		20°C	30°C	40°C	50°C
10%	3.43	1.29	1.56	1.82	2.07
20%	7.40	1.22	1.49	1.76	1.98
30%	12.05	1.16	1.42	1.67	1.89
40%	17.57	1.12	1.34	1.58	1.78
50%	24.23	1.07	1.28	1.48	1.65

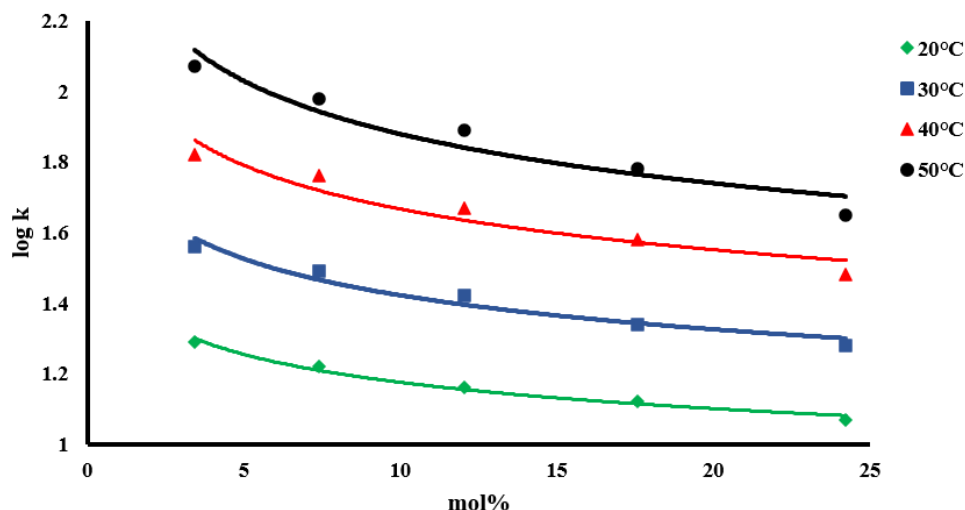


Fig 1 Variation of log k value with mol % of ethylene glycol at different temperatures

Determination of iso-composition activation energy

TABLE 3 Variation of log k with $10^3/T$ (in K^{-1}) for the alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol media.

Temperature in °C	$10^3/T$	log k at different compositions				
		10%	20%	30%	40%	50%
20°C	3.41	1.29	1.22	1.16	1.12	1.07
30°C	3.30	1.56	1.49	1.42	1.34	1.28
40°C	3.19	1.82	1.76	1.67	1.58	1.48
50°C	3.09	2.07	1.98	1.89	1.78	1.65

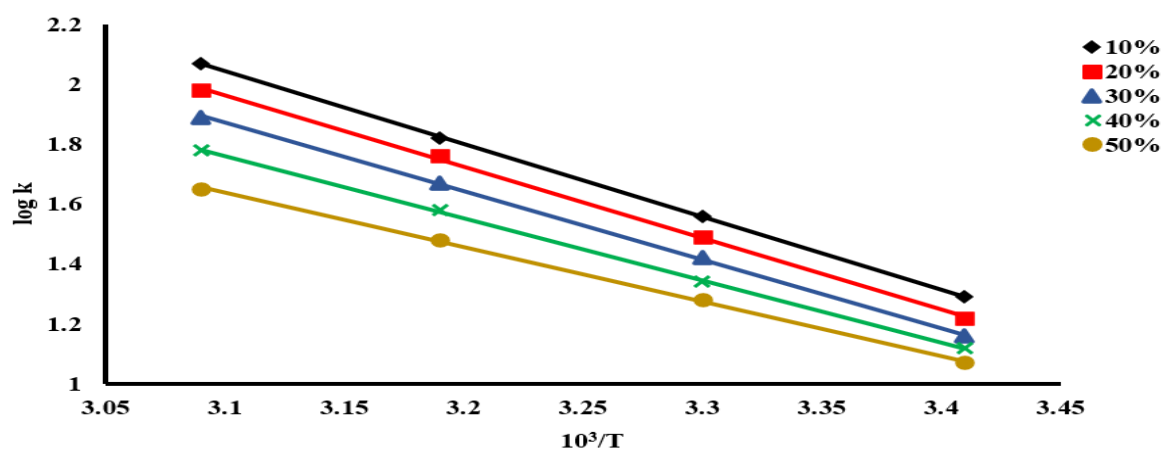


Fig 2 Plot of log k value with $10^3/T$ for alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol media.

TABLE 4 Iso-composition activation energy (E_c) for the alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol mixtures.

% of ethylene glycol (v/v)	10%	20%	30%	40%	50%
E_c (kJmol ⁻¹)	46.50	45.64	43.67	39.73	34.73

The temperature dependence of the specific rate constants was analysed using the Arrhenius equation. Plots of $\log k$ against $10^3/T$ were constructed for each ethylene glycol composition shown in Table-3 and (Fig-2), and the corresponding iso-composition activation energy were calculated from the slopes of the linear plots. The iso-composition activation energy values obtained at different ethylene glycol compositions are listed in Table 4. The experimentally determined iso-composition activation energy decreases with increasing ethylene glycol concentration, this behaviour indicates a reduction in the apparent energy barrier in the modified solvent environment^[12,13]. Such a change may arise from altered solvation of hydroxide ion and changes in the stabilization of the activated state.

Effect of dielectric constant on iso-dielectric activation energy

TABLE 5 Iso-dielectric activation energy (E_D) for the alkaline hydrolysis of ethyl pyruvate at different dielectric constants in aqueous ethylene glycol media.

Value of D	64	68	72	76	80
E_D (kJmol ⁻¹)	54.53	57.93	63.10	66.19	68.64

The results indicate a progressive increase in iso-dielectric activation energy with increasing dielectric constant of the reaction medium (Table-5). The observed variation suggests that the dielectric properties of the aqueous ethylene glycol system influence the energetic requirements of the hydrolysis process. Changes in solvent composition modify the solvation environment of the reacting ionic species and may affect ion-dipole interactions and transition-state stabilization. These solvent-dependent interactions provide insight into the relationship between the dielectric properties of the medium and the reaction mechanism^[14,15].

Effect of water concentration on the specific rate constant

TABLE 6 Variation of $\log k$ with $\log[H_2O]$ for the alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol at different temperatures.

% of Ethylene glycol (v/v)	% of H ₂ O	$\log[H_2O]$	$\log k$ at different temperatures			
			20°C	30°C	40°C	50°C
10%	90%	1.70	1.29	1.56	1.82	2.07
20%	80%	1.64	1.22	1.49	1.76	1.98
30%	70%	1.56	1.16	1.42	1.67	1.89
40%	60%	1.52	1.12	1.34	1.58	1.78
50%	50%	1.44	1.07	1.28	1.48	1.65

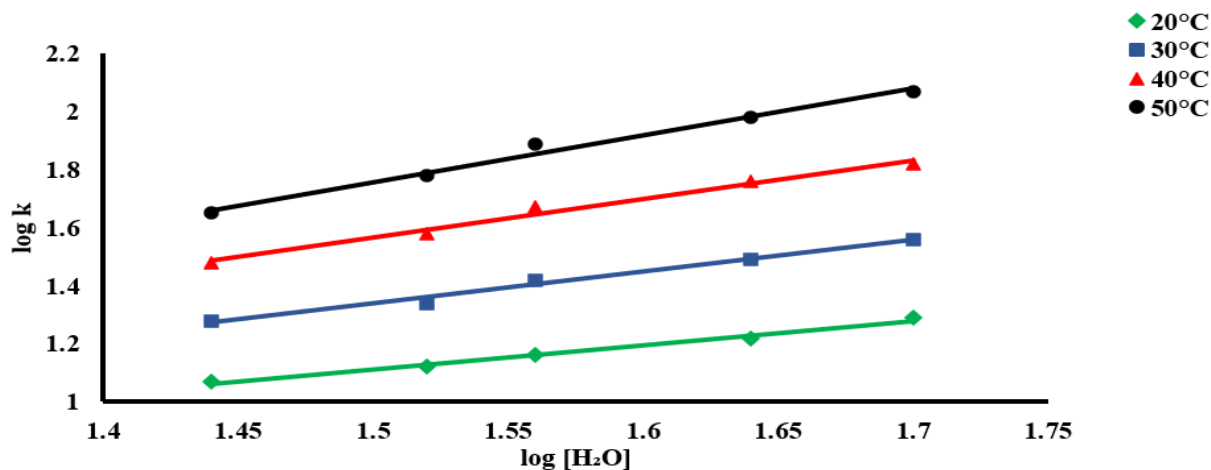


Fig 3. Variation of log k with log [H₂O] for the alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol media.

Determination of solvation number

TABLE 7 Slope values obtained from the plots of log k versus log[H₂O] at different temperatures in aqueous ethylene glycol media.

Temperature	20°C	30°C	40°C	50°C
Slope	0.840	1.097	1.334	1.612

To obtain additional information concerning the role of the aqueous component, the dependence of the reaction rate on water concentration was examined by plotting log k against log [H₂O] shown in Table-6 and Fig-3. The resulting relationship provides an empirical measure of the sensitivity of the reaction rate to changes in water concentration. The slope (Table-7) obtained from these plots may be expressed as an apparent solvation parameter^[16]. Changes in this parameter with temperature or solvent composition indicate that the organization of the solvent surrounding the reacting species changes during the reaction. The observed dependence of the rate on water concentration can therefore be interpreted in terms of changes in the solvation environment accompanying formation of the activated state^[17].

Thermodynamic Activation Parameters

TABLE 8 Thermodynamic activation parameters (ΔH^* , ΔS^* , ΔG^*) for the alkaline hydrolysis of ethyl pyruvate in aqueous ethylene glycol media. ΔH^* , ΔG^* in kJmol⁻¹, ΔS^* in Jmol⁻¹K⁻¹.

% of ethylene glycol (v/v)	Thermodynamic Activation Parameters								
	ΔH^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
		20°C	20°C	30°C	30°C	40°C	40°C	50°C	50°C
10%	44.21	74.62	-103.79	75.65	-103.77	76.67	-103.72	77.65	-103.54
20%	43.46	75.01	-107.70	76.06	-107.60	77.03	-107.26	78.20	-107.56

30%	40.99	75.28	-117.05	76.48	-117.13	77.56	-116.86	78.74	-116.89
40%	37.20	75.52	-130.79	76.91	-131.06	78.09	-130.66	79.41	-130.70
50%	32.24	75.78	-148.63	77.26	-148.61	78.67	-148.35	80.21	-148.52

The thermodynamic activation parameters (Table-8), namely enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), and Gibbs free energy of activation (ΔG^*), were evaluated to obtain further insight into the reaction process^[18]. The enthalpy of activation provides information about the energetic requirement for formation of the activated complex. The entropy of activation reflects changes in molecular organization during the transition from reactants to the activated state. The Gibbs free energy of activation represents the free-energy barrier associated with the reaction under the experimental conditions. Variations in these parameters with ethylene glycol concentration may be associated with changes in solvent organization, hydrogen-bonding interactions, and solvation of the reacting species^[19]. The combined analysis of kinetic and thermodynamic parameters provides a broader understanding of the influence of aqueous ethylene glycol on the alkaline hydrolysis of ethyl pyruvate^[20].

CONCLUSION

The present study investigates the influence of aqueous ethylene glycol on the kinetics and thermodynamic characteristics of alkaline hydrolysis of ethyl pyruvate. The reaction rate constants were evaluated at different solvent compositions and temperatures using conductometric measurements. The kinetic analysis provides information about the temperature dependence of the reaction and the influence of solvent composition on its activation barrier. Evaluation of the thermodynamic activation parameters further helps to interpret the energetic and molecular characteristics of the activated complex. The findings can contribute to a better understanding of solvent-dependent ester hydrolysis and the role of hydrogen-bonding interactions, solvation effects, and solvent composition in controlling reaction kinetics.

Acknowledgements

The authors gratefully acknowledge the Department of Chemistry, Patna University, Patna, India, for providing the laboratory facilities and infrastructure necessary to carry out this research.

Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. Smith, M. B., & March, J. (2006). *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure* (1st ed.). Wiley. <https://doi.org/10.1002/0470084960>
2. Fink, M. P. (2007). Ethyl pyruvate: A novel anti-inflammatory agent. *Journal of Internal Medicine*, 261(4), 349–362. <https://doi.org/10.1111/j.1365-2796.2007.01789.x>
3. Reichardt, C. (2002). *Solvents and Solvent Effects in Organic Chemistry* (1st ed.). Wiley. <https://doi.org/10.1002/3527601791>
4. Atkins, P. W., & de Paula, J. (2006). *Atkins' physical chemistry* (8. ed). Oxford University Press.
5. Clayden, J., Greeves, N., & Warren, S. (2012). *Organic chemistry* (2nd ed). Oxford university press.
6. Diorazio, L. J., Hose, D. R. J., & Adlington, N. K. (2016). Toward a More Holistic Framework for Solvent Selection. *Organic Process Research & Development*, 20(4), 760–773. <https://doi.org/10.1021/acs.oprd.6b00015>
7. Singh, A. K. (2023). Water-DMSO Co-Solvent effect and kinetics of acid catalyzed Hydrolysis of butyl formate and Influence on Activation Parameters. *Asian Journal of Research in Chemistry*, 159–162. <https://doi.org/10.52711/0974-4150.2023.00026>

8. Hughes, E. D., & Ingold, C. K. (1935). 55. Mechanism of substitution at a saturated carbon atom. Part IV. A discussion of constitutional and solvent effects on the mechanism, kinetics, velocity, and orientation of substitution. *Journal of the Chemical Society (Resumed)*, 244. <https://doi.org/10.1039/jr9350000244>
9. Sharma, S., Ramani, J., Bhalodia, J., & Vyas, B. (2013). Kinetic study of specific base catalyzed hydrolysis of ethyl acrylate in water-ethanol binary system. *Russian Journal of Physical Chemistry A*, 87(5), 730–736. <https://doi.org/10.1134/S0036024413050348>
10. Singh, A. K., & Bano, A. (2019). Kinetics and Solvent effect on Aquo-dipolar protic organic-solvent system of Hexanoate ester. *Asian Journal of Research in Chemistry*, 12(6), 341. <https://doi.org/10.5958/0974-4150.2019.00064.6>
11. Rani, R., Verma, D. K., Kumar, P., & Shahi, A. (2026). Investigating Solvent Effects on the Kinetics and Mechanism of Alkaline Hydrolysis of Ethyl Pyruvate in Aqueous Dimethyl Sulfoxide. *International Research Journal of Pure and Applied Chemistry*, 27(5), 207–215. <https://doi.org/10.9734/irjpac/2026/v27i51038>
12. Singh, A. K. (2024). Study of Aqueous Solvent effect and Kinetics in Hydrolysis of Butyle Salicylate in Alkaline Medium of Water and DMF. *Research Journal of Science and Technology*, 176–180. <https://doi.org/10.52711/2349-2988.2024.00026>
13. Singh, A. K. (2019). Activation Parameter and Solvent effect on solvolysis of Ethyl benzoate in Aquo-organic Solvent System. *Asian Journal of Research in Chemistry*, 12(2), 99. <https://doi.org/10.5958/0974-4150.2019.00022.1>
14. Singh, L., Gupta, A. K., Singh, R. T., Verma, D. K., & Jha, R. C. (1984). Effect of DMSO on the kinetic behavior of alkali catalyzed hydrolysis of methyl salicylate. *Reaction Kinetics and Catalysis Letters*, 24(1–2), 161–165. <https://doi.org/10.1007/BF02069621>
15. Akerlof, G. (1932). DIELECTRIC CONSTANTS OF SOME ORGANIC SOLVENT-WATER MIXTURES AT VARIOUS TEMPERATURES. *Journal of the American Chemical Society*, 54(11), 4125–4139. <https://doi.org/10.1021/ja01350a001>
16. Robertson, R. E., Heppollette, R. L., & Scott, J. M. W. (1959). A SURVEY OF THERMODYNAMIC PARAMETERS FOR SOLVOLYSIS IN WATER. *Canadian Journal of Chemistry*, 37(4), 803–824. <https://doi.org/10.1139/v59-108>
17. Singh, A. K. (2021). Kinetics Investigation of Solvent Polarity on Reaction Rate for Solvolysis of Ethyl Caprylate Ester in Binary Solvent System. 2021 10th International Conference on System Modeling & Advancement in Research Trends (SMART), 676–679. <https://doi.org/10.1109/SMART52563.2021.9676306>
18. Wynne-Jones, W. F. K., & Eyring, H. (1935). The Absolute Rate of Reactions in Condensed Phases. *The Journal of Chemical Physics*, 3(8), 492–502. <https://doi.org/10.1063/1.1749713>
19. Ak, S. (2017). Solvent Effect on the Enthalpy and Entropy of Activation for the Hydrolysis of Ethyl Cinnamate in Mixed Solvent System. *Journal of Physical Chemistry & Biophysics*, 07(01). <https://doi.org/10.4172/2161-0398.1000238>
20. Tommila, E., Murto, M.-L., Jerslev, B., Hatanaka, A., & Munch-Petersen, J. (1963). The Influence of the Solvent on Reaction Velocity. XXIII. The Alkaline Hydrolysis of Ethyl Acetate in Dimethyl Sulphoxide-Water Mixtures. *Acta Chemica Scandinavica*, 17, 1947–1956. <https://doi.org/10.3891/acta.chem.scand.17-1947>