A Kinetic Study on the Solvent Effect of Aquo-DMSO Solvent Systems on the Medicinal Efficiencies of Cinnamate Esters

Zeba Parween [1], and R. T. Singh[2]
1. Assistant Professor of Chemistry, College of Commerce, Arts and Science, Patna
2. Professor & Formerly HOD Chemistry and the Dean of the Faculty of Science, V. K. S. University, Ara

Received:Sep 29, 2026 Accepted:Oct 26, 2026 Published:Nov 10, 2026

ABSTRACT

With a view to study the Solvent effect of dipolar-aprotic solvent on the. medicinal efficiency of an unsaturated acid ester (Cinnamate), the kinetics of alkali catalysed hydrolysis of methyl cinnamate was studied in aquo-DMSO Solvent System.

From enhancement in ΔH* and ΔS* values with simultaneous increase in ΔG* values of the reaction, it has been inferred that the reaction is enthalpy dominated and entropy controlled.

From the enhancement in E_C values with increase in DMSO content in the reaction media and from depletion in E_D values with increase in D values of the aquo-DMSO media, it has been concluded that the initial state and the transition state of the reaction are solvated and desolvated respectively.

From the evaluated numerical values of the Iso-kinetic temperature of the reaction which comes to be 319.0, it is concluded that there is strong and appreciable interaction between solvent and solute in aquo-DMSO reaction media.

KEYWORDS: Solvent Systems, Medicinal efficiencies, Machanistic pathways, Solvation, Initial and Transition States, Dense and Bulky form. Cinnamate, Dielectric effect, Iso-kinetic temperature.

INTRODUCTION

Though a large number of researchers of earlier[1-2] have reported their researches on the solvent effect on different solvolysis reactions, but the study of solvent effect of dipolar aprotic solvent like DMSO, on the usefulness of the cinnamate ester on its medicinal efficiencies have not been paid a wide attention so far.

So, in order to high light the above noted idea, it was thought essential and useful to study the solvent effect of DMSO on the medicinal behaviour and efficiency of methyl cinnamate so that principle for manufacturing medicine of desired potential from cinnamate be formulated.

The kinetics of alkali catalysed solvolysis of methyl cinnamate was studied by adding different concentration of the aprotic organic co-solvent (DMSO) from 20 to 80% (v/v) in the reaction media at five different temperatures, i. e., 20, 25, 30, 35 and 40^oC by using previously reported methods[3-4]. The specific rate constants were evaluated using second order kinetic equation and have been mentioned in Table – I.

The thermodynamic activation parameters namely free energy of activation (ΔG*), enthalpy of activation (ΔH*) and entropy of activation (ΔS*) of the reaction were determined by using wynne-Jones and Eyring equation[5] and are synchronised in Table - II.

From the slopes of the Arrhenius plots of log k versus 1/T and that of log k_D (obtained from interpolation of the plots of log k against D values of aquo-DMSO solvent system) versus 1/T the values of Iso-composition activation energy (E_C) and Iso-dielectric activation energy (E_D) of the reaction have been evaluated and are recorded respectively in Tables- III and IV.

Solvent effect on the Thermodynamic Activation Parameters of the Reaction: The evaluated values of the three thermodynamic activation parameters namely ΔH*, ΔG* and ΔS* are synchronised in Table-II and from their variations with mol% of the organic content (DMSO) of the reaction media, it is found that the values of free energy of activation (ΔG*) increases with increasing DMSO content of the reaction at all the temperature at which the reaction was studied. At 30°C, values of ΔG* were recorded increasing from 81.58 kJ/mol to 83.65 kJ/mol with increasing proportion of DMSO from 20 to 80% (v/v). Though the enhancement in ΔG* values is not very high, however, it is liable to be taken into consideration.

Similar variations in ΔG* values with increasing mol % of organic solvent of the reaction media have also been reported earlier by Kiranmayee & Singh[6], Monalisa & Singh et at.[7] and Singh & Kumar et al.[8]. From the plot of ΔG* against mol % of organic co-solvent, it is found that ΔG* values increases smoothly and non-linearly with gradual addition of DMSO in the reaction media. This finding is indicative of desolvation of reactants as explained and also supported by Elsemongy et al.[9].

So far as the variation in ΔH* and ΔS* values are concerned, on going through Table-IV, it is interestingly observed that both of them decrease with gradual increase in the concentration of DMSO in the reaction media at all the temperatures.

On the basis of the relation:-

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

it can be concluded that simultaneous enhancement in ΔG* values with increase in the values of both the ΔH* and ΔS* values is only possible when the extent of increase in ΔH* is more than that of ΔS*. The regular enhancement to the greater extent in ΔH* values clearly indicates that the alkali catalysed hydrolysis of methyl cinnamate in aquo-DMSO media is enthalpy dominated and entropy controlled. Moreover, non-linear variation in ΔH* and ΔS* values with increasing mol% of DMSO in the reaction media, gives information of the fact that the specific solvation is taking place in aquo-DMSO systems, similar to that as reported by Saville et al.[10] and it also indicates that the random distribution of the components are not permissible.

The similar non-linear variations in ΔS* and ΔH* values with increasing mol % of the organic component in the reaction media have also been reported earlier by Kumar[11], Svati & Singh et al.[12]. The enhancement in both ΔH* and ΔS* values also justifies that transition state of the reaction is desolvated and its initial state is solvated in aquo-DMSO reaction media.

Solvent Effect on the Iso-composition Activation Energy (E_C) of the Reaction: From the slopes of the Arrhenius plots of log k versus 10^3/T, the values of Iso-composition activation energy (E_C) of the reaction have been evaluated and recorded in Table-III. From Table-III, it is obvious that iso-composition activation energy values of the reaction go on increasing from 96.55 kJ/mol to 135.82 kJ/mol with increasing concentration of DMSO in the reaction media from 20 to 80% (v/v).

The enhancing trend in the E_{exp} value may be due to either of the following three causes:

(i) The initial state is solvated and the transition state is desolvated,

(ii) The transition state is more desolvated than the initial state, and

(iii) The initial state is more solvated than the transition state.

Out of these three causes, the first factor seems to be operative in this case as both ΔH* and ΔS* values of the reaction as mentioned in Table-II, are found to increase. Such findings have been reported earlier by

Singh & Wats et al.[14] and Singh & Parween et al.[15]. Similar interpretations have also been found in support of the recently reported views of K Kishore & Singh et al.[16].

Solvent effect on the Iso-dielectric Activation Energy (E_D) of the reaction:

Similar to Iso-composition activation energy (E_C) , the values of Iso-dielectric activation energy (E_D) were also calculated from the slopes of the Arrhenius plots of log k_D versus 10^3/T.

From the recorded values of the Iso-dielectric activation energy (E_D) of the reaction in Table-IV, it is apparent that with increase in D values of the reaction media from D=62.5 to D=75, the E_D values go on decreasing from 140.95 kJ/mol to 108.21 kJ/mol respectively.

Since with increase in DMSO content of the reaction media there is decrease in its dielectric (D) values, hence in reverse way it may be inferred that with decrease in D values of the reaction media or with increasing DMSO concentration in it, E_D values also increase similar to increase in E_C values. Thus, E_C and E_D values are complementary to each other.

Similar interpretations for such effect of concentration of the added organic content of the media or of the effect of change in dielectric constants of the reaction media have also been reported earlier by Singh & Singh et. al.[17], Rashmi & Singh et al.[18] and Priyanka & Singh et al.[24] and in recent years by Raghaw & Singh[19].

Solvent effect on the Iso-kinetic Temperature of the Reaction and Solvent-solute Interaction in the Aquo-DMSO Reaction Media:

The values of the Iso-kinetic temperature of the reaction were evaluated by using Barclay and Butler relationship[20] which is as follows:

$$\delta m(\Delta H^*) = \beta \delta m(\Delta S^*)$$

It is a straight line equation presenting the relationship between enthalpy and entropy of activation. $'\beta'$ is iso-kinetic temperature. From the data available in Table-V, the plots of ΔH^*versus ΔS^*at 30^oC were made. From the slope of the obtained straight line, the value of iso-kinetic temperature was found to be 318.84≈319.0. In the light of Leffler's[21] guidelines, from the value of iso-kinetic temperature which is much higher than the standard value 300, it is concluded that in aquo-DMSO media, there is appreciably strong solvent-solute interaction for alkali catalysed solvolysis of methyl cinnamate. Similar observations, inferences and interpretations have also been reported earlier by Singh & Navendu et al.[22], Kumar[23], and Singh & Singh et. al.[24]. Recently Chaudhary & Singh[25] have reported similar findings.

References:

1. Singh, Lallan, Gupta, A.K., Singh, R.T., Verma, D.K. and Jha, R.C. : React. Kinet. Catal. Lett.,**24**, No.(1-2), 161-165, 1984
2. Singh, B, Gupta, A. K., Pathak, D. B., Singh, V. K., Singh, Y. P. and Singh, R. T.: J. Indian Chem. Soc., **66**, 372 – 379, 1989
3. Singh R.T., Kumari, M., Chaudhary, K. K. and Namrata : ARJ Phys. Sci., **16**, No,(1-2), 105-115, 2013
4. Singh, R.T., Navendu, K. S., Henry, W. and Hafizee, N. K.: NIRJ Sci., **14**, 53-61, 2014 (June)
5. Wynne Jones W.F.K. and Eyring H.: J. Chem. Phys., **3**, 492, 1935
6. Kiranmayee and Singh, R. T.: Asian Journal of Chemistry, **18**, No. (2), 1050-1054, 2006
7. Monalisa, Verma, S., Singh, D. K. and R. T. Singh: NIRJ Sci., **17**, 35-47, 2015 (June)
8. Singh, R. T., Singh, P., Kishor, K. and Singh, S. K.: ARJ Phys. Sci., **14**, No. (1-2), 84-95, 2014

9. Elsemongy, M.M., Elamayem, M.S. and Moussa, M.N.H. : Z. Physik. Chem. Neue Folge, **94**, 69, 1975
10. Saville B.J. and Hudson R.F.: J. Chem. Soc., 4114, 1955
11. Kumar, N. : NIRJ Sci. **20**, 51-64, 2016 (June)
12. Kumari, Svati, Kamal, K. K., Singh, H. and Singh, R. T.: NIRJ Sci., **21**, 59-72, 2016 (Dec.)
13. Abhay A., and Singh R. T.: GIS Science Journal, **11**, No. (2), 70-77, 2024
14. Singh, R.T., Wats, K., Kishor, K. and Kumar, D. : NIRJ Sci., **16**, 33-42, 2014
15. Singh, R.T., Kumar, S., Perween, Z. and Singh, R. I.: ARJ Phys. Sci.; **16**, No.(1-2), 117-128, 2013
16. K. Kishore and Singh R. T.: Journal of Xidian University, **19**, No. (1), 212-224, 2025.
17. Singh R. K., Sudhanshu, N. S., K. Mrityunjay, and Singh R. T.: NIRJ Sci., **14**, 43-52, 2014
18. Rashmi, Singh, V. K., Singh, P. and Singh, R. T.: ARJ Phys. Sci., **19**, No. (1-2), 93-102, 2016
19. K. Raghaw and Singh R. T.: Journal of Xidian University, **9**, No. (1), 87-94, 2025
20. Barclay, I. A. and Butler, J. A.: Trans. Faraday Soc., **34**, 1445, 1938
21. Leffler, J.E. : J. Org. Chem., **20**, 1201, 1955
22. Singh R.T., Navendu K. S., Lal V. K. and Singh R. I.: ARJ Phy. Sci., **17**, Nos. (1-2), 187-200, 2014
23. Kumar, N.: NIRJ Sci., **21**, 73-86, 2016 (Dec.)
24. Singh, R., Nazia, S., Kumari, S. and Singh R. T.: ARJ Phys. Sci., **19**, No. (1-2), 75 – 87, 2016
25. Chaudhary K. and Singh R. T.: GIS Science Journal, **12**, No. (10), 1-6, 2025

Table – I

Specific rate constant values of Alkali catalysed hydrolysis of Methyl cinnamate in water-DMSO media

$k \times 10^2$in $(dm)^{-1}min^{-1}$

Temp In ^oC	% of DMSO (v/v)						
	20%	30%	40%	50%	60%	70%	80%
20^oC	91.71	74.15	60.56	49.87	40.75	32.73	23.69
25^oC	172.90	147.30	125.17	107.42	90.51	75.65	58.87
30^oC	327.57	287.47	256.33	228.45	204.27	175.71	144.08
35^oC	600.07	542.88	506.76	469.14	431.42	385.83	837.13
40^oC	1116.35	1031.10	994.49	955.21	925.12	856.66	794.15

Table – II

Consolidated Values of Activation parameters (ΔH^* ΔH^* of the reactionIn water-DMSO system at different temperatures.

ΔH^* and ΔG^* in kJ/mol, ΔS^* in J/K/mol

% of DMSO (v/v)	Mole % of DMSO	ΔH^* in kJ/mol	20^oC		25^oC		30^oC		35^oC		40^oC	
			ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*	ΔG^*	ΔS^*
20%	5.94	91.98	81.91	34.36	81.78	34.23	81.58	34.31	81.42	34.27	81.17	34.53
30%	9.77	98.93	82.43	56.32	82.18	56.22	81.91	56.16	81.68	56.01	81.38	56.08
40%	14.40	102.97	82.92	68.42	82.58	68.42	82.20	68.54	81.86	68.55	81.47	68.68
50%	20.17	108.77	83.40	86.60	82.96	86.62	82.49	86.73	82.05	86.75	81.58	86.88
60%	27.49	116.20	83.89	110.29	83.38	110.13	82.77	110.32	82.27	110.18	81.66	110.36
70%	37.09	122.29	84.42	129.24	83.83	129.07	83.15	129.17	82.55	129.02	81.86	129.18
80%	50.27	131.56	85.47	157.30	84.45	158.09	83.65	158.12	82.90	157.99	82.06	158.15

Table – III

Evaluated values of Iso-composition Activation Energy ($E_c or E_{exp}$) of the reaction in water-DMSO media.

% of DMSO (v/v)	20%	30%	40%	50%	60%	70%	80%
E_c value In kJ/mol	96.65	101.18	108.09	113.41	119.37	125.32	135.82

Table – IV

Evaluated values of Iso-Dielectric Activation Energy (E_D) of the reaction at different desired 'D' values of the water-DMSO media.

D values	D = 62.5	D = 65	D = 67.5	D = 70	D = 72.5	D = 75
E_D values In kJ/mol	140.95	131.39	124.17	118.07	115.47	108.21

Table – V

Variation of ΔH^*, ΔG^* and ΔS^* values of the reactionwith mol % of DMSO in water-DMSO media

% of DMSO (v/v)	Mole % ofDMSO	ΔH^* in kJ/mol	ΔG^* In kJ/molat 30^oC	ΔS^* In J/K/molat 30^oC
20%	5.94	91.98	81.58	34.31
30%	9.77	98.93	81.91	56.16
40%	14.40	102.97	82.20	68.54
50%	20.17	108.77	82.49	86.73
60%	27.49	116.20	82.77	110.32
70%	37.09	122.29	83.15	129.17
80%	50.27	131.56	83.65	158.12