A Kinetic Study of the Solvent Effect of Aquo-EG reaction media on the Solvolysis of Methyl Iso-Butyrate

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ABSTRACT

The kinetic study of the solvent effect of alkali catalysed hydrolysis of mehyl iso-butyrate was studied in water-Ethylene Glycol media having varying composition of EG (from 0 to 60%). The rate of the reaction was found depleting with gradual addition of the organic content (EG) of the reaction media. All the three thermodynamic activation parameters of the reaction were found to be enhanced simultaneously with the addition of more and more Ethylene Glycol in the reaction media. From the simultaneous enhancement in three thermodynamic parameters, it has been inferred that the said reaction is enthalpy dominating and entropy controlled. From the plots of ΔH^* against ΔS^*, the iso-kinetic temperature of the reaction has been evaluated from the slope of the plot. The numerical value of its kinetic temperature of the reaction has been found to be $308.20 \approx 309$. From the value of iso-kinetic temperature, which is greater than 300, it has been inferred that there is considerable solvent-solute interaction in the reaction media in presence of EG in it.

Key Words:
Reaction media, Methyl Iso-Butyrate, Activation Energies, Thermodynamic Activation parameters, Iso-kinetic temperature.

Introduction:

Though the solvent effect on the rate and mechanism of the various types of the reaction have been reported[1-3], but very little attention has been paid towards the study the solvent effect on the thermodynamic activation parameters and solvent-solute interaction, particularly for ion-dipolar reaction. In order to highlight the above noted idea, it has been proposed to make a kinetic study of the solvent effect on the alkali catalysed hydrolysis of methyl iso-butyrate in water-EG media of various compositions ranging from 0 to 60% (v/v).

Experimental:

The kinetics of alkail catalysed hydrolysis of methyl isobutyrate has been carried out in water-EG media having different concentration of the EG varying from 0 to 60% (v/v) and at four different temperatures ranging from 25 to 40^{o}C at regular interval of 5^{o}C. The second order specific rate constant values of the reaction have been found decreasing with increase in EG content in the reaction media and these have been mentioned in Table - I.

The evaluated thermodynamic activation parameters have been tabulated in Table-II. The values of ΔH^* and ΔS^* at 30^{o}C have been inserted in

Table – III in order to evaluate the values of iso-kinetic temperatures of the reaction.

Results and Discussion:

Solvent effect on the Thermodynamic Activation parameters:

Like iso-composition and iso-dielectric activation energies (E_C and E_D), the other thermodynamic parameters such as enthalpy of activation ΔH*, entropy of activation ΔS* and free energy of activation ΔG* are also the better indicators of the solvent effects exerted by the solvent on the solvolysis reactions. These thermodynamic activation parameters have been calculated with the help of Wynne Jones and Eyring[4] equation. In order to evaluated ΔH*, log k/T values were plotted against -1/T. The plots were found to be linear and from the slopes of the straight lines which is equal to ΔH*, values were evaluated for different compositions of water EG media. For determining the values of $\frac{\Delta S^*}{2.303R}$, the equation of Absolute Rate Theory[5] in the following form was used:

$$\log k/T = \log\frac{\hbar}{h} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT}$$

By putting the values of $\log\frac{k}{T}, \log\frac{\hbar}{h}, \Delta H^*$, R and T in the above equation ΔS^* values were calculated. The free energy of activation were evaluated with the help of the equation:

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

The values of all these three thermodynamic parameters i.e. ΔH^*, ΔS* and ΔG* at different mol % of the organic component of the reaction media have been synchronized in Table - II. On careful observation of the data, it is found that ΔG* values increase from 71.77 kJ/mol to 77.15 kJ/mol with change of proportion of EG from 0 to 60%(v/v) at 30°C. Though the enhancement is not very large, however it cannot be ignored, rather it is quite considerable.

The report of Yagil and Anbar[6] indicated that OH^- ion of NaOH is hydrated with three molecules of water. In mixed aquo-organic co-solvent mixtures, organic component molecules are expected to contribute to the process of desolvation as they may be regarded as poor anion solvator in comparison to water. A similar variation in ΔG* values with increasing mol% of the organic co-solvent has also been reported in the past by Singh et al[7,8] , Rai et. al.[9], Cleavel[10] and Tommila[11]. It is obvious that ΔG* values increases smoothly with increasing mol% of EG. This gradual linear increase in ΔG* values with increase in mol% of the organic component in the reaction media is indicative of solvation or desolvation of reactants as explained by Absolute Reaction Rate Theory[5] and also reported by Elsemongy et. al.[12].

So far as the variation in ΔH* and ΔS* are concerned, it is clear from Table - II that both of them increase with increasing mol% of EG in the reaction media. However, on perusal of the Table - II, it is interestingly observed that all the three thermodynamic parameters of the reaction namely ΔG*, ΔH* and ΔS* are found to increase simultaneously with increase in mol % of organic component of the reaction media.

According to the relation,

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

it can be easily concluded that simultaneous increase in ΔG* values with increase in ΔH* and ΔS* value is only possible when the extent of enhancement in ΔH* values is greater than that found in ΔS* values. The regular enhancement to the greater extent in ΔH* values in comparison to the ΔS* values clearly indicates that the alkali catalysed hydrolysis of methyl iso-butyrate in water-EG media is enthalpy dominating and entropy controlled. Moreover, as found, the non linearity found in ΔS* curves with mol% of ΔG^* gives information of the fact that specific solvation is taking place in water-EG systems as reported by Saville et al.[13] and it also indicates that the random distributions of the components are not acceptable.

The similar non linear variations in ΔH* and ΔS* values with increasing mol % of the organic component in the reaction media have also been reported earlier by Tommila et al.[14], Singh and Jha[15] and in recent years by Sabita & Singh[16] and Hafizee and Singh[17].

Iso-Kinetic Relationship

Barclay and Butler[18] have developed an iso-kinetic relationship between enthalpy of activation ΔH* and entropy of activation ΔS* as follows:

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

where 'β' is a constant called iso-kinetic temperature and also known some times before as Leffler Grunwald[19] & Solvent stabilizer operator. Leffler[20] has pointed out that plot of ΔH* against ΔS* results in a straight line and the slope of the line gives the value of iso-kinetic temperature (β). He pointed out that many solvolysis reactions the values of slope of plots of ΔH* versus ΔS* come in between 300 and 400 and this foretells about the considerably interaction between solvent and solute of the reaction mixture.

In the present study also, plots of ΔH* versus ΔS* has been found linear which is conformity with Barclay-Butler relationship. The numerical value of the slope of the straight line is found to be 308.70 which is greater than 300. Thus in light of Leffler's guidelines, from the value of the slope, it can easily be concluded that there is considerable change in the structure of the reactant or in the solvent or in both the reactant and the solvent due to appreciable interaction between solvent and solute present in the reaction mixture (water-EG media) in the similar way as reported by Rakesh & Singh et. al[21], Raghaw & Singh[22] and Azad & Singh et. al.[23]. The structural changes with increasing proportion of the EG in water-EG media are responsible for the decrease in the specific rate constant values.

References

1. Singh B., Gupta A. K., Pathak D.B., Singh V. K., Singh Y.P and Singh R.T. : J. Indian. Chem. Soc., **66**, 377-379, 1989.
2. Singh, R.K., Kaushalendra, Sahay S. J. and Singh R. T. : A.R.J Phys. Chem., **8**, 77-80,2005
3. Mishra S. K. and Singh, R.T. : ARJ Phys. Chem., **2**, 119-122, 2006
4. Wynne-Jones W.F. K. and Eyring H.: J. Chem. Phys., **1**, 492, 1953
5. Glasstone S., Laidler K. J., and Eyring H. : “The Theory of Rate Process”McGraw Hill, : New York, 1941.
6. Yagil, Y. and Anbar, N.: J. Am. Chem. Soc., **85**, 2376, 1963
7. Singh A. K., Singh P. H., Singh S. B. and Singh R. T.: ARJ Phys. Soc., **1**, 75-78, 1998
8. Singh D. K., Sinha R., Singh R. I. and Singh R. T.: Ibid, **1**, 65-67, 2000

9. Rai C. L. and Singh R. T.: Ibid, **2**, 97-99, 1999
10. Cleave, NJ: Soumen Kemi **458**, 285, 1972
11. Tommilla E: Acta. Chem. Scand: **20**, 923, 1966
12. Elsemongy, M. M., Abu Elamayem, M. S. and Moussa, M. N. HZ.: Physik Chem. (Neue Folge) **94**, 69, 1975
13. Saville, B. J. and Hudson, R. F.: J. Chem. Soc., 4114, 1955
14. Tommila, E. and Mevikallio, E: Soumen Kemi, **26B**, 79, 1953
15. Singh Lallan, Singh, R. T. and Jha, R.C.: J. Indian. Chem. Soc., **57**, 1089, 1980
16. K. Sabita and Singh R. T.: GIS Science Journal, **10**, No. (8), 569-595, 2023
17. Hafizee N. K. and Singh R. T.: GIS Science Journal, **9**, No. (7), 417 – 429, 2022
18. Barclay, I. A and Butler, J. A.: Trans Faraday, Soc., **4**, 1445,1938 .
19. Leffler, J. E. and Grunwald, E.: "Rates of Equilibris in Organic Reactions" John Wiley & Sons, New York, 1963
20. Leffler J. E. : J. Org. Chern. 2P 1201, 1955
21. Singh R. K., Singh O.P. and Singh R.T.: Strad Research Journal, **10**, No (5), 01-07, 2023
22. K. Raghaw and Singh, R. T.: Journal of Xidian University, **9**, No. (1), 87-94, 2025
23. Azad R. K., Sharma S. P., Kumar N. and Singh R. T.: Journal of Xidian University, **19**, No. (8), 1190 – 1197, 2025

Table – I

Specific Rate Constant values of Alkali Catalysed Hydrolysis of Methyl Iso-butyrate in Water-EG media

$\mathbf{k \times 10^2 \, in \, (dm)^3 mol^{-1} \, min^{-1}}$

Temp in ^{0}C	**% of Ethylene Glycol (v/v)**						
	0%	**10%**	**20%**	**30%**	**40%**	**50%**	**60%**
25°C	142.00	103.00	58.00	36.00	24.00	14.00	7.45
30°C	204.00	154.00	100.90	71.00	47.00	32.00	19.00
35°C	295.00	251.00	160.70	129.00	85.90	65.00	47.00
40°C	381.00	340.00	276.00	224.00	170.00	131.00	115.00

Table – II

Values of ΔH^* in kJ/mol and $(\Delta S^* + 100)$ in J/K/mol at 30^{o}C in Water-EG Media

% of EG	Mol%	ΔH^* in k/J mol	$\Delta S^* + 100$ in J/K mol
0	0	52.30	32.82
10	3.47	58.24	55.64
20	6.96	78.16	117.19
30	12.16	89.90	153.35
40	17.73	97.70	175.31
50	24.42	110.71	215.10
60	32.64	138.28	301.72

Table – III

Variation of Thermodynamic Activation Parameters $(\Delta H^{*}, \Delta G^{*}$and $\Delta S^{*})$ with mol% of Ethylene Glycol in Water-EG media at different temperatures for alkali catalysed hydrolysis of methyl Iso-Butyrate of the reaction

$\Delta H^{*}$and ΔG^{*}in kJ/mol, ΔS^{*}in J/K/mol

% of Ethylene Glycol	Mol%	ΔH^{*} in kJ/mol	25^{O}C		30^{O}C		35^{O}C		40^{O}C	
			ΔG^{*}	ΔS^{*}	ΔG^{*}	ΔS^{*}	ΔG^{*}	ΔS^{*}	ΔG^{*}	ΔS^{*}
0%	0	52.30	70.88	-62.16	71.17	-62.18	71.46	-62.07	71.96	-62.78
10%	3.47	58.24	71.67	-44.94	71.88	-44.96	71.88	-44.17	72.30	-44.80
20%	6.96	78.16	73.09	17.04	72.93	17.19	73.01	16.71	72.80	17.04
30%	12.16	89.90	74.26	52.81	73.85	53.35	73.55	53.34	73.39	53.12
40%	17.73	97.70	75.27	75.38	74.05	75.31	74.64	74.97	74.10	75.52
50%	24.42	110.71	76.61	110.46	75.86	115.10	75.40	116.89	74.79	115.06
60%	32.64	138.28	78.15	201.72	77.15	201.72	76.15	201.68	75.10	201.82