STUDIES ON THE EFFECT OF WATER-DMF SOLVENT SYSTEMS ON THE THERMODYNAMIC FUNCTIONS OF AN ION-DIPOLAR SOLVOLYSIS REACTION

Namami Shankar Sudhanshu

Research Scholar, Department of Chemistry, V.K.S. University, Ara

Abstract

For studying the solvent effect of DMF, on the thermodynamic functions of alkali catalysed hydrolysis of methyl butyrate ester (Ion-dipolar reaction) the kinetics of the reaction was studied in different aqua-DMF media containing 30 to 80% DMF (v/v) at temperatures varying from 20 to 40°C.
The values of Iso-composition activation energy of the reaction were found to decrease with increasing proportion of DMF in the reaction media. The plausible explanation for such depletion is due to solvation and desolation of transition and initial states of the reaction respectively.
From the enhancement observed in ΔG* values with simultaneous decrease in the values of ΔH* and ΔS* of the reaction, it is inferred that the organic co-solvent DMF acts as entropy controlling solvent. The numerical value of Iso-kinetic temperature of the reaction. Which comes to be nearly 300 indicates that there is considerable solvent-solute interaction in the reaction media.

Key words: Organic content, Dielectric, Depletion, Solvation changes, Solvation and Desolvation, Entropy controlling, Mechanistic path ways, Solvent-solute interaction.

INTRODUCTION:

Though various researchers[1-4] in the field of kinetics have reported the effect of solvents on the rates, mechanism and the thermodynamic properties of simple esters, but, a little attention has been paid towards the studies of solvent effect of dipolar aprotic solvents on the thermodynamic activation functions, mechanism of the reaction and solvent-solute interaction for alkali catalysed solvolysis of esters having their biochemical utility in preparing scented food products and soft drinks.

In order to highlight the above noted facts, it has been proposed to study the kinetics of alkali catalysed hydrolysis of methyl butyrate, having the fruity smell in water DMF reaction media.

Experimental & Calculation: The kinetics of alkali catalysed hydrolysis of methyl butyrate was carried out separately in the different aqua-organic Co-solvent media (water-DMF) prepared by adding different volumes of organic co-solvent (30 to 80% v/v). The strength of the solution was kept 0.1 M with respect of NaOH and 0.05 M with respect to the ester. The

reaction was found to follow the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table - I.

Using Arrhenius equation, the iso-composition activation energy values of the reaction were evaluated and are recorded in Table - II.

The thermodynamic activation parameters such as ΔH^*, ΔG^* and ΔS^* have been evaluated using Wynne-Jones and Eyring equation[5]. And their consolidated values have been shown in Table - III.

RESULTS AND DISCUSSION:

Effect of Solvent on the Specific Rate Constant:

In order to elaborate the effect of the solvent on the specific rate constant values of the reaction, the log k values were plotted against the mole % of the organic co-solvent (DMF) and were found to follow decreasing trends. However, the depletion found in the rate with increasing mole % of the organic co-solvent at all the temperatures follows smooth path following two intersecting straight lines having different numerical values of the slope (of similar nature) before and after the point of intersection at about 26 mole % of DMF in the reaction media. From the plots, it was found that with increasing the temperature of the reaction, the rate of depletion in the rate becomes deeper or sharper. After all, in the light of the views of Elsemongy[6] and Singh et[7,8]. The decrease observed in the specific rate constant values with different values of slopes may be attributed partly due to the dielectric effect of the media and partly due to solvation changes taking place in the reaction media.

Effect of Solvent on the Iso-composition Activation Energy:

On perusal of the data mentioned in Table - II, it is observed that the value of iso-composition activation energy of the reaction go on decreasing from 69.46 kJ/mole to 17.31 kJ/mole with increasing concentration of DMF from 30 to 80% (v/v), in the reaction media.

The depleting trend in E. values of the reaction in water-DMF media may be due to either of the following three causes:

(i)   The transition state is solvated and the initial state is desolated.

(ii)   The initial state is more desolated than the transition state.

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

Among these three factors, the third factor seems to be operative in this case as from the values of thermodynamic activation parameters of the reaction in Table-III both ΔH^* and ΔS^* values of the reaction are found to decrease with increasing proportion of DMF in the

reaction media (ΔH^* values decreases from 62.63 kJ/mole to 13.92 kJ/ mole and ΔS^* values deplete from -85.81J/K/mole to -258.18J/K/mole at 30°C). Similar such findings and their interpretations also are in accordance with Kumari & Singh et al[9].

Solvent Effect on Thermodynamic Activation Parameters:

From Table-III on perusal of the values of thermodynamic activation parameters, namely $\Delta G^*, \Delta H^*$ and ΔS^*, it is found that ΔG^* values (free energy of activation) of the reaction increases with simultaneous decrease in its ΔH^* and ΔS^* values. At 30°C, ΔG^* values have been observed increasing from 88.63 k cal/mole to 92.15 k cal/mole with increasing concentration of dimethyl form amide (DMF) from 30 to 80% (v/v) in the reaction media. Though this enhancement is not very large, however, it is quite considerable.

From the plots of ΔG^* values against mole % of DMF, it is found that ΔG^* values go on increasing non-linearly with gradual addition of DMF in the reaction media. This finding is indicative of desolation of reactants as explained by Elsemongy et al[10].

So far as the variations in ΔH^* and ΔS^* are concerned on observing their values from Table it is interestingly found that both of them decrease with gradual addition of DMF in the reaction media.

From the thermodynamic relation:

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

it can be easily concluded that simultaneous increase in ΔG^* values, with decrease in both of ΔH^* and ΔS^* is only possible when ΔS^* values deplete more than AH* values. From such findings, it is inferred that in presence of DMF in the reaction media, the alkali catalysed hydrolysis of methyl butyrate becomes entropy controlled reaction.

Moreover, non-linear variations in ΔH^* and ΔS^* values with increasing mole % of DMF in the reaction media gives information of the fact that the specific solvation is taking place in water-DMF systems similar to that as reported by Saville et al[11]. and recent report of Singh et al.[17]

Solvent Effect on Iso-kinetic Temperature and Solvent-Solute Interaction in the Reaction Media:

The value of the Iso-kinetic temperature of the reaction was evaluated by using Barcley-Butler relationship[13] which is expressed as-

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

It is a straight line equation representing the relationship between enthalpy and entropy of activation values of the reaction. 'β' is known as iso-kinetic temperature. From the values of ΔH* and ΔS* values available in Table - IV, the plots of ΔH* versus ΔS* at 30°C were made. From the slope of the straight line of the plots, the value of the kinetic temperature was evaluated to be 298.4 = 300. Thus, in the light of Lefller's[14] guidelines, from the values of the iso-kinetic temperature (which is approximately 300), it can safely be concluded that there is considerable change in the structure of the reactant or in the solvent or in both the reactant and solvent due to considerable interaction between solvent and solute present in the reaction media (water - DMF) in the similar way as reported earlier by Singh & Singh et al[15] and recently also by Sushma & Singh et al[16].

References:

1.   *Singh, Lallan, Singh, R.T.,*   :   *J. Indian Chem. Soc.,*
     Singh, R. and Jha, RC   **55**, *372, 1978*
2.   *Kiranmayee and Singh, R. T. :   Asian Journal of Chemistry,*
                                      18, *No. 2, 1050-1054, 2006*
3.   *Tauheed, S., Haider, S.R.*   :   *ARJ Phys. Sci.,* **10**, *No. (1-2)*
     and Singh, R.T.   *201-204, 2007*
4.   *Tabassum, N., Upadhyay, M. K.,* :   *NIRJ Sci.,* **1**. *No.(1), 115-118,*
     Singh, A. K. and Singh, R. T.   2008
5.   *Wynne-Jones, W. F.K.   :   J. Chem. Phys.* **3**, *492, 1935*
     and Eyring, H.
6.   *Elsemongy, M.M.*   :   *Z. Physik. Chem. (Neue Folge)*
                                      84, *295, 1973*
7.   *Singh, Lallan, Singh, R. T. :   J. Indian Chem. Soc,*
     and Jha, R. C.   **58**, *966-969, 1981*
8.   *Singh, A. K., Rai, C. L., :   ARJ Phys. Sci.,* **11**, *No. (1-2),*
     Singh, Y. P. and Singh, R. T.   167-170, 2008
9.   *Kumari, K., Pandey, S., :   NIRJ Sci.,* **4**, *87-94, 2010*
     Singh, A. and Singh, R.T.
10. *Elsemongy, M. M.*   :   *Z. Physik. Chem. (Neue Folge)*
     Elamayam, M. S. and   **84**, *295, 1973*
     Moussa, M. N. H.
11. *Saville, B.J. and Hudson, R. F.: J. Chem. Soc.,* **4114**, *1955*
12. *Kumari, K., Upadhyay, M. K., : NIRJ Sci.,* **4**, *65-72, 2010*
     Kumar, A. and Singh, R.T.

13. *Barclay, 1. A. and Butler, J. A. V. : Trans, Faraday Soc.,* **34**, *1445,1938*
14. *J. E. Leffler   : J. Org. Chem.,* **20**, *1201, 1955*
15. *Singh, P., Pathak, S.N.   : ARJ Phys. Sci.,* **11**, *No. (1-2)*
     Singh, A. K. and Singh, R. T.   151-154, 2008
16. *K Sushma, Ranjan R.K and Singh RT: IJESM* **7**, *No(2), 147-162 2018(Feb)*

Table-1 Alkali catalysed hydrolysis of Methyl-butyrate in water-DMF media

$k \times 10^2$ **in** $(dm)^3$ **mole^{-1} min^{-1}**

Temp in ^{o}C	% of t-butanol					
	30%	40%	50%	60%	70%	80%
20° C	83.33	61.94	53.22	48.89	44.78	39.36
25° C	128.97	93.78	77.62	63.74	55.33	44.59
30° C	199.89	151.57	115.12	85.27	61.92	49.45
35° C	316.96	219.28	152.34	97.86	83.37	56.36
40° C	493.17	316.00	208.15	135.52	92.07	60.94

Table –II Values of Iso-composition Activation Energy of the reaction at different concentrations of DMF media.

% of DMF	30%	40%	50%	60%	70%	80%
E_C value in kJ/mole	69.46	61.45	50.98	37.02	27.65	17.31

Table -III

Consolidated Values of Free energy activation (∆G*), Enthalpy of activation (DH*) and

Entropy of activation (∆S*) in water-DMF media.

∆H* and ∆G* in kJ/mole, ∆S* in J/K/mole

% of DMF (v/v)	Mole % of DMF	∆H*	20°C		25°C		30°C		35°C		40°C	
			∆G*	-∆S*	∆G*	-∆S*	∆G*	-∆S*	∆G*	-∆S*	∆G*	-∆S*
30%	9.12	62.63	87.74	85.70	88.21	85.84	88.63	85.81	88.96	85.49	89.29	85.18
40%	13.50	60.74	88.48	94.68	89.00	94.83	89.32	94.32	89.90	94.67	90.45	94.92
50%	18.96	50.63	88.85	130.44	89.47	130.34	90.02	130.00	90.83	130.52	91.54	130.70
60%	25.98	37.34	89.06	176.52	89.96	177.58	90.77	176.34	91.96	177.34	92.65	170.71
70%	35.27	25.82	89.27	216.55	90.35	216.54	91.58	217.03	92.38	216.16	93.66	216.74
80%	48.29	13.92	89.58	258.22	90.84	258.12	92.15	258.18	93.38	257.99	94.73	258.18