

The Comparative Kinetic Studies of the solvating efficiencies of Mano and Dihydric Alcohols on the catalysed Hydrolysis of Butyrate Ester

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Abstract

The solvating efficiencies of two different organic co-solvents namely methyl alcohol and ethylene glycol have been studied by studying the kinetics of alkali catalysed hydrolysis of methyl butyrate in water-MeOH and water-EG media having different concentrations of two different organic co-solvents. The solvating efficiency of the two different organic co-solvents were compared by evaluating the number of water molecules associated with the activated complex. and also by determining the activation energies of the reaction in the two reaction media. It has been inferred that MeOH in water-MeOH media causes the equilibrium of water to be shifted from its bulky form to dense form while ethylene glycol in water-EG media acts in the reverse manner. It has also been concluded that MeOH in water-MeOH media solvates the initial state but desolvates the transition state, but Ethylene glycol in water-EG media has the opposite solvating power to that of methyl alcohol (MeOH).

Keywords: Solvation efficiencies, dihydric alcohol, solvation number, specific solvation, dielectric and solvation effect, Mechanistic path, Iso-composition and iso-dielectric, Enhancement, Depletion.

Introduction

The alkali catalysed hydrolysis of methyl butyrate was kinetically studied separately in the two reaction media namely water-MeOH and water-EG having different concentration (from 30 to 80%(v/v)) of the organic co-solvent (MeOH and EG) at five different temperatures ranging from 20 to 40°C.

The reaction was found to follow the second order kinetic path in both the reaction media. The specific rate constant values of the reaction have been reported in Table-I and II for water-MeOH and water-EG media respectively. The number of the water molecules associated with the activated complex of the reaction were evaluated using Robertson Equation' and have been mentioned the Table-III and IV for water-MeOH and water-EG media respectively. Similarly, the values of iso-composition activation energy of the reaction in the two media have been calculated

Table – I Values of Specific Rate Constant for Alkaline Hydrolysis of Methyl Butyrate in water-MeOH media.
 $k \times 10^2$ in $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$

Temp in °C	Percentage concentration of MeOH (v/v)					
	30%	40%	50%	60%	70%	80%
20°C	106.70	89.8	66.07	51.12	37.33	20.95
25°C	154.61	130.20	110.61	77.45	57.69	37.76
30°C	220.14	180.20	150.11	125.02	98.41	62.20
35°C	319.84	268.41	225.21	190.10	160.23	102.58
40°C	461.20	399.40	325.40	300.05	244.91	169.43

Table – II Values of Specific Rate Constant for Alkaline Hydrolysis of Methyl Butyrate in water-Ethylene glycol (EG) media.
 $k \times 10^2$ in $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$

Temp in °C	Percentage concentration of EG (v/v)					
	30%	40%	50%	60%	70%	80%
20°C	85.50	67.60	50.85	33.19	20.89	11.75
25°C	114.40	92.50	70.40	43.65	28.19	14.45
30°C	159.00	130.10	90.50	54.20	34.10	16.98
35°C	208.93	165.40	118.40	72.61	42.30	20.40
40°C	296.71	218.40	163.20	95.63	52.58	24.01

From the Arrhenius plots of $\log k$ values against $1/T$ and have been shown in Table-V and VI for water-EG media respectively.

Results and Discussion

Effect of solvating efficiency of the solvent on the rate of reaction

From table I and II, it is obvious that in both the reaction media, the rates of reaction go on depleting with addition of more and more organic co-solvent (MeOH/EG) in the reaction media. In water-MeOH media, the extent of depletion is more than that observed in water-EG media. At 30°C, the rates of the reaction depletes from $220.14 \times 10^2 \text{ dm}^3 \text{ mole}^{-1}$ to $62.10^2 \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$ with increasing concentration of MeOH from 30 to 80% (v/v) in water-MeOH media. On the other hand, in water-EG media, the rate of the reaction depletes from $159.00 \times 10^2 \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$ to $16.98 \times 10^2 \text{ dm}^3 \text{ mole}^{-1} \text{ min}^{-1}$ with increasing concentration from 30 to 80% (v/v) of EG in water-EG media. Thus in water-MeOH media, there is depletion of 157.94 units in the rate where as water-EG media the rate of reaction decreases up to 142.02 unit with increasing organic content from 30 to 80% (v/v) in the reaction media at 30°C. Thus, in the light of the above noted observations, it is inferred that MeOH in water-MeOH media has more retarding capacity in the rate of reaction than that of ethylene glycol in water-EG media.

Effect of Solvating Power on the number of water molecules associated with the activated complex and on the mechanism of the reaction

The effect of water concentration $[\text{H}_2\text{O}]$ of the water-MeOH mixture, on the rate and mechanism of alkaline hydrolysis of methyl butanoate has been studied in the light of the guidelines and observations rendered by Tommila et al., Lane and Elsemongy et al. They have established an idea of the number of water molecules taking part in the formation of activated complex. The number of water molecules associated with the activated complex has been determined by plotting $\log k$ against $\log [\text{H}_2\text{O}]$ according to the relation proposed by Robertson¹.

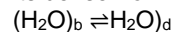
$$\log k = \log k_0 + n \log [\text{H}_2\text{O}]$$

Here, 'n' is the solvation number which tells about the criteria for studying about the mechanism of the reaction.

It is obvious from the plots of $\log k$ versus $\log [\text{H}_2\text{O}]$ that at all the five temperatures at which the kinetics were studied, straight lines with different

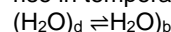
values as mentioned in Table-III are obtained. From the values of slopes as mentioned in Table-III, it is inferred that the number of water molecules associated with the activated complex vary from 1.48 to 0.88 with rise of temperature,

These observations may be attributed to the fact that equilibrium shifts from bulky form of water to its dense form with the rise of temperature.



The numerical values of straight lines for the plots of $\log k$ versus $\log [\text{H}_2\text{O}]$ in water-EG media for each temperature have been tabulated in Table-IV.

From the above noted values of the slopes in Table -IV, it may be inferred that in water-EG media, the number of water molecules involved in the formation of activated complex varies from 1.6 to 2.1 as the temperature rises from 20 to 40°C. These inferences may be attributed to the fact that equilibrium shifts from dense water to bulky water with rise in temperature.



These observations and accordingly the inferences are against to that found in the case of water-MeOH media,

Table-III The values of slopes of the plots of $\log k$ versus $\log [\text{H}_2\text{O}]$ in water-MeOH media.

Temp.in °C	Slopes
20°C	1.476 (1.48)
25°C	1.240
30°C	1.128
35°C	0.994
40°C	0.878 (0.88)

Table-IV The values of slopes of the plots of $\log k$ versus $\log [\text{H}_2\text{O}]$ in water-EG media.

Temp.in °C	Slopes
20°C	1.61
25°C	1.75
30°C	1.92
35°C	2.00
40°C	2.10

From depleting and enhancing trends in the number of molecules of water associated with the activated complex of the reaction respectively in the water-MeOH and water-EG media, it is inferred that presence of MeOH in water-MeOH media shifts the equilibrium of water from bulky form to dense form and similarly ethylene glycol in water-EG media shifts the water equilibrium from its dense form to bulky form with rise of temperature of the reaction from 20 to 40°C.

In the light of findings of Robertson¹ and Mishra et al⁵ and from above noted trends, it is also concluded that solvating power of MeOH changes the mechanism of the reaction from unimolecular to bimolecular and that of ethylene glycol changes the mechanism of the reaction in water EG media in opposite manner i.e., from bimolecular to unimolecular.

Effect of Solvation power of the solvent on Iso-composition Activation Energy:

Using Arrhenius formula,

$$k = A e^{-E/RT}$$

The iso-composition activation energy for alkaline hydrolysis of methyl butanoate in aquo-MeOH water-EG media were evaluated from the values of slopes of the linear plot of log k values against 1/T. From the value of slopes of the straight lines, the values of the iso-composition activation energy have been calculated and are enlisted in Table - V and VI respectively for water-MeOH and water-EG media.

After Inaking observation of the values of E_{exp} values of the reaction in water-MeOH Inedia from Table -V, it is clear the E_{exp} values increase with increase in the concentration of MeOH in the reaction media. With the addition of methyl alcohol from 30 to 80%(v/v) in the reaction media, there is enhancement in the E_{exp} values from 56.36 kJ/mole to 82.45 kJ/mole. It

Table - V

Values of Iso-composition Activation Energy(E_{exp}) at different composition of water-MeOH media.

% of MeOH (v/v)	30%	40%	50%	60%	70%	80 %
E_{exp} in K/J/mole	56.3 6	60.8 9	64.6 1	68.2 2	74.4 1	82. 45

Table - VI

Values of Iso-composition Activation Energy (E_{exp}) at different composition of water-EG media.

% of EG (v/v)	30%	40%	50%	60%	70%	80%
E_{exp} in k/J/mole	51.1 9	47.2 4	45.5 3	41.9 9	37.0 3	27.0 6

has been established that changes in the values of activation energy are obviously noticeable only when the solvation changes take place either at initial state level or at the transition state level or at both the levels. The increase in the activation energy with decrease in the specific rate constant value seems to be quite natural. The following three possibilities may be held responsible for increase in the E_{exp} values :

1. The initial state is more solvated than the transition state,
2. The transition state is more desolvated than the initial state, and
3. The initial state is solvated and the transition state is desolvated.

Out of the three factors, the third one seems to be applicable in our case and this factor is supported by the increase in the values of entropy of activation [(from-181.10 J/k/mole to -9.52 J/k/mole at 30°C with increase in MeOH content from 30 to 800/0 (v/v)) in the reaction media. This Conclusion has also been supported by Singh et al.⁵

From the data mentioned in Table-VI, it is interesting to note that E_c values decreases from 51.19 kJ/mole to 27.06 kJ/mole with increasing proportion of EG in the waterEG mixtures.

The depleting trend in the E_{exp} values can be explained by either of the following three situations:

1. The transition state is less desolvated than the initial state
2. The initial state is less solvated than the transition state, and
3. The initial state is' desolvated and the transition state is solvated.

Out of these three factors (situations), the third factor seems to be operative as both ΔH^* and ΔS^* values of the reaction were found to decrease with increasing EG content in the water-EG media. ΔH^* depletes

from 46.99 kJ/mole to 26.02 kJ/mole and ΔS^* depletes from-120.31 J/k/mole to - 207.53 J/k/mole with increasing content of EG from 30 to 80% in the reaction media at 30°C. Our inference has also been in support of the findings of Sinha et al⁶.

On the basis of enhancement and depletion in the values of activation energy of the reaction due to addition of Methyl alcohol and ethylene glycol respectively in water-MeOH and water-EG media, it is inferred that methyl alcohol has the solvating power to solvate the initial state and to desolvate the transition state where as ethylene glycol has the opposite solvating power to that of methyl alcohol. these inferences have been reported earlier by Elsemongy⁷ Kiranmeyee and Singh⁸ and recently also by Rashmi & Singh et al⁹ and also by Abhay & Singh et al¹⁰, Namrata & Singh et al¹¹ and Sunita & Singh et al¹².

Aim of the study

On hydrolysing, Butyrate ester, butyric acid is produced, which is widely used for manufacturing food and perfume additives in the form of flavouring agent.

The aim of the present study (research) is to identify a solvent whose solvating efficiency is such that on hydrolysing the ester (methyl butyrate) in presence of that solvent in the reaction media, more and more butyric acid is produced.

Conclusion

After making Comparative kinetic studies on the alkali catalysed hydrolysis of methyl butyrate separately in aquo-methanol(monohydric alcohol) and aquo-Ethylene glycol (dihydric alcohol) it is concluded that monohydric alcohol has more solvating efficiency than dihydric alcohol.

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