Studies on the effect of Dielectric constants of Aquo-DMF Solvent- System of the Solvolysis Products of Nicotinates

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Abstract

From the enhancement observed in ΔG* values with simultaneous decrease in the values of ΔH and ΔS* of the reaction, it is concluded that the organic co-solvent dimethyl formamide (DMF) acts as entropy controller and enthalpy stimulator solvent for alkali catalysed solvolysis of Methyl nicotinate.

Form the evaluated values of water molecules associated with the activated complex of the reaction which are found to increase with increase in the temperature of the reaction, it is inferred that the bimolecular mechanistic path is changed to unimolecular in presence of the organic component (DMF) of the reaction media. The numerical value of Iso-Kinetic temperature of the reaction which comes to be nearly 287.5 (below 300) indicates that there is weak but considerable solvent-solute interaction in the aquo-DMF solvent system.

Key words: Dielectric Constants Solvent- Systeme, Solvolysis, Mechanism, Solvation number, unimolecular, Biomolecular, Transition State.

Introduction

Though a large number of kineticists¹² of the kinetic have reported the effect of solvents on the rates, mechanism and the thermodynamic properties of hydrolysis of simple esters, but, a little attention has been paid towards the studies of solvent effect of dipolar aprotic solvent-Dimethyl formamide (DMF) on the rate, mechanism and thermodynamic activation parameters of the reaction and solvent-solute interaction for alkali catalysed solvolysis of nicotinate esters which has medicinal potential and industrial uses for being used as insecticides which enhance yield of agricultural products.
Experimental & Calculation

The kinetics of alkali catalysed hydrolysis of Methyl nicotinate was carried out separately in the different aquo-organic co-solvent media (aquo-DMF) prepared by adding different volumes of DMF (20 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 1. For studying the effect of changes of concentration of organic component (DMF), the variation of log k values of the reaction with mol% of acetone in the reaction media has been enlisted in Table 2. Using Arrhenius equation, the iso-composition and iso-dielectric activation energies values of the reaction were evaluated and are recorded respectively in Table 3 & 4. The thermodynamic activation parameters such as $\Delta H^*$, $\Delta G$ and $\Delta S^*$ have been evaluated using Wynne-Jones and Eyring equation and their consolidated values have been shown in Table 5.

For studying the mechanism of the reaction, the number of water molecules associated with the transition state of the reaction in reaction media at different temperatures have been evaluated by the use of Robertson equation and are depicted in Table 6.

### Table 1

Specific rate constant values of Alkali catalysed hydrolysis of Methyl nicotinate in water-DMF media

| Temp in °C | % of DMF (v/v) | $k \times 10^2$ in $(dm)^3$ mole$^{-1}$min$^{-1}$ |
|------------|----------------|---------------------------------------------|
|            | 20%            | 30%            | 40%            | 50%            | 60%            | 70%            | 80%            |
| 20°C       | 40.82          | 37.72          | 34.86          | 32.82          | 30.70          | 27.87          | 25.12          |
| 25°C       | 86.38          | 77.37          | 68.85          | 62.13          | 55.26          | 47.91          | 41.51          |
| 30°C       | 184.29         | 157.62         | 136.36         | 118.09         | 99.68          | 83.14          | 67.78          |
| 35°C       | 371.19         | 306.97         | 257.22         | 213.99         | 174.22         | 138.23         | 108.02         |
| 40°C       | 741.65         | 605.48         | 488.43         | 391.20         | 302.41         | 234.15         | 170.70         |

### Table 2

Variation of log k values of the reaction at different temperatures with mol% of DMF in water-DMF media.

| % of DMF (v/v) | Mol % of DMF | 2 + log k values |
|----------------|--------------|-----------------|
|                |              | 20°C            | 25°C            | 30°C            | 35°C            | 40°C            |
| 20%            | 5.53         | 1.1609          | 1.9364          | 2.2655          | 2.5696          | 2.8702          |
| 30%            | 9.12         | 1.5766          | 1.8886          | 2.1976          | 2.4871          | 2.7821          |
| 40%            | 13.50        | 1.5423          | 1.8379          | 2.1347          | 2.4103          | 2.6888          |
| 50%            | 18.96        | 1.5161          | 1.7933          | 2.0722          | 2.3304          | 2.5924          |
| 60%            | 25.99        | 1.4871          | 1.7424          | 1.9986          | 2.2411          | 2.4806          |
| 70%            | 35.27        | 1.4451          | 1.6802          | 1.9198          | 2.1406          | 2.3695          |
| 80%            | 48.29        | 1.4000          | 1.6182          | 1.8311          | 2.0335          | 2.2314          |
Table 3.
Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction in water-DMF media

| % of DMF (v/v) | 20% | 30% | 40% | 50% | 60% | 70% | 80% |
|---------------|-----|-----|-----|-----|-----|-----|-----|
| E_c value in kJ/mol | 111.04 | 106.52 | 101.73 | 96.26 | 88.72 | 81.97 | 73.61 |

Table 4
Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction at Different Desired "D" values of the water-DMF media

| D values | D = 50 | D = 55 | D = 60 | D = 65 | D = 70 | D = 75 |
|----------|--------|--------|--------|--------|--------|--------|
| E_c value in kJ/mol | 78.91 | 88.52 | 96.74 | 107.00 | 115.36 | 124.39 |

Table 5
Consolidated Values of Enthalpy of activation (\(\Delta H^*\)), Free energy of activation (\(\Delta G^*\)) and Entropy of activation(\(\Delta S^*\)) of the reaction at different mol % of DMF in water-DMF media

| % of DMF (v/v) | Mole | \(\Delta H^*\) in kJ/mol | 20°C | 25°C | 30°C | 35°C | 40°C |
|----------------|------|--------------------------|------|------|------|------|------|
|                |      |                          | \(\Delta G^*\) | \(\Delta S^*\) | \(\Delta G^*\) | \(\Delta S^*\) | \(\Delta G^*\) | \(\Delta S^*\) | \(\Delta G^*\) | \(\Delta S^*\) | \(\Delta G^*\) | \(\Delta S^*\) | \(\Delta G^*\) | \(\Delta S^*\) | \(\Delta G^*\) | \(\Delta S^*\) |
| 20%            | 5.53 | 107.73                   | 83.88 | 81.38 | 83.50 | 81.31 | 83.03 | 81.50 | 82.65 | 81.42 | 82.23 | 81.45 |
| 30%            | 9.12 | 104.19                   | 84.08 | 68.66 | 83.77 | 68.52 | 83.43 | 68.54 | 83.14 | 68.36 | 82.76 | 68.47 |
| 40%            | 13.50| 98.60                    | 84.27 | 48.91 | 84.06 | 48.78 | 83.75 | 49.00 | 83.59 | 48.73 | 83.32 | 48.81 |
| 50%            | 18.96| 92.22                    | 84.42 | 26.65 | 84.32 | 26.54 | 84.15 | 26.63 | 84.06 | 26.49 | 83.90 | 26.60 |
| 60%            | 25.98| 86.39                    | 84.58 | 6.17  | 84.61 | 5.98  | 84.58 | 5.96  | 84.59 | 5.84  | 84.57 | 5.81  |
| 70%            | 35.27| 79.79                    | 84.81 | -17.16| 84.96 | -17.36| 85.04 | -17.33| 85.18 | -17.52| 85.24 | -17.41|
| 80%            | 48.29| 71.08                    | 85.07 | -47.73| 85.32 | -47.76| 85.55 | -47.83| 85.81 | -47.86| 86.06 | -47.86|

Table 6
Values of the slopes of the plots of log k versus log [H_2O] values at different temperatures

| Temperature in °C | Slope - IBefore log [H_2O] value 1.398 | Slope - IIAfter log[H_2O] value1.398 |
|-------------------|------------------------------------------|-------------------------------------|
| 20°C              | 0.369                                    | 0.453                               |
| 25°C              | 0.413                                    | 0.752                               |
| 30°C              | 0.558                                    | 1.072                               |
| 35°C              | 0.676                                    | 1.177                               |
| 40°C              | 0.816                                    | 1.447                               |
Results and Discussion

Effect of Solvent on the Specific Rate Constants of the Reaction:

In order to highlight 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 (their values from Table 2) 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 follow smooth path following two intersection straight lines at about 21.00 mol % of DMF having different numerical values of the slope (of similar nature) before and after the point of intersection (at about 21.00 mol % DMF in the reaction, the degree of depletion in the rate constants of the reaction becomes slower or shallow.

However, the possible rate depleting factors in the rate can be listed as follows:
(i) decrease in the bulk dielectric constant value of the medium.
(ii) decrease in the polarity of the reaction media on adding less polar DMF to it.

The above noted two depleting factors are quite in operation and this is quite in agreement with the theory of Hughes and Ingold that the rate ought to decrease with decreasing dielectric constant of the reaction media.

Such decrease in rate constant with increasing proportion of the organic co-solvent like DMF have also been reported earlier by Anantkrishnan et al. Essemongy et al and recently also by Akanksha & Singh et al. However, the decrease observed in the specific rate constant values with different numerical values of slopes may be attributed partly due to the dielectric effects of the reaction media and partly due to solvation changes taking place in it (aquo-DMF) reaction media.

Effect of Solvent on the Iso-composition Activation Energy (EC) of the Reaction:

On perusal of the data mentioned in Table 3, we observe that the value of Iso-composition activation energy of the reaction go on decreasing from 111.04 kJ/mol to 73.61 kJ/mol with increasing concentration of DMF from 20 to 80% (v/v), in the reaction media. The depletion Ec values of the reaction in water-acetone media may be due to either of the following three causes:
(i) The transition state is solvated and the initial state is desolvated,
(ii) The transition state is more solvated than the initial state, and
(iii) The transition state is less desolvated than the initial state.

Among these three factors, the first factor seems to be operative in this case as from the values of thermodynamic activation parameters of the reaction in Table 5, both DH* and DS* values of the reaction are found to decrease with increasing proportion of DMF in the reaction media (DH* values decreases from 107.18 kJ/mol to 71.08 kJ/mol and DS* values decreases from 81.50 J/K/mol to -47.76 J/K/mol at 30°C).

Our such findings and their interpretations have been found in accordance with the earlier reports of Singh & Perween et al. and also with the recent reports of Sharma & Singh et al.

Solvent Effect on the Iso-dielectric energy (ED) of the reaction:

From the values recorded in Table 4, it appears that ED values of the reaction go on increasing with increasing dielectric constant values of the aquo-DMF reaction media. The ED value is 78.91 kJ/mol at D value 50 and increases to 124.39 kJ/mol at D value 75. The enhancement in the ED values with increase in D values of the reaction media is in accordance with depletion in Ec or Eexp values of the reaction with increasing mol % of DMF in the reaction media. These findings and conclusions have been found in support of the earlier reports of Wolford and also with the recently reported findings by Haider & Singh et al.

Solvent Effect on Thermodynamic Activation Parameters of the Reaction:
From Table 5, on perusal of the values of thermodynamic activation parameters, namely $\Delta G^*$, $\Delta H^*$ and $\Delta S^*$, it is observed that $\Delta G^*$ values (free energy of activation) of the reaction increases with simultaneous decrease in its $\Delta H^*$ and $\Delta S^*$ values. At 30°C, $\Delta G^*$ values have been observed increasing from 83.03 k cal/mol to 85.55 k cal/mol with increasing concentration of DMF from 20 to 80% (v/v) in the reaction media. Though this enhancement is not very large, however, it is quite considerable and acceptable too. In order to highlight the effect of changing concentration of the organic content (acetone) in the reaction media, $\Delta H^*$, $\Delta G^*$ and $\Delta S^*$ values were plotted against the changing mol % of DMF in the reaction. From the plots of $\Delta G^*$ values against mol % of DMF, it is found that $\Delta G^*$ values go on increasing non-linearly with gradual addition of acetone in the reaction media. This finding is indicative of desolvation as explained by Elsemongy et al.\textsuperscript{14}

So far as the variation in $\Delta H^*$ and $\Delta S^*$ are concerned on observing their values from Table 5 and their plots against mol % of DMF, it is interestingly found that both of them decrease linearly and non-linearly respectively 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 increase in $\Delta G^*$ values with simultaneous decrease in both of $\Delta H^*$ and $\Delta S^*$ values is only possible when $\Delta S^*$ values decreases more than $\Delta H^*$ value. From such findings, it is inferred that in presence of acetone in the reaction media, the alkali catalysed hydrolysis of Methyl nicotinate becomes entropy controlled and enthalpy stimulate reaction. moreover, linear variation in $\Delta H^*$ and non-linear variation in $\Delta S^*$ values with increasing mol % of DMF, gives information of the support of the recent observation and inferences of Dheeraj & Singh et al.\textsuperscript{16}.

Conletion

Due to weak but considerable intection in aquo-DMF reaction media the solvent DMF is acceprable solvent for nicotinates and it will act effectively as in secticide in presence of DMF.

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