

A Thermodynamic Study of the Reaction between Two Hypiodite Ions in Ethanol-water Mixed Solvents

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Summary: The rate of reaction between two hypiodite ions in aqueous ethanol mixtures at 275 K is retarded by increasing the ethanol content of the medium. The closest distance of approach of reacting ions indicate that the shape of the activated complex is more similar to a double sphere model. Electrostatic and non-electrostatic (kJ/mole) contributions to the changes in free energy of activation are 12.4 and 80.45 in 0.156 mole fraction of ethanol and 7.54 and 82.66 in water. A change in entropy from -34.9 J/K/mole in water to -57.40 J/K/mole in 0.156 mole fraction of ethanol indicate that a highly ordered activated complex is formed at a higher concentration of ethanol in the mixed solvents. The logarithm of the rate constant is found to be a linear function of $1/E^{1/2}$ in the proposed equation.

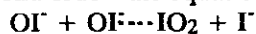
Introduction

The thermodynamic parameters which are affected by the transfer of electrolytes from aqueous to organo-aqueous mixtures have been shown to vary with the bulk property namely, the dielectric constant (E) of the medium [1]. Significant changes in the structure and dielectric properties of water occur upon the addition of alcohol to it. Several expressions based on different models of ionic interactions have been proposed by many research workers for predicting the rate of reaction to the variations of dielectric constant of the medium [2]. These expressions predict a linear relationship between the logarithm of the rate constant and $1/E$ or $E-1/2E+1$. For ion-dipole interactions, "Amis" equation relate the logarithm of rate constant to $1/E$ and to the dipole moment (μ) of the activated complex [3].

The effect of the addition of ethanol to aqueous solutions in the evaluation of thermodynamic parameters for the iodate-bromide reaction was reported in the previous study [4]. In the present study, the effect of dielectric constant variations on the kinetics and on the changes in activation parameters of the reaction between two hypiodite ions in aqueous ethanol mixed solvents is reported. Also, the application of the modified form of "Amis" equation on the kinetics of ionic reaction has been examined in the above reaction.

The reaction between two hypiodite ions in solution takes place at measurable rates at 275 K. The kinetics and the mechanism of the reaction has

been reported in literature [5]. The reaction follows a second order rate equation,



Hence,

$$k = 1/t \cdot x/a(a-x).$$

Where,

a = initial concentration of iodite ion,

x = conversion of iodite ion after time 't'.

Experimental

A Unicam SP 8000 Spectrophotometer with thermostatic attachment was used to follow the reaction, and a maximum wavelength of 365 nm was used to estimate iodite estimation. The molar absorptivity and maximum absorption wavelength of IO_2^- in aqueous and aqueous ethanol mixtures were predetermined with standard solutions. Independent experiments showed that the "Beer's Law" is obeyed in aqueous ethanol mixed solvents. All absorption measurements were taken within half an hour each experimental run. Matched quartz cuvettes were used for all absorption measurements. Sodium hydroxide was used to maintain a constant ionic strength. The reactions were carried out at different ionic strengths ($\mu = 0.1$ to 0.4) and the rate constant values were extrapolated to zero ionic strength. Sodium iodite solutions ($3 \times 10^{-3} M$ to $10^{-4} M$) were prepared by dissolving iodine crystals in sodium hydroxide ($0.1 M$). Deionised water was distilled twice before preparing the solutions. The values of dielectric constants for different aqueous ethanol mixtures were taken from literature [8]. All

experiments were carried out in a thermostatic bath and the reaction temperature was held constant within 0.2°C.

The ethanol concentrations used in the reaction media were, 2.0, 4.8, 7.2, 10.4, 13.2 and 16.0 mole percent.

The reagents used were sodium iodite, iodine, sodium hydroxide of analaR grade and absolute alcohol.

Calculations

Free energy of activation was calculated by using the expression;

$$\Delta G_{\text{tot}} = RT(\ln KT/h - \ln k_D)$$

where; K , is the Boltzmann's constant; h , is Planck constant; T , is the absolute temperature; R , is the gas constant; and k_D is the rate constant at a given dielectric constant of the medium.

The free energy contribution due to electrostatic interactions ($\Delta G_{e.s}$) was calculated by using the equation;

$$\Delta G_{e.s} = N.Z_a.Z_b. e^2/E.R_{ab}$$

Where; N , is the Avagadro's number; Z_a and Z_b are the charges on ions, a and b ; e , is the electrostatic charge; E , is the dielectric constant; and R_{ab} is the radius of the activated complex.

The free energy contribution, due to non-electrostatic attractions ($\Delta G_{n.e.s}$) was evaluated from the relationship;

$$\Delta G_{\text{tot}} = \Delta G_{e.s.} + \Delta G_{n.e.s.}$$

The free entropy of activation was calculated by using the expression;

$$\Delta S_{e.s.} = \Delta G_{e.s.} \ln E/dT.$$

A constant value for $d. \ln E/dT$ as -0.0043 was taken [6].

The values for standard enthalpy ΔH° and entropy ΔS° were deduced by using the expression [7].

$$\Delta S^\# = \Delta S^\circ + 1/E$$

$$\Delta H^\# = \Delta H^\circ + 1/E$$

Results

Table-1 provides the data for the activation parameters of the iodite reaction at various concentrations of ethanol in aqueous solutions. Table-2 represents the data for the rate constants at two different temperatures at various dielectric constant values of aqueous ethanol mixtures. Fig. 1 and 2 depict the variations of logarithm of the rate constant with $1/E$ and $E-1/2 E + 1$ respectively, while, Figure 3, demonstrates the change in the logarithm of the rate constant in relation to $1/E^{1/2}$. The

Table-1: Activation Parameters at Different Ethanol Concentrations.

Ethanol mole fraction X_m .	$\Delta_{e.s}$ -J $K^{-1}\text{mole}^{-1}$	$\Delta G_{e.s.}$ kJ mole^{-1}	$\Delta G_{n.e.s.}$ kJ mole^{-1}	$\Delta H^\# + \Delta H^\circ$ kJ mole^{-1}	$\Delta S^\# + \Delta S^\circ$ kJ $K^{-1}\text{mole}^{-1}$
0.00	34.91	7.54	82.66	408.84	0.831
0.032	39.77	8.59	82.14	410.05	0.834
0.072	45.46	9.82	81.56	411.53	0.837
0.0104	50.00	10.82	81.17	412.87	0.839
0.140	55.09	11.90	80.66	414.20	0.842
0.156	57.40	12.40	80.45	414.88	0.844

Table-2: Rate constant values at various dielectric constants; $\mu = 0$

Dielectric Constant $1/E \cdot 10^3$	Constants ^(a)	
	Rate $K_a \cdot 10^{-3}$ $\text{mole}^{-1} \cdot \text{sec}^{-1}$	$K_b \cdot 10^{-3}$ $\text{mole}^{-1} \cdot \text{sec}^{-1}$
(8)	275 K	280 K
12.3	3.16	3.69
14.0	2.57	2.96
16.0	1.99	2.33
17.6	1.58	1.89
19.4	1.26	1.50
20.2	1.12	1.36

(a) - Average of three readings.

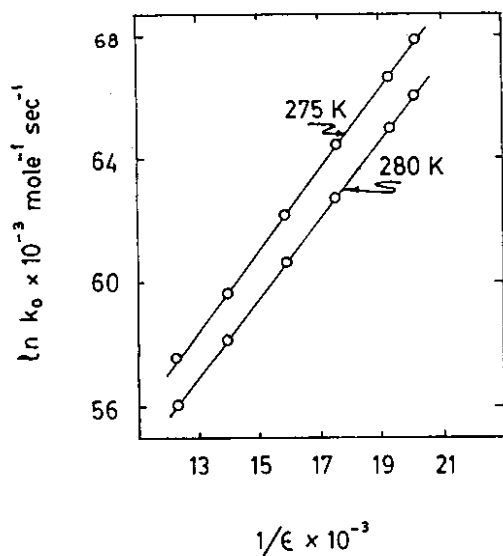
 μ - Ionic strength. $(IO^-) - 3 \times 10^{-3} M$.

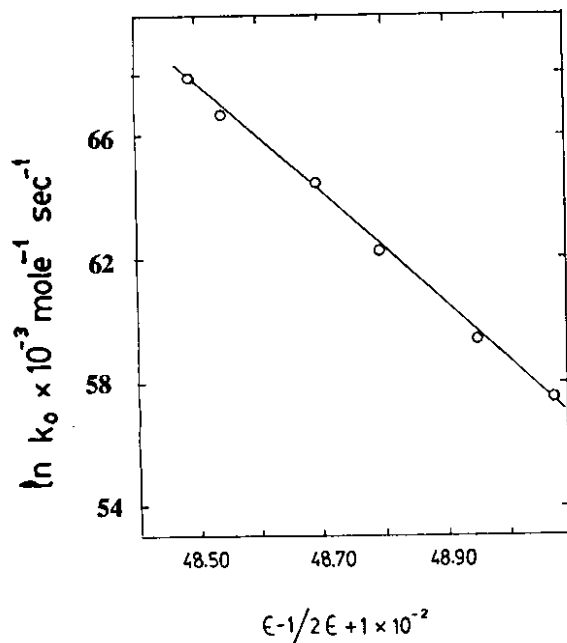
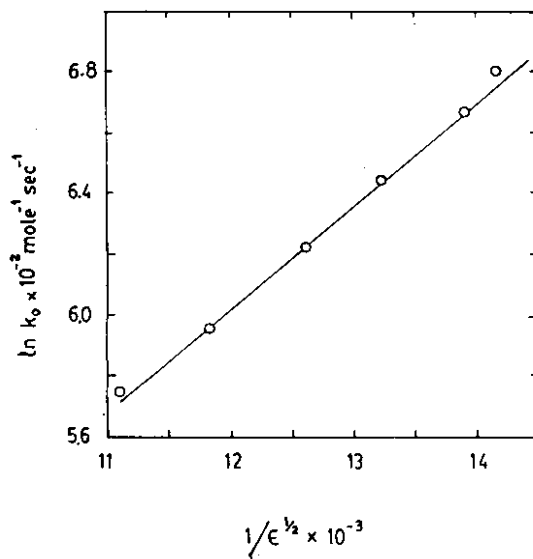
Fig.1: Linear relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant.

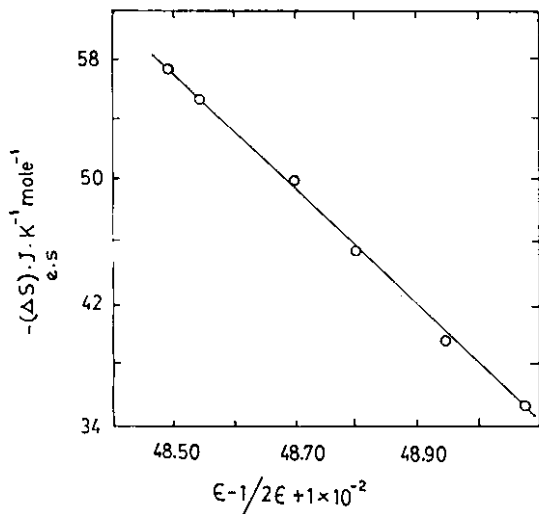
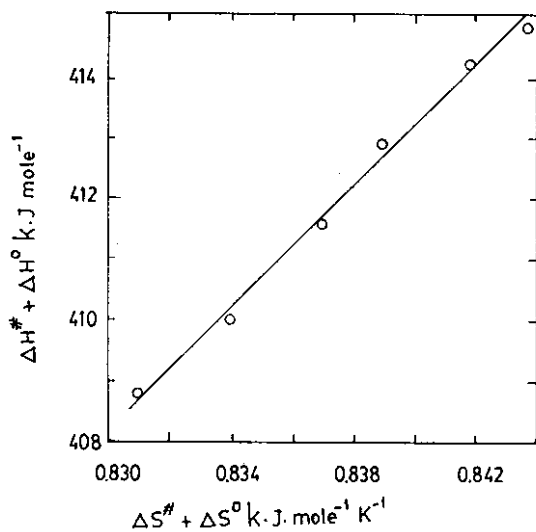
entropy changes with solvent polarity in relation to $E^{-1/2} E + 1$ is shown in Fig. 4. Fig. 5, represents the compensation relationship between $\Delta H^\ddagger + \Delta H^\circ$ and $\Delta S^\ddagger + \Delta S^\circ$.

Discussion

As seen in Fig. 1, a linear plot between the logarithm of the rate constant and $1/E$ was obtained, which indicates that both the electrostatic

and non-electrostatic interactions are contributing to changes in the total free energy of activation of the hypoiodite reaction. An increase in the values of the free energy of activation with a decrease in the dielectric constant of the medium (Table-1) is possibly due to the approach of like charges in the formation of activated complex. A fairly constant value of $\Delta G_{n.e.s.}$ ($81.44 \text{ kJ mole}^{-1}$) indicates making and breaking of the bonds of the transient species

Fig.2: Linear relationship between the logarithm of the rate constant and $E^{-1/2} E + 1$.Fig.3: Linear relationship between the logarithm of the rate constant and $1/E^{1/2}$.

Fig. 4: Variation of entropy changes with $E-1/2 E + 1$.Fig. 5: Plot of the relationship between $\Delta H^\ddagger + \Delta H^\circ$ and $\Delta S^\ddagger + \Delta S^\circ$.

in solution. Moreover, higher values of $\Delta G_{n.e.s.}$ than those of $\Delta G_{e.s.}$ ($7-12 \text{ kJ mole}^{-1}$) appears to be associated with the configurational orientation of the ions in the formation of the activated complex.

As seen in Table-1, large changes in the values of entropy of activation were observed with increasing amounts of ethanol mole fraction in the mixed solvent. The negative values for the entropy of activation are possibly due to the electrostatic freezing of solvent molecules around the charged

activated complex [9]. Higher negative values of entropy for increasing mole fractions of ethanol ($-57.40 \text{ JK}^{-1} \text{ mole}^{-1}$ in 0.156 mole fraction) in mixed solvent indicate a large reorganisation of the solvent molecules in solution and the formation of a highly ordered activated complex. It is evident from Fig. 4 that entropy of activation depends to the same extent as the free energy of activation on the variations of the dielectric constant of the medium. Moreover, it was observed (Fig. 5) that the sum of standard and activated enthalpies ($\Delta H^\ddagger + \Delta H^\circ$) exhibits a linear relationship with $(\Delta S^\ddagger + \Delta S^\circ)$ which indicates a compensation effect in the reaction.

The rate of reaction between hypoiodite ions at zero ionic strength increases with an increase in the dielectric constant of the aqueous ethanol mixture (Table-2). An increase in the rate of the reaction is expected as the electrostatic interactions between reacting ions are increased at a higher dielectric constant of the medium.

The plot of the logarithm of the rate constant at zero ionic strength versus the reciprocal of the dielectric constant (Fig. 1) is a straight line with a positive slope. The value for the radius of the activated complex obtained from the slope of the line and by using the Laidler-Eyring expression [9] is 4.52 \AA° at 275 K.

The theoretical value of the radius of the activated complex for single sphere model was calculated by using the expression: $T^* = (T_{a3} + R_{b3})/3$ as 3.11 \AA° . The radius of the activated complex (R_{ab}) for the double sphere model was calculated theoretically on the assumption that r_{ab} is the sum of the reactants as 4.66 \AA° . The radius of the iodite ion was taken as 2.33 \AA° from Cotton [10]. A comparison of the experimental value of the activated complex, i.e., $r = 4.52 \text{ \AA}^\circ$ with the theoretical value indicates, that the shape of the activated complex is more similar to a double sphere model.

The radius of the activated complex changed from 4.74 \AA° to 4.85 \AA° , when the reaction temperature was raised from 308 K to 313 K. This increase in the size of the activated complex is possibly due to the lack of solvation between transient species and the solvent molecules at higher temperatures.

Amis [3] has proposed an expression for the variations in the rate of reaction with the dielectric constant of the medium as:

$$\ln.k = \ln.k_0 + Z.e/EKT. \mu/r_{ab}^2 \quad (1)$$

The above equation was modified [4] by considering the inductive interactions between the highly polar activated complex and the solvent molecules to the following expression;

$$\ln.k = \ln.k_0 + Z.e/KT.r_{ab}. 1/E^{1/2} \quad (2)$$

Whereas, other equations based on ion-ion, and dipole-dipole interaction models relate the logarithm of the rate constant to $1/E$ and $E-1/2$ $E+1$, the equation (2) predicts the logarithm of the rate constant to vary with $1/E^{1/2}$. This relationship is found valid for ionic reactions carried out in mixed solvents of high dielectric constants [4]. A linear dependence of the logarithm of the rate constant on $1/E$ or $E-1/2E+1$ and on $1/E^{1/2}$ depicted in Fig. 1-3 respectively, indicate that the first order Coulombic forces are largely responsible for the formation of the activated complex in mixed solvents of dielectric constants above 40.

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