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CHEMICAL KINETICS
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Kinetic Study of Specific Base Catalyzed Hydrolysis of Ethyl Acrylate in Water–Ethanol Binary System[1]

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Abstract—Kinetic study of hydroxide anion catalyzed hydrolysis of ethyl acrylate has been carried in ethanol–water (10–50% v/v) binary systems at the temperature range 30 ± 0.1, 35 ± 0.1, 40 ± 0.1, and 45 ± 0.1°C. Calculated specific rate constant values decreases with increasing proportion of ethanol at all temperatures. The observed retardation of a base catalyzed hydrolysis reaction is explained on the basis of fact that the formation of polarized transition state is disfavored with increase in % of ethanol. The relation between the change in dielectric constant due to variation in binary mixtures and change in specific rate constant are explained on the basis of electrostatic and non electrostatic contributions of solvent mixtures. The variation of ΔG^*, ΔH^*, ΔS^* with solvent composition and the specific effect of water on the reaction rate kinetics are also discussed.

Keywords: kinetics, alkaline hydrolysis, ethyl acrylate, binary system.

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INTRODUCTION

In organic synthetic chemistry, hydrolysis is considered as the reverse or opposite of condensation, (a reaction in which two molecular fragments are joined for each water molecule produced). As hydrolysis may be a reversible reaction, condensation and hydrolysis can take place at the same time, with the position of equilibrium determining the amount of each product. The hydrolysis process is involved in saponification in soap manufacturing, plant and animals metabolism [1], enzymatic reactions, biosynthetic reactions, inorganic ligand exchange reactions [2]. Esters can be hydrolyzed to carboxylic acids by nucleophilic acyl substitution mechanism either in basic or acidic condition. Hydrolysis involves replacing the alkoxy group of the ester with a hydroxyl group. It occurs when the nucleophiles (e.g., water or hydroxyl ion) attacks the carbon of the carbonyl group of the ester [3] has been extensively reported by number of workers [4–14].

Ethyl acrylate is extensively used in the production of polymers including plastics, adhesives, resins, safety glass, plastic bottles and dental restorations [15]. When consumed can cause a number of physical problems like eye, nose, throat irritation, eye redness, pain, minor burns, skin redness, irritation of the skin and rashes, loss of memory and headache [16]. Literature survey reveals that there is only one review based on kinetics and mechanism in vinyl esters reported in Russian by Rekasheva [17]. So, it is planned to carry out a detailed study on hydrolysis of ethyl acrylate in ethanol–water (10–50% v/v) binary systems at the temperature range 30 ± 0.1, 35 ± 0.1, 40 ± 0.1, and 45 ± 0.1°C. The variation of ΔG^*, ΔH^*, ΔS^* with solvent composition and the specific effect of water on the reaction is studied here.

EXPERIMENTAL

Material. All chemicals used were of A. R. grade and conductivity water was used throughout the work. The purity of ethyl acrylate was checked by distillation at reduced pressure. Ethanol was purified by the method reported earlier [18].

Kinetic measurements. Conductometric method [19–21] was employed for the calculating hydrolytic rate constant for ethyl acrylate at different temperatures using μ-Conductivity meter-306 with cell constant 1 ± 0.01. Before the use, the new conductivity cell was immersed in distilled water for at least 24 h. The cell was kept in distilled water between the measurements. This distilled water was changed frequently in order to avoid formation of algae, which tends to cling to the pores of the platinum-black layer of the cell, reducing the active surface. It was ensured that there are no air bubbles between the plates of the conductivity cell. Conductivity cells of different cell constants were chosen mainly to ensure that the actual resistance between the plates, when cell is immersed in the solution, is within practical measurable range.

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[1] The article is published in the original.

Inaccuracy can occur in the results if the resistance to be measured is too high or too low. A safe practical range is 10 μS/cm to 100 mS/cm.

In the present study High Precision Water Bath Ca. No. MSW-274 with the readability of 0.01°C is used for maintaining the temperatures. Depending on the experimental being done, two or four sets of apparatus can be operated in a single bath of this size.

The reactions were initiated by mixing thermally equilibrated solution of 0.02 N NaOH and 0.02N the ester (in ethanol–water, % v/v) at the required temperature. Beakers of the base and esters were maintained at the temperature of 30 ± 0.1, 35 ± 0.1, 40 ± 0.1, and 45 ± 0.1°C respectively in water bath. After equilibration, 20 mL of ester solution was delivered in reaction vessel and similar amount of sodium hydroxide solution was added to it. Measurement of time was started only when one half of base was added to the ester solution. The course of the reaction was followed by measuring the conductance (C_t) of the reaction mixture at regular time intervals using a conductivity bridge in the temperature range from 30 ± 0.1 to 45 ± 0.1°C.

The reaction is found to be first order with respect to [nucleophiles] and also first order with respect to [substrate]. The second order rate constant (k_{obs}) are calculated from the linear plot of $(C_0 - C_t)/(C_t - C_\infty)$ vs time, where C_0, C_t, C_∞ are the conductance of the reaction mixture at zero, t and infinite time intervals [22]. The rate constants determined were found to be reproducible within ±1% error. The possibility of esters undergoing hydrolysis in ethanol–water (% v/v) binary mixtures was checked by conducting an independent study under similar experimental conditions. The rate constants for the hydrolysis of ethyl acrylate in different solvents mixtures were determined at different selected temperatures. A personal computer was used to carry out the multiple regression analysis.

Calculation of rate constant (k). The second order rate expression for a reaction in which the two reactants are at equal concentration, a, is,

$$k = \frac{1}{a} \times \frac{x}{a(a-x)}.$$

The amount of reaction that has occurred, x, and the amount of reactants remaining, $(a - x)$, can be deduced from the conductance (C). The total amount of reaction possible is proportional to total change of conductivity, i.e., a $\alpha(C_0 - C_\infty)$. Therefore the amount of reaction after time, t, namely, x is proportional to $C_0 - C_t$. Substituting the above expression,

$$k = \frac{1}{a} \times \frac{(C_0 - C_t)}{(C_t - C_a)}.$$

A graph (Fig. 1) of $(C_0 - C_t)/(C_t - C_\infty)$ against t (time) should therefore give a straight line of slope equal to $[a]k$. The units of k_2 are $dm^3 mol^{-1} min^{-1}$ and k_2 are calculated using linear regression analysis with $r^2 = 0.918$–0.995. A representative data for alkaline hydrolysis of ethyl acrylate in water at 30 ± 0.1°C is given in Table 1 and graphical presentation is given in Fig. 1.

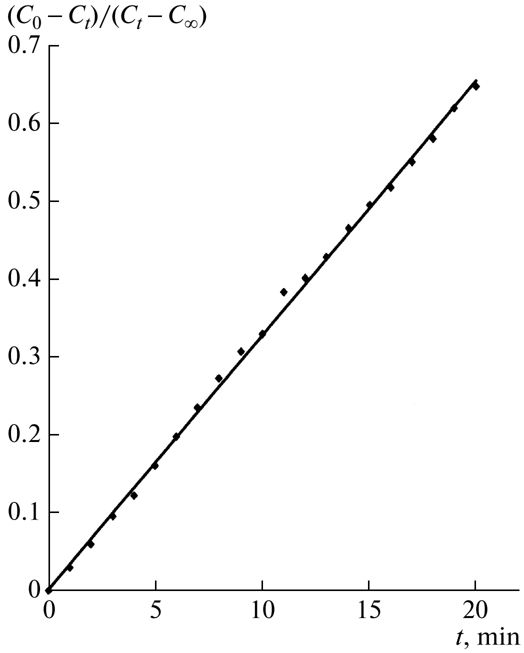

Fig. 1. Conductance measurement for the rate constant of ethyl acrylate at 30 ± 0.1°C.

RESULTS AND DISCUSSION

Table 2 gives the specific rate constant values at various composition of aqueous-organic solvent system at different temperatures. The Arrhenius equation was obeyed within the limits of experimental error in selected systems. The plots of log$k$ against $1/T$ were linear in all cases. Values of activation entropy ΔS^* and ΔG^* were calculated from the following well known equations

$$K = \frac{kT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT},$$

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

$$k = K_t e^{-\Delta G^*/RT}/h.$$

The calculated values of activation parameters E_a, ΔG^*, ΔH^*, ΔS^* are presented in Table 2.

The results of present investigation can be summarized as follows:

(I) The rate of hydrolysis are much smaller in the water–ethanol mixtures than in water–DMSO mixtures [23]. The k_2 values decrease with increase in the organic cosolvent content in the reaction medium at all temperatures. The graphical presentation in Fig. 2 shows that the fall is only gradual at first but when the mole fraction of ethanol become greater than 0.062

Table 1. Conductance measurements for calculation of rate constant of ethyl acrylate at 30 ± 0.1°C in water

t, min	$C_t \times 10^3$, S	$\frac{C_0 - C_t}{C_t - C_\alpha}$
0	0.742	0
1	0.720	0.030
2	0.700	0.060
3	0.678	0.095
4	0.662	0.122
5	0.640	0.161
6	0.621	0.198
7	0.602	0.236
8	0.585	0.273
9	0.570	0.307
10	0.560	0.330
11	0.539	0.383
12	0.532	0.402
13	0.522	0.429
14	0.509	0.466
15	0.499	0.496
16	0.492	0.518
17	0.482	0.550
18	0.473	0.580
19	0.462	0.619
20	0.454	0.648

Note: $C_0 = 0.742 \times 10^{-3}$ S; concentration of reactants is equal 2×10^{-2} mol/dm^3; $C_\alpha = 0.01 \times 10^{-3}$ S, $k_2 = 1.60$ dm^3 mol^{-1} min.

(water in the solvent less than 800 mL/L) the fall becomes very steep.

(II) Figure 3 shows the curves plotting the Arrhenius parameter E_a as function of solvent composition have the same form as the alkaline hydrolysis of ethyl acetate in dioxane–water and acetone–water mixture [24].

(III) The reaction rate decreases with decrease in dielectric constant of the solvent mixture. The trend of change in k_2 values is thus just opposite to the results of some workers [25, 26] but same as the results obtained in alkaline hydrolysis of ester in aquo-DMSO mixtures.

(IV) Plot of log$k$ against log[ethanol] reveals nothing of specific interest, so plot of log$k$ against log[H_2O] is presented at 30 ± 0.1°C. Figure 4 shows that the plot of log$k$ vs. log[H_2O] for ethanol is a straight line whose slope approaches the value 1.11 as the temperatures rises indicates that reaction is first order with respect to [H_2O].

Reaction rate. Alkaline hydrolysis of several esters has been studied in aqueous-organic solvent system [27–29]. Retardation of specific rate constant for hydrolysis of 2 carbomethoxy propionate ion under alkaline condition supports the results of the present study [30, 31]. At very high concentration [32, 33] of organic solvent, the rate of alkaline hydrolysis of esters decreases with decreasing water concentration in acetone, dioxane and alcohol binary systems. The results of investigations [31, 32] of alkaline hydrolysis of substituted ethyl benzoates in acetone–water and ethanol–water mixtures are similar to observations made by Rawat and Rama [33]. The observed retardation of a base catalyzed hydrolysis reaction with increase in ethanol content in mixture may be explained on the basis of fact that the formation of polarized transition state is disfavored with increasing % of ethanol [34]. This is in accordance with the qualitative prediction of Houghes–Ingold theory [35].

According to Tommila et al. [36], the first and rate determining step in alkaline ester hydrolysis is the addition of hydroxide ion to the carbon of carbonyl group of ester, after which a rapid reaction with water follows. Thus if the activity of hydroxide ion is decreased, the reaction rate must decrease. The lower rates in ethanol–water mixtures suggest that the ethanol water interaction significantly increase the concentration of "free" water available for solvation of hydroxide ions. The curve representing the rate constant as a function of solvent composition (Fig. 2) begins to reduce rapidly when the mole fraction of eth-

Table 2. The alkaline hydrolysis of ethyl acrylate in ethanol-water mixtures

Water in the solvent				k_2, dm^3 mol^{-1} min^{-1}			
mL/L	wt %	x_w	ε	30°C	35°C	40°C	45°C
1000	100	1.000	78.54	1.60	2.50	4.71	5.69
900	90	0.972	71.23	7.00	8.35	9.70	11.05
800	80	0.938	65.23	6.90	7.35	8.35	9.45
700	70	0.890	59.68	5.30	6.15	6.75	7.85
600	60	0.850	53.78	4.30	4.85	5.40	6.05
500	50	0.716	47.84	3.75	4.25	4.75	5.30

Note: Initial concentration of the ester and NaOH was 0.02 mol/dm^3, ε is the dielectric constant at 30 ± 0.1°C.

anol exceeds a value of greater than 0.062 i.e., when the ratio of water molecule to ethanol molecules is 4 : 1 or less, the reaction rate decreases vary rapidly with increasing ethanol concentration. This is the point where the amount of free water decreases rapidly with increasing ethanol concentration. This implies that the solvation of hydroxide ions being strong in this range of ethanol - water binary mixtures and hydrolysis constant values decreases.

The values of ΔG^*, ΔH^*, ΔS^*. Variation of E_a with solvent composition is plotted in Fig. 3, plots reveals that with the increase in the proportion of ethanol in the medium, activation energy of reaction has decreased with decrease in water content (increase in methanol content). Results observed here is in agreement with those of earlier investigations [37]. Thus, it is anticipated that there is greater desolvation of the initial state than the transition state.

Values of ΔG^* depends on the rate constant and has increased smoothly with increase in ethanol content in binary mixtures reflecting the decrease in hydrolysis constants (Fig. 5). Tommila and his coworkers [38, 39] reported that the curves representing variation of ΔG^* and ΔH^* with mole fraction of solvent in binary mixtures are much more complicated.

In Fig. 6, plot of ΔH^* against ΔS^* in aqua—ethanol media is straight line, which is in accordance with Barclay—Butler rule [40]. These relations have been observed [24, 41] in many cases and have often been discussed. The behavior of curves in plots of ΔH^* and ΔS^* as functions of solvent composition have been attributed to changes in the solvation of the reactants and the transition state as the composition of the solvent is gradually varied [24].

The orientation of the solvent molecules around the solute particles affects its reaction with reacting molecules, and thus solvation of reacting species lowers the entropy of the system. Solvation is a spontaneous process, and so its $\Delta G^* = \Delta H^* - T\Delta S^* < 0$, so $\Delta S^* < 0$. In aqueous solvent mixtures the water molecules have a specific attraction for the hydrophilic part and the organic molecules a specific attraction for the alkyl or other groups of solute. Thus a variation in the composition of the solvent leads in general to changes in the solvation of the solute particles, i.e., in a reaction system in the solvation of the reactants and the transition complex. The decrease in ΔS^* values again suggests the formation of non mobile transition state indicating solvation of transition state or desolvation of initial state.

In Table 3 shows sharp increase in the values of ΔS^* and ΔH^* from 10 to 20% increase in content of ethanol co solvent in selected binary mixtures. But reversal trend is observed in their values up to 50% of the ethanol co solvent. This is indicative of strong structural and solvation changes resulting in rearrangement and reorientation of solvent particles around reactant molecules sharply affecting the activation process. Complex behavior in thermodynamic activation parameters towards variations in solvent composition have been reported by many workers [42].

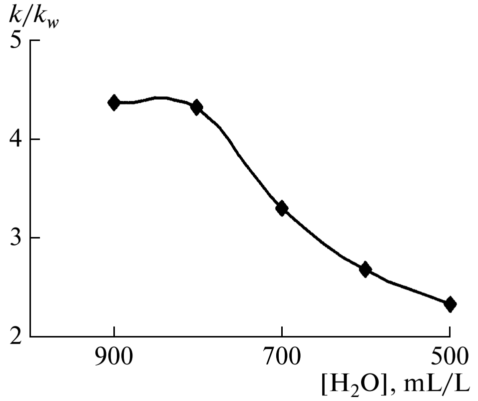

Fig. 2. Variation of k/k_w with solvent composition.

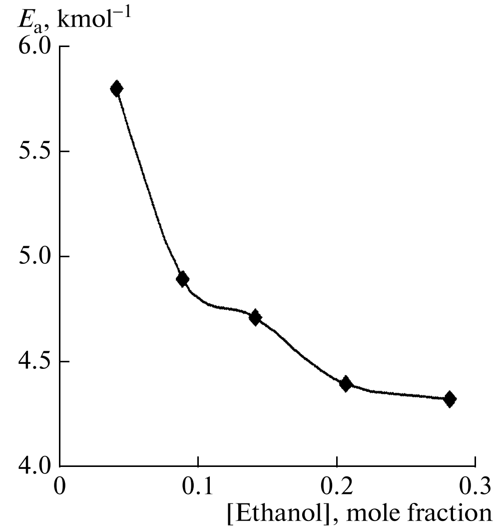

Fig. 3. Variation of E_a with solvent composition.

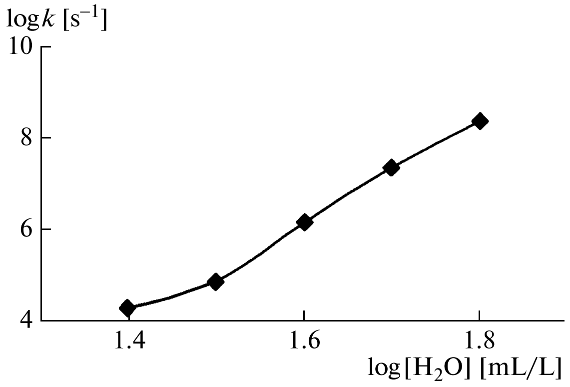

Fig. 4. Plot of log$k$ against log$[H_2O]$.

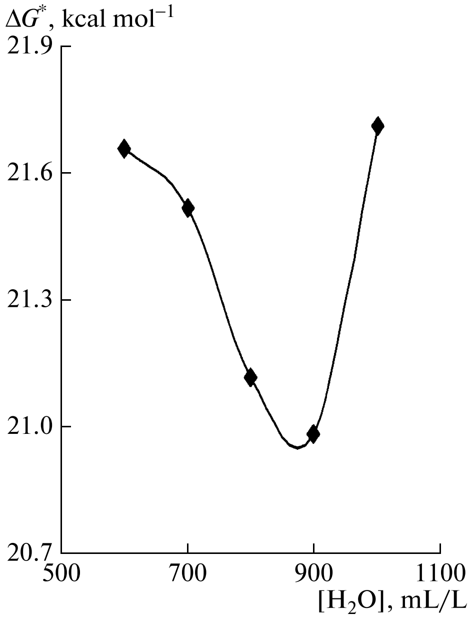

Fig. 5. Variation of ΔG^* with solvent composition at 30°C.

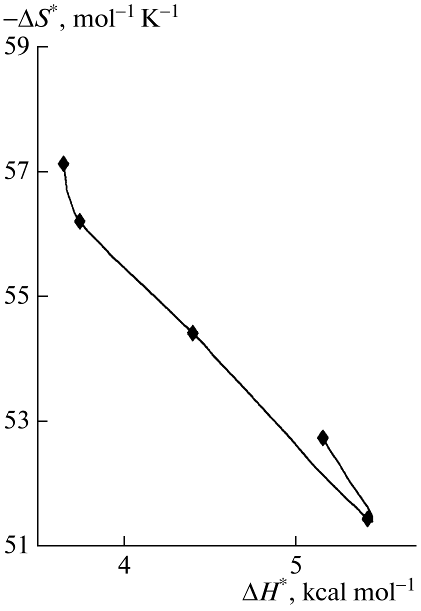

Fig. 6. Plot of ΔS^* against ΔH^*.

According to Winstein and Franberg [43], in binary solvent mixtures two types of solvent molecules interact with reactants both in ground state and transition state. Solvent–solvent interaction is also very complicated. Alcohol–water mixtures are probably the most complex binary solvent systems. In water, a solute molecule builds a structure of a considerable number of water molecules around itself. Such a structure formation around ethyl acrylate is quite likely due to electron releasing α-methyl group in the vinyl ester [44]. The structure formation around solute molecules must compete for water molecules with the existing water-structure. When a small amount of another solvent like alcohol is added, the solute molecules also compete with the structures built by the alcohol molecules. This leads to the decrease in entropy and enthalpy of activation. When the water structure built around solute molecules have essentially disappeared, further addition of alcohol decreases entropy and enthalpy of activation. This is in consistent with Frank and Evans [45] concept.

Table 3. Thermodynamic activation parameters for the hydrolysis of ethyl acrylate in alkaline aqueous ethanol medium

E_a, kcal mol^{-1}	ΔG^*, kcal mol^{-1}	ΔH^*, kcal mol^{-1}	$-\Delta S^*$, cal mol^{-1}K^{-1}
5.796	21.710	5.160	52.76
4.896	20.997	5.415	51.46
4.715	21.120	4.401	54.40
4.408	21.521	3.741	57.02
4.334	21.666	3.644	57.09

The relation between the rate constant and dielectric constant of the solvent. With the increase in the proportion of ethanol in the medium, the dielectric constant values decrease; this has more pronounced effect than the solvation factor. The plot of log$k$ again $1/\varepsilon$ being approximately linear over a wide range of mixtures [46]. The plot of log$k$ against $1/\varepsilon$ is a straight line for mixtures that contain less water than 850 mL/L and its slope value is negative (Fig. 7).

According to Laidler [47], the slope of the plot of log$k$ against $1/\varepsilon$ for an ion(A^-) dipole(B) reaction with net charge $Z_BE = 0$ is given by the equation

$$\frac{d\ln k}{d(1/\varepsilon)} = \frac{1}{k_B T}\left[\frac{Z_A^2 e^2}{2}\left(\frac{1}{r_A} - \frac{1}{r^*}\right) + \frac{3}{4}\left(\frac{\mu A^2}{rA^3} + \frac{\mu B^2}{rB^3} - \frac{\mu^{*2}}{r^{*3}}\right)\right],$$

where k_B is the Boltzmann constant and the μ's and r's are the dielectric constants and radii of the reactants and the transitions complex, respectively. In all cases $r^* < r_A$, so that if the terms involving $Z_A^2 e^2$ predominate and the slope value would be negative, i.e., the reaction rate would decrease with increasing dielectric constant. The higher value of μ^* arise from an ionization of carbonyl group in transition state. The r_A value is large in present study and hydroxide ion will be strongly solvated. The ethanol molecules can fit easily around the carbonyl oxygen, the ionization of carbonyl group become more complete, thus transition state will be more polarized. This factor leads to negative value of slope of log$k$ against $1/\varepsilon$. In present work, the slope value is not larger (–48.34), which in accor-

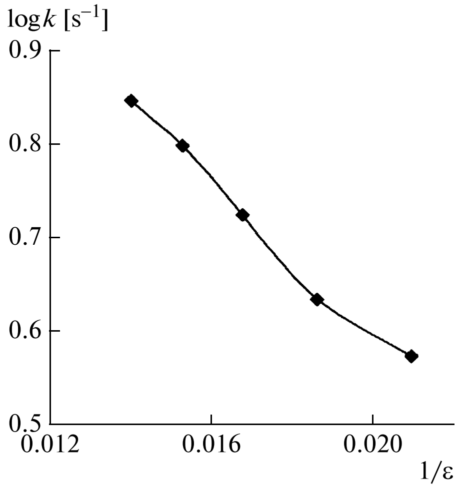

Fig. 7. Plot of log$k$ against 1/ε at 30°C.

dance with the fact that the solvation of hydroxide ion increases gradually with increasing composition of ethanol and hydrolysis constant values decrease.

Role of water. As suggested by Tommila [48] and Lane [49] the variation of log$k$ with log[H_2O] gives the idea of the number of water molecule associated with the activated complex. Laidler and Landskroener [50] assumed that the rate governing step in alkaline hydrolysis consists of a simultaneous attack of a hydroxide ion on carbonyl and of a water molecule on the ester oxygen. From Fig. 4 it is seen that the plot of log$k$ against log[H_2O] for ethyl acrylate is a straight line whose slope values nearly 1.11. This result indicates that one water molecule takes part in the formation of the transition state. Robertson [51] proposed the equation,

$$\log K = \log K_0 + n\log[H_2O],$$

where n gives the average value of slopes up to 30% (v/v) of organic co-solvent and its value was found to be 1.11. This value reduced to 0.94 beyond this composition. If we assume that the activity of hydroxide ions in ethanol-water mixtures is proportional to the mth power of molar water concentration and that the water participation order is n, we may write,

$$k_{\text{exp}} = k[H_2O]^{m+n}.$$

If n has the value 1, we obtain $k_{\text{exp}} = [H_2O]^{m+1}$. We see from Fig. 2 that $m + 1 = -1.11$, and thus $m = -2.11$ or the activity of hydroxide ions is proportional to about $1/[H_2O]_2$ in the range where the plot is linear. This explains the progressive desolvation of the activated complex with the increase in the organic co-solvent content.

CONCLUSIONS

There is gradual decrease in the rate and also same effect for the ΔS* and E_a values with successive increase in ethanol proportion in the aqua-organic solvent system. It may be attributed to the greater solvation of polarized transition state relative to the reactant. Sharp increase in the values of ΔS* and ΔH*, in support to the placid behavior of ΔG*, indicates the changes resulting in rearrangement and reorientation of solvent molecules around reactant molecules, sharply affecting the activation process. The plot of ΔH* against ΔS*, gave straight lines confirming the justification of iso-kinetic relationship. The decrease in the rate with decreasing dielectric constant of the medium can be attributed to the fact that the formation of more polarized transition state. The plot of log$k$ against log[H_2O] was found to be straight line with slope close to 1.11, which is indicative of the fact that the reaction going on is first order with respect to [H_2O] and overall bimolecular in nature.

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