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Solvent's Effect on Specific Rate Constant by The Addition of Zno-Nanoparticles in Alkali Catalyzed Hydrolysis of Ethylnicotinate

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Abstract: The Solvent effect of aqueous aprotic solvent was expressed by studying the kinetics and mechanism of alkali catalyzed hydrolysis of ethylnicotinate in aqueous 1,4-dioxane system having various compositions (20% to 80% v/v) and different temperature range 20°C, 30°C and 40°C affected by the addition of ZnO-nanoparticles. ZnO-nanoparticles increase surface area, catalytic property and polarity of the alkali catalyzed hydrolysis reaction, hence, rate and the specific rate constant value changes. From the kinetic study we found that decrease of rate and specific rate constant (k) of the reaction with gradual addition of organic co-solvent.

The change in iso-composition activation energy (E_C), iso-dielectric activation energy (E_D), solvation and desolvation of initial state and transition state, the number of associated water molecules with activated complex were also calculate and explained.

The thermodynamic parameters enthalpy of activation (ΔH^*), entropy of activation (ΔS^*) and free-energy of activation (ΔG^*) were also calculated. The addition of ZnO-nanoparticles in reaction mixture enhances conductivity specific rate constant E_C, E_D and other above given parameters.

Key Words: ZnO-nanoparticles, Rate, Specific rate constant, Ethylnicotinate, 1,4-dioxane, activated complex, Hydrolysis, Solvolysis, Transition state, iso-composition activation energy, iso-dielectric activation energy, etc.

I. Introduction:

The effect of solvent on the kinetics and mechanism of alkali catalyzed hydrolysis reactions of ester was explained by several researchers but solvent effect on the rate and specific rate constant by the addition of ZnO-nanoparticles in alkali catalyzed hydrolysis of biologically active ester ethylnicotinate in aqueous 1,4-dioxane media are quite interesting and not studied earlier.

The nicotinic acid, nicotinic amide and nicotinic ester are useful pharmacologically active molecule, hence used as pro drugs since long times. Thus the present investigation of the hydrolysis of biologically active ester ethylnicotinate is important from the point of kinetic study and biological activities.

Experimental:

Analytical grade 1,4-dioxane and ethylnicotinate were used. The Merck grade ZnO-nanoparticles was used. All other chemicals used were either of Merck grades or BDH. Conductivity meter was used to measure conductivity of the reaction mixture. Double distilled D.M. water was used.

Water thermostate maintain the temperature control to ±0.01°C. A water thermostate will be set up to evaluate the solvent effect on specific rate by the addition of ZnO-nanoparticles in alkali cotalyzed hydrolysis of biologically active ester in aquo-1,4-dioxane media.

The strength of NaOH was N/5 and strength of ester was N/5, organic solvent and water are mixed in different ratio (i.e. 20%, 40%, 60% and 80%) at different temperature 20°C, 30°C and 40°C . 1 gram ZnO-nanoparticles added in reaction mixture. Its total volume became 22 mL. After few minutes, 1 mL N/5 NaOH solution was added and finally 1 mL ethylnicotinate was added in the solution with the help of pipette followed by constant stirring. The total volume of the solution is 24 mL.

The alkali catalyzed hydrolysis reaction was second order kinetics and the evaluated values of specific rate constant is given in Table-1.

Table-1 Values of specific rate constant ($dm^3 mol^{-1} min^{-1}$) of alkali catalyzed hydrolysis of ethylnicotinate in aquo-1,4-dioxane with ZnO-nanoarticles

Temp. in °C	Value of K			
	20%	40%	60%	80%
20°C	16.60	13.02	9.38	7.05
30°C	32.78	25.98	16.70	12.31
40°C	64.11	50.26	30.03	20.20

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Variation of log k value against mole % of aquo-1,4-dioxane media is shown in Table-2.

Table–2

Variation of log K value against mole% of aquo-1,4-dioxane system with ZnO-nanoparticles

% of 1,4-dioxane	**Log K**			
	mole%	**20°C**	**30°C**	**40°C**
20%	4.99	1.2201	1.5156	1.8069
40%	12.21	1.1146	1.4146	1.7012
60%	23.98	0.9722	1.2227	1.4775
80%	45.65	0.8481	1.0902	1.3057

Variation of log k values against $10^3/T$ is shown in Table-3.

Table–3

Variation of log K values against $10^3/T$ of aquo-1,4-dioxane system with ZnO-nanoparticles

Temp. in °C	**Log K**				
	$10^3/T$	**20%**	**40%**	**60%**	**80%**
20°C	3.41	1.2201	1.1146	0.9722	0.8481
30°C	3.30	1.5156	1.4146	1.2227	1.0902
40°C	3.19	1.8069	1.7012	1.4775	1.3057

Variation of log k vs log [H_2O] of aquo-1,4-dioxane media at different temperature with ZnO-nanoparticles is shown in Table-4.

Table–4

Variation of log K with log [H_2O] of water-1,4-dioxane at different temperature with ZnO-nanoparticles

% of 1,4-dioxane	**% of H_2O**	**log [H_2O]**	**log K**		
			20°C	**30°C**	**40°C**
20%	80%	1.6478	1.2201	1.5156	1.8069
40%	60%	1.5229	1.1146	1.4146	1.7012
60%	40%	1.3468	0.9722	1.2227	1.4775
80%	20%	1.0458	0.8481	1.0902	1.3057

Variation of E_C and E_D values are given in Table-5 and Table-6 respectively.

Table–5

Iso-composition activation energy of alkaline hydrolysis of ethylnicotinate with ZnO-nanoparticles in aquo-1,4-dioxane media

% of 1,4-dioxane	**20%**	**40%**	**60%**	**80%**
E_C value in kJ/mole	50.70	49.88	44.35	42.14

Table–6

Iso-dielectric activation energy of alkaline hydrolysis of ethylnicotinate with ZnO-nanoparticles in aquo-1,4-dioxane media

D values	**D = 50**	**D = 55**	**D = 60**	**D = 65**	**D = 70**	**D = 75**
E_D value in kJ/mole	83.87	80.14	76.31	72.68	68.17	61.24

Slope of log k vs mole % of aquo-1,4-dioxane media with ZnO-nanoparticles is shown in fig.-1.

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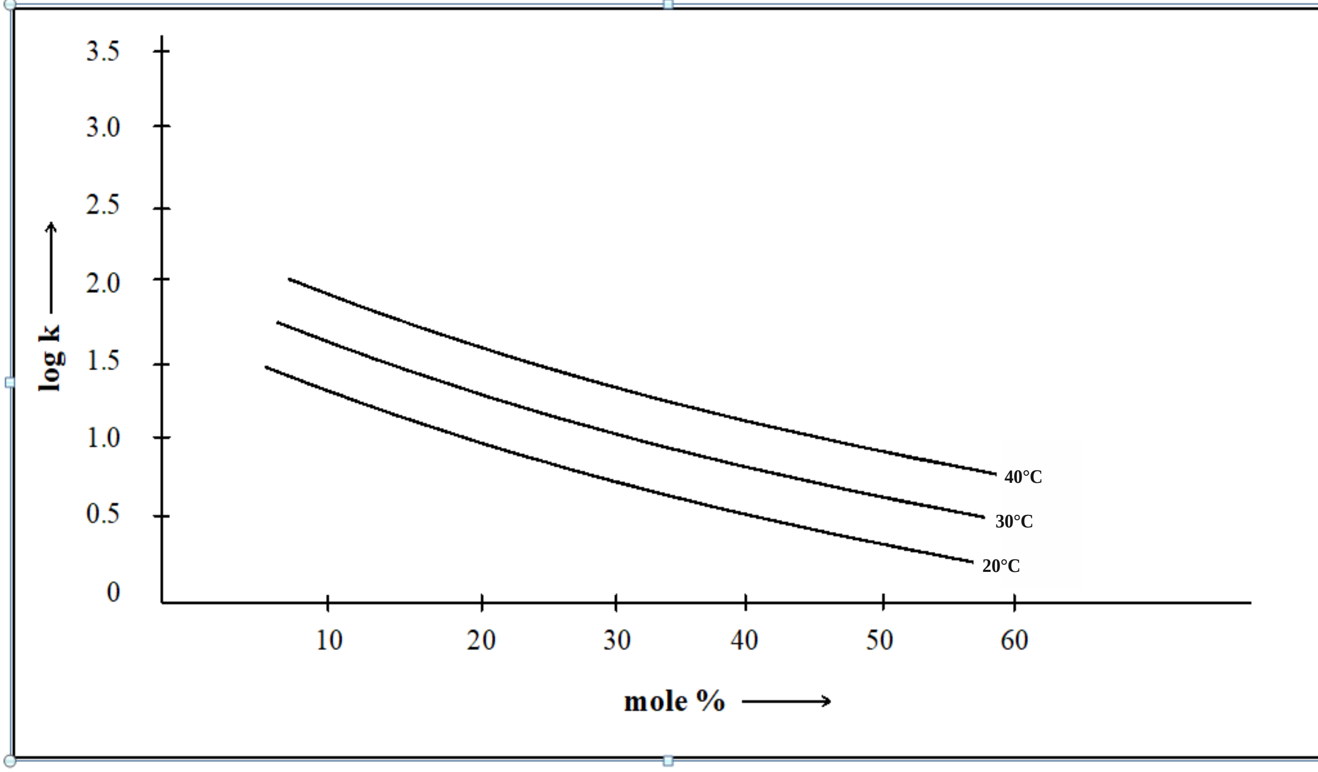

Fig.- 1: Variation of log K with mole% of aquo-1,4-dioxane media with ZnO-nanoparticles

Arrhenius slop of log k vs $10^3/T$ of aquo-1,4-dioxane media with ZnO-nanoparticles is shown in fig.-2.

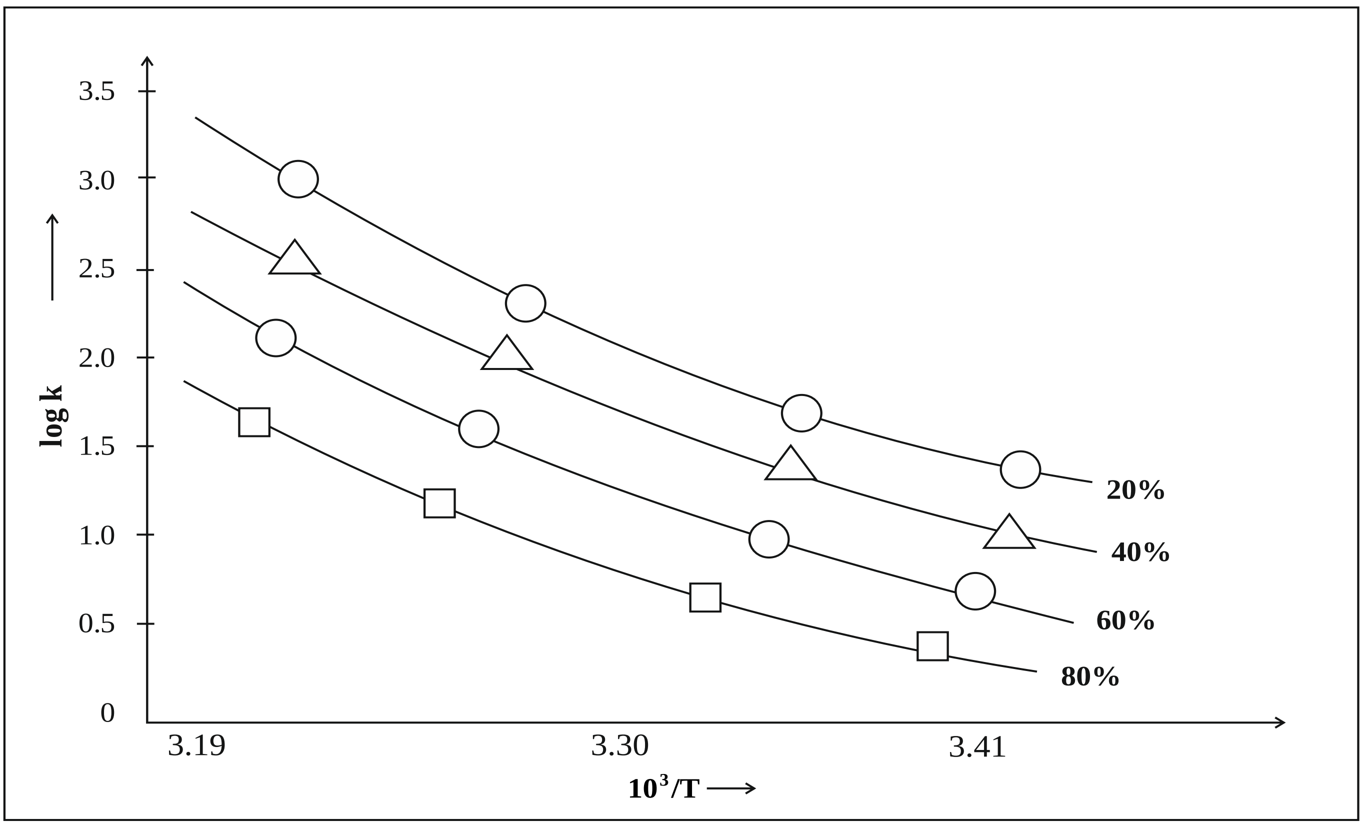

Fig.- 2: Slope of log k vs $10^3/T$ of aquo-1,4-dioxane media with ZnO-nanoparticles

Slope of log k vs log [H_2O] of aquo-1,4-dioxane media with ZnO-nanoparticles is shown in fig.3.

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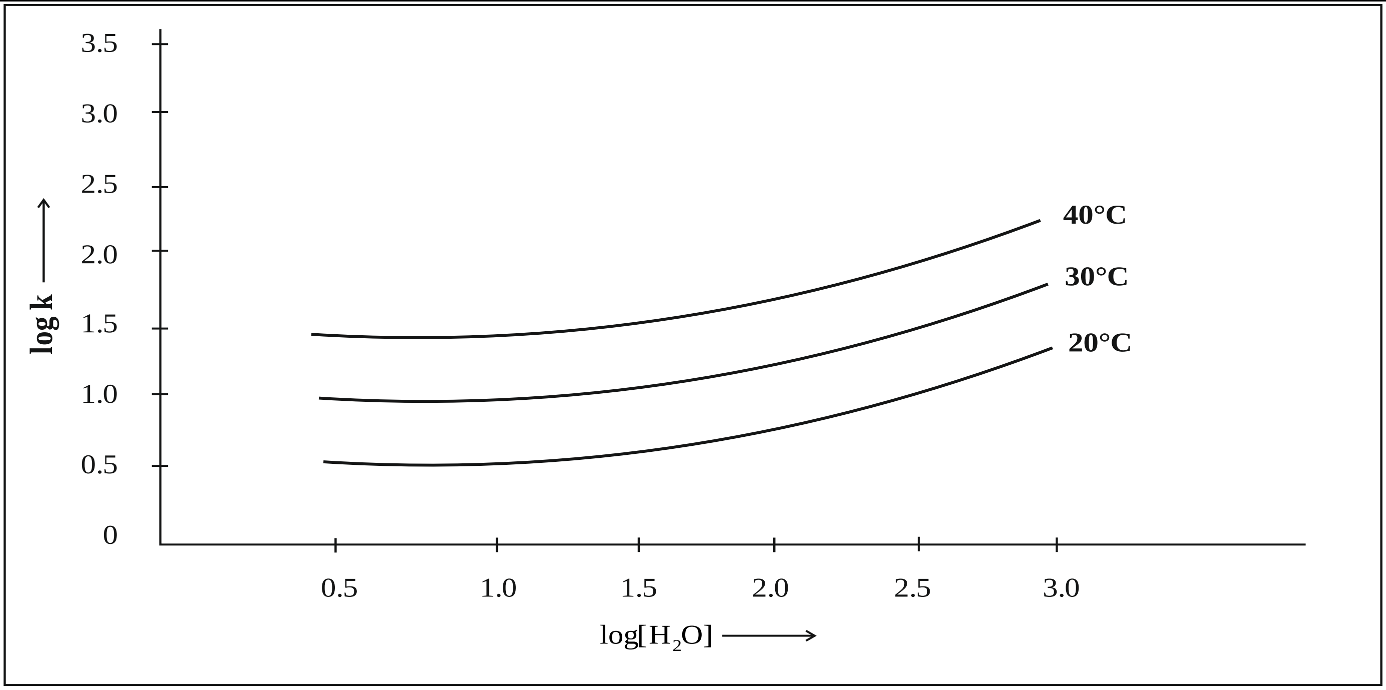

Fig.-3 : Variation of log k vs log [H_2O] of aquo-1,4-dioxane media with ZnO-nanoparticles

The iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) were calculated. The various thermodynamic activation parameter, i.e. ΔG*, ΔS* and ΔH* values calculated with the help of Wynne-Jones and Eyring equation.

II. Results and Discussion:

The second order rate constant for alkali catalyzed hydrolysis of ethylnicotinate in aquo-1,4-dioxane media with the addition of ZnO-nanoparticles were calculated at 20°C, 30°C and 40°C. The specific rate constant (K) values increase with temperaure beacuse effective collisions between reacting molecules increases.

The depletion in rate and specific rate constant is due to decrease in polarity of the reaction media by adding less polar organic solvent or decrease in bulk dielectric constant value, is in good agreement with the Hughes and Ingold theory. Such decreases in rate was also reported by Elsemongy and recently by several researchers. Similar results are obtained with the addition of ZnO-nanoparticles. It enhances the specific rate constant values at various composition and different temperature.

The value of E_C is calculate from Arrhenius equation plots of log k versus 10^3/T. Its value decreases with the increases in organic solvent, this is due to solvation change in the initial state or transition state or in the both states. The thermodynamic parameters like ΔH* and ΔS* decreases with addition of organic co-solvents, but ΔG* values increases, supported recently by several researchers.

The value of E_D is calculated by plotting Arrhenius plot of log K_D against 1/T. Solvation number (n) is associated water molecules in the activated complex is determined with the help of Robertson equation,

$$\log k = \log k_0 + n \log (H_2O)$$

The solvation number is calculated by plotting log k versus log [H_2O].

With the addition of organic solvents to water, the bimolecular reaction change to the unimolecular reaction path in similar way studied as previous workers like Parker and Tomillinson.

Iso-kinetic relationship between ΔH* and ΔS* was developed by Barclay and Butler as

$$\delta_m (\Delta H^*) = \beta\, \delta_m (\Delta S^*)$$

The plot of ΔH* versus ΔS* is a straight line and this slope gives the iso-kinetics temperature (β) value, which is pointed out by Leffler.

The structural changes occurs with the increase in the concentration of organic solvent, which is responsible for the decrease in the values of specific rate constant. Such interactions are reported by many researchers.

Alkaline hydrolysis reaction with metal nano-particles is quite interesting than normal alkaline hydrolysis reaction because metal nano-particles shows surface activity, catalytic activity and also increases the polarity of the reaction medium, which enhances rate, specific rate constant and other kinetic parameters.

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III. Conclusion:

In the alkali catalyzed hydrolysis reaction of ethylnicotinate in aquo-1,4-dioxane media with the addition of ZnO-nanoparticles, the specific rate constant decreases at all the temperatures with the gradual addition of organic solvent.

The iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) values are also changes. It indicated that solvation and desolvation occurs. Solvating power of 1,4-dioxane change the reaction mechanism from bimolecular to unimolecular due to increase in the number of associated water molecule. The various thermodynamics parameters like ΔG^*, ΔS^* and ΔH^* values are also changes with the gradual addition of organic co-solvent at different temperature.

Addition of ZnO nano-particles in the reaction medium increase the surface area, catalytic activity and polarity of the medium, which influences kinetic parameters.

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