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Comparative Study of the Kinetics of Base Catalysed Hydrolysis of Methyl Salicylate in Aquo-Ethylene Glycol, Aquo-*n*-propyl Alcohol and Aquo-Tertiary Butyl Alcohol

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The rate of alkali catalysed hydrolysis of methyl salicylate in aquo-ethylene glycol, aquo-*n*-propyl alcohol and aquo-tertbutyl alcohol of composition ranging from 10% to 40% of ethylene glycol, *n*-propyl alcohol and tertiary butyl alcohol respectively at temperature varying from 15 to 35°C has been studied. The rate constant decreases with increasing percentage of ethylene glycol, *n*-propyl alcohol and tertiary butyl alcohol respectively in water. The isocomposition activation energy E_c was calculated using Arrhenius equation and other thermodynamic parameters such as change in enthalpy of activation ΔH*, change in free energy of activation ΔG*, and change in entropy of activation ΔS* were evaluated using Wynne Jones and Erying equation. The variation in rates and thermodynamic parameters of the reactions in the aquo co-solvent media has been compared with each other.

INTRODUCTION

The present work is in continuation of our previous work.[1–3] It is well understood that solvents play a very important role[4–7] in deciding the course and rate of reaction performed in it. In recent years kinetics of various types of reactions have been attempted by chemists particularly in mixed aquo-organic solvent systems in a bid to explore various aspects of interaction of solvent molecules with reacting substances in it but its explanations put forward are not satisfactory. The work of Laidler[4] and Ingold[5] showed that the rate of hydrolysis of ester decreases with decreasing dielectric constant value of the medium. The decrease in rate constant of ester hydrolysis upon the addition of co-organic solvents in aqueous solvents has also been observed[6–8] and, therefore, more work is needed as to how the reacting solute species and the transition state are affected when co-organic solvent proportion of the reaction medium is gradually changed. In our laboratories and elsewhere several alkali catalysed hydrolyses of simple aliphatic aromatic esters, and of amides, have been probed in mixed aquo-organic solvent system but only limited cases of hydrolysis of substituted esters of benzoic acid have been attempted. It is, therefore, thought worth-while to study the kinetics of alkali hydrolysis of methyl salicylate in aquo-ethylene glycol, aquo-*n*-propyl alcohol and aquo tertiary butyl alcohol solvent systems at different compositions and temperatures to arrive at some definite conclusions.

EXPERIMENTAL

Ethylene glycol, *n*-propyl alcohol, tertiary butyl alcohol, methyl salicylate and other required chemicals were of BDH/E. Merck. Organic co-solvents (ethylene glycol, *n*-propyl alcohol and tertiary butyl alcohol) were purified by standard processes. Double distilled water free from CO_2 was used wherever required. Methyl salicylate was first distilled under reduced pressure and was further purified by repeating the distillation process and the fraction between 221–224°C was collected. The boiling point of distilled product was found to be 223°C which confirmed its purity. The standard solutions of NaOH (0.2N) and methyl salicylate (M/6) were made. Varying compositions of co-solvents were 10–40%. Reaction mixture except methyl salicylate was thermostated for $\frac{1}{2}$ h. 10 mL of methyl salicylate was added to the thermostated reaction mixture and quickly 10 mL of this reaction mixture was removed and added to a cleaned conical flask containing 20–25 mL of ice-cold water and 10 mL standard HCl, and finally titrated with baryta solution.

Reproducible results were obtained. The rate constant values (k) were determined at temperatures varying from 15 to 35°C at intervals of 5°C for compositions varying from 10–40% co-organic solvents in water and are produced in Table-1.

TABLE-1

SPECIFIC RATE CONSTANT (k) FOR ALKALINE HYDROLYSIS OF METHYL SALICYLATE IN AQUO-ETHYLENE GLYCOL, *n*-PROPYL ALCOHOL AND TERT. BUTYL ALCOHOL

[$k \times 10^1$ in dm^3 $mole^{-1}$ min^{-1}]

Temp. °C	Ethylene Glycol (Vol %)				Tertiary butyl alcohol (Vol. %)				*n*-propyl alcohol (Vol%)			
	10	20	30	40	10	20	30	40	10	20	30	40
15	6.40	5.51	4.42	3.61	—	—	—	—	—	—	—	—
20	10.30	8.71	7.72	10.70	—	—	—	—	—	—	—	—
25	16.32	14.50	13.52	12.70	8.60	7.90	7.10	6.70	1.940	1.83	1.74	1.66
30	23.50	22.40	21.50	20.40	12.40	11.40	10.70	9.90	2.980	2.89	2.77	2.65
35	—	—	—	—	18.10	16.50	15.80	14.20	4.150	4.05	3.96	3.86
40	—	—	—	—	25.40	23.50	22.30	21.10	—	—	—	—

RESULTS AND DISCUSSION

The rate constant values are remarkably decreasing with the gradual increase of co-organic solvents in water. The observed decrease in the rate is the overall effect of decreasing dielectic constant value of the medium and the transition state and it is supported by the theory of Hughes[9] and Ingold[5] and also from the prediction of Laidler Landskroener[4] and Fradenbagen[10]. The increases in the activation energy is due to more desolvation of transition state than its initial state.

Table-2 shows that of the two esters *viz.* methyl salicylate and iso-amyl salicylate reported earlier the rate for the former has been found to be higher than that for the latter under identical experimental conditions.

TABLE-2

SPECIFIC RATE CONSTANTS (k) FOR ALKALINE HYDROLYSIS OF ISO-AMYL SALICYLATE AND METHYL SALICYLATE IN AQUO-ETHYLENE GLYCOL, AQUO-*N*-PROPYL ALCOHOL AND AQUO-TERTIARY BUTYL ALCOHOL AT 25°C

($K \times 10^1$ in dm^3 $mole^{-1}$ min^{-1})

Esters	Ethylene glycol (Vol. %)				*n*-Propyl alcohol (Vol. %)				Tert. butyl alchol (Vol. %)			
	10	20	30	40	10	20	30	40	10	20	30	40
Iso-amyl salicylate	12.60	11.50	9.50	8.50	1.[illegible]	1.72	1.61	1.51	7.10	6.10	5.50	4.70
Methyl salicylate	16.32	14.50	13.52	12.70	1.94	1.83	1.74	1.76	8.60	7.90	7.10	6.70

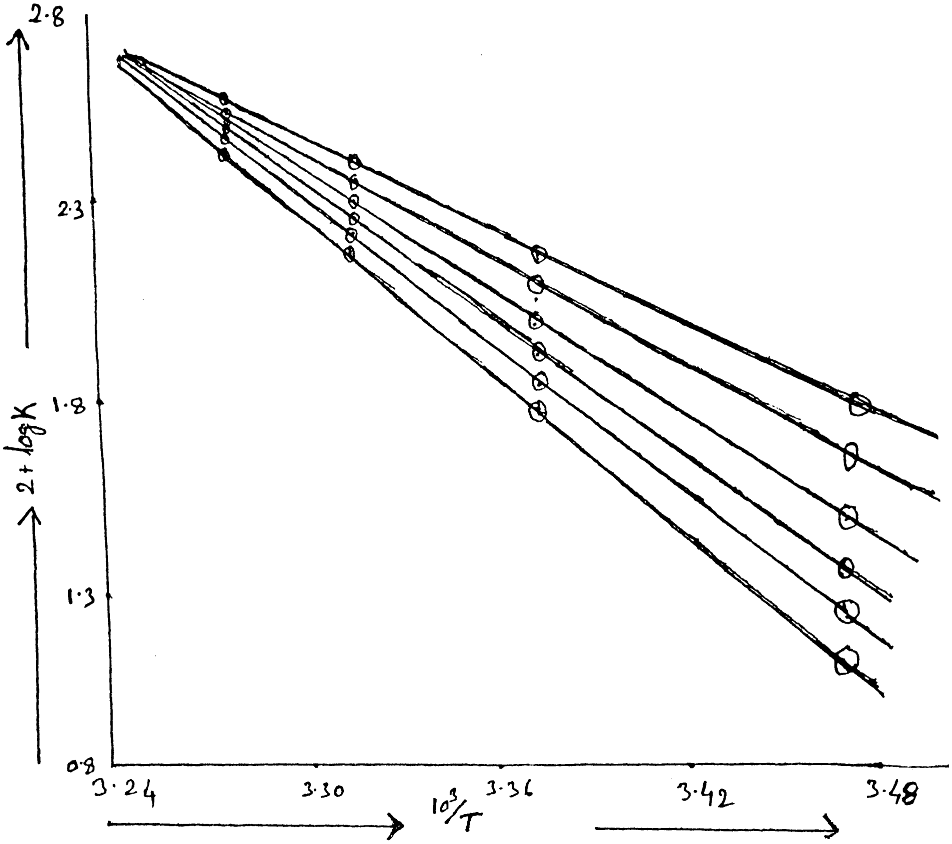

Fig. 1. Plot of 2 + log k *vs.* $10^3/T$ for alkaline hydrolysis of methyl salicylate in aquo-ethylene glycol medium.

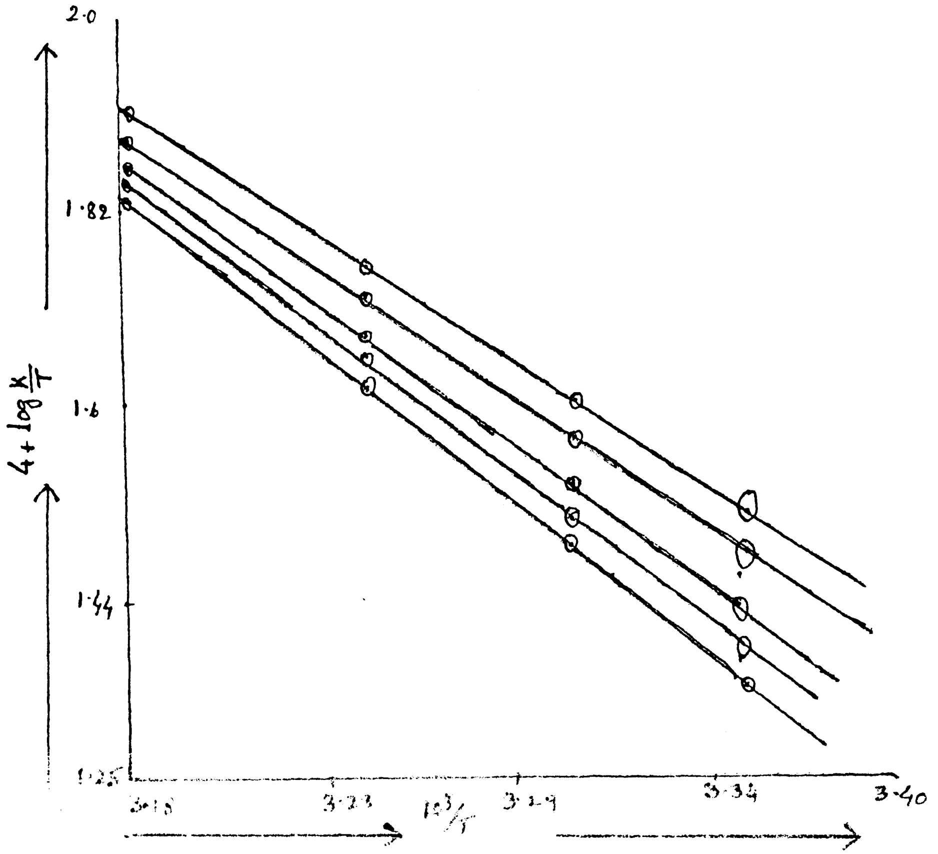

Fig. 2. Plot of 4 + log k *vs.* k/T for alkaline hydrolysis of methyl salicylate in aquo-tertiary butyl alcohol medium.

Iso-amyl group being more bulky than methyl group, it is expected that alkaline hydrolysis which involves attack by OH^- anion on the —COOR part of the esters will be sterically more hindred in case of iso-amyl group as compared to methyl group. This would lead to slower rate of hydrolysis of iso-amyl salicylate as compared to methyl salicylate. Our experimental results fail in this line.

Effect of temperature

Specific rate constant values are found to increase with increasing temperature according to the Arrhenius law, yielding a good straight line for log K *vs.* 1/T (Fig. 1 and 2). The value of iso-composition activation energy, E_C, and iso-dielectric activation energy, E_D, found to increase in all the cases, *i.e.*, in aquo-glycol, aquo-*n*-propyl alcohol and aquo-tertiary butyl alcohol solvent system which is supported by Worlford.[11] These values are tabulated in Tables 3 and 4.

TABLE-3
ISO-COMPOSITION ACTIVATION ENERGIES (E_C)

Vol. %	Ethylene glycol				*n*-Propyl alcohol				Tertiary butyl alcohol			
	10	20	30	40	10	20	30	40	10	20	30	40
E_C in kJ mole^{-1}	60.85	66.27	72.16	76.58	56.10	58.97	59.73	63.18	55.23	57.44	59.26	62.43

TABLE-4
ISO-DIELECTRIC ACTIVATION ENERGIES (E_D)

Dielectric constant values	Aquo-ethylene glycol				Aquo-*n*-propyl alcohol				Aquo tert. butyl alcohol			
	62	63	64	65	58	62	66	70	48	52	56	60
E_D in kJ mole^{-1}	10.34	10.26	10.21	9.89	9.95	11.87	10.72	10.91	57.40	58.27	58.27	59.26

Other Activation Parameters

Table-5 presents the values of change in free energy of activation (ΔG^*), change in enthalpy of activation (ΔG^*) and change in entropy of activation (ΔS^*) in each aquo-organic co-solvent system. The increase in ΔG^* although

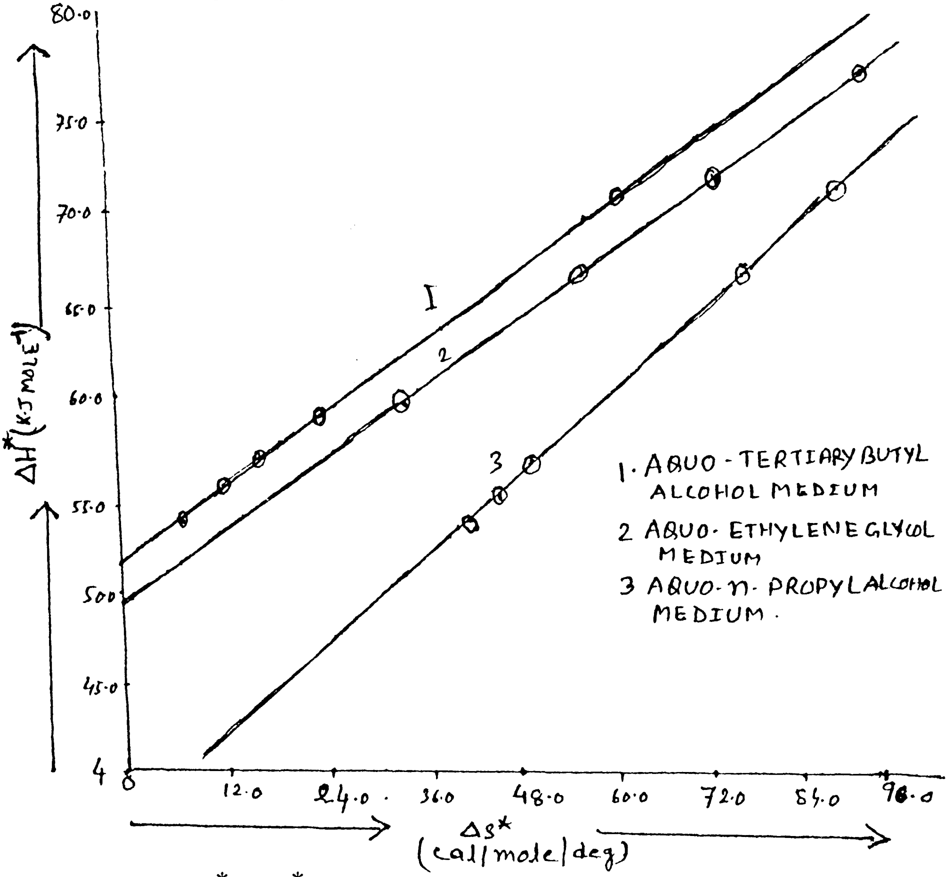

Fig. 3. Plot of ΔH^* *vs.* ΔS^* for alkaline hydrolysis of methyl salicylate in aquo-tertiary butyl alcohol, aquo-ethylene glycol and aquo-*n*-propyl alcohol media.

very small, is indicative of specific desolvation of the transition state. This is in accordance with our view that the transition state is less solvated or more desolvated than the reactants in initial state with addition of co-organic solvent in mixture which is supported by Cleve[12] and Eslemongy.[13]

TABLE-5

ACTIVATION PARAMETERS FOR ALKALINE HYDROLYSIS OF METHYL SALICYLATE IN AQUO-ETHYLENE GLYCOL, AQUO-*n*-PROPYL ALCOHOL AND AQUO-TERT, BUTYL ALCOHOL

(ΔH^* in kJ mole^{-1}, ΔG^* in the mole^{-1} and ΔS^* in cal mole^{-1} deg^{-1})

Vol. %	Ethylene Glycol Temp. (°C)					*n*-propyl alchol Temp. (°C)			Tertiary butyl alcohol Temp. (°C)				
		15	20	25	25		25	25		25	30	40	25
	ΔH^*	ΔG^*	ΔG^*	ΔG^*	ΔS^*	ΔH^*	ΔG^*	ΔS^*	ΔH^*	ΔG^*	ΔG^*	ΔG^*	ΔS^*
10	61.27	44.48	49.25	49.00	41.15	50.54	71.17	–239.15	52.65	50.55	50.53	50.45	7.02
20	66.28	49.89	49.64	49.29	57.00	50.93	71.33	–239.52	53.18	50.77	50.76	50.63	8.01
30	72.17	50.39	49.98	49.46	76.19	53.61	71.49	–240.09	55.42	51.06	50.93	50.75	14.83
40	79.52	50.94	50.26	49.63	99.63	54.18	71.60	–240.47	56.12	51.17	57.09	50.93	16.55

When ΔH^* is plotted against ΔS^* an excellent straight line (in each aquo-cosolvent system) is obtained which is indicative of isokinetic relations relationship between ΔH^* obeying Barclay and Butter rule[14] (Fig. 3). The increase of ΔS^* suggests the formation of more mobile transition state which supports contention of desolvation of the transition state.

Effect of ionic strength

There is a very small influence of ionic strength of the reaction rate. It is, therefore, indicative of the fact that hydrolysis relations under study are not ion-ion type but an ion-dipolar molecule type of reactions which is supported by Hughes.[10]

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