

## KINETIC STUDIES IN ESTER HYDROLYSIS

### Part III. Acid Hydrolysis of Ethyl Acetate in Mixed Solvents\*

By P. MADHAVAN NAIR AND S. V. ANANTAKRISHNAN, F.A.Sc.

(Department of Chemistry, Madras Christian College, Tambaram)

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#### INTRODUCTION

In Part II<sup>2</sup> of these studies, it was noticed that the rate of the reaction under investigation showed interesting variations in aqueous glycerol media when the solvent composition was progressively changed from 20% water to 20% glycerol. The present communication deals with a part of a systematic investigation of the nature of solvent effect in acid catalysed and alkaline hydrolysis of esters. The reaction rate has been determined in various dioxane-water and acetone-water mixtures.

#### RESULTS AND DISCUSSION

The results presented in Tables I and II give the bimolecular rate constants and dielectric constants for the various media.

TABLE I  
*Velocity constants in dioxan-water mixtures*

Compo- sition Vol. % dioxan	Temperature °C.					
	35		45		55	
	Dielectric constant	$k$ $\times 10^5$	Dielectric constant	$k$ $\times 10^5$	Dielectric constant	$k$ $\times 10^5$
0	74.93	28.06	71.49	63.39	68.24	137.5
10	66.13	26.25	63.35	62.81	59.89	134.4
20	57.32	25.82	55.31	59.96	51.70	128.7
40	40.67	21.63	38.48	48.56	36.40	106.8
60	24.82	16.14	23.44	37.20	22.14	82.08
80	10.34	10.96	9.81	27.84	9.31	61.03
90	5.40	11.47	5.20	28.98	5.01	63.30

\* The material presented here is part of a thesis of P.M.N., accepted for M.Sc. Degree of Madras University.

TABLE II  
Velocity constants in acetone-water mixtures

Compo- sition Vol. % Acetone	Temperature °C.					
	35		45		55	
	Dielectric constant	$k$ $\times 10^5$	Dielectric constant	$k$ $\times 10^5$	Dielectric constant	$k$ $\times 10^5$
0	74.93	28.06	71.49	63.39	68.24	137.50
10	70.63	25.87	67.41	59.21	(64.2)	123.50
20	66.17	23.31	63.14	54.03	(59.3)	110.10
40	56.29	18.17	53.73	40.19	(51.3)	83.71
60	44.99	13.67	42.93	28.76	(41.3)	65.21
80	32.12	9.365	30.62	22.62	(29.0)	49.73
90	25.22	9.649	24.07	24.46	(23.02)	53.46

The dielectric constant values in Tables I and II have been obtained by interpolation using data taken from Akerlof.<sup>1</sup> Values within brackets are computed from the values at lower temperature.

Since it has been well established by Harned and Ross<sup>4</sup> that the first order rate constant is proportional to the catalyst concentration even for media containing extremely high proportions of dioxane, the measurements made are under strictly comparable conditions. Figs. 1 and 2 show the variation of reaction rate with composition of the medium. As can be readily seen from the curves, while in general a lower dielectric constant is associated with a reduced reaction rate, this behaviour does not persist right through and the rate constant passes through a minimum in region of 80% organic solvent. Also, the values obtained make it evident that the two series of solvents have marked specific influence on the reaction rate. Thus, at 35° C. while a change in dielectric constant from 74.93 to 10.34 depresses the value of  $k \times 10^5$  from 28.06 to 10.96, in dioxane-water systems, a much smaller change, namely from 74.93 to 32.12 is sufficient to bring about a greater drop (to 9.365) in rate constant in acetone-water systems. The behaviour is the same for higher temperatures. The reaction velocity is, therefore, found to be far more sensitive to changes in dielectric constant in acetone-water mixtures than in mixtures of dioxane and water. The significance of the trend of velocity constants with changing composition of the medium is more fully considered in a separate communication.

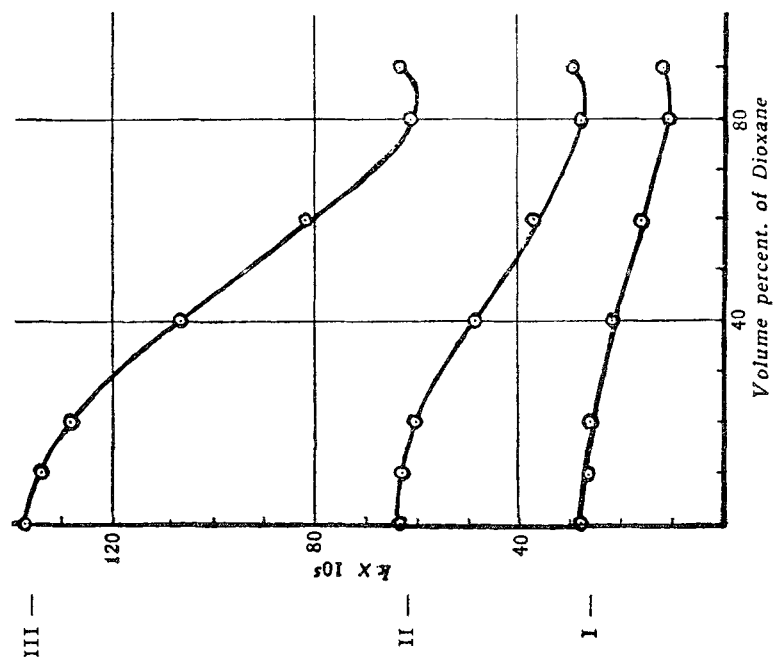


FIG. 2. Velocity-composition curves for Dioxane-water mixtures.  
 Curve no. I II III  
 Temp. 35° C. 45° C. 55° C.

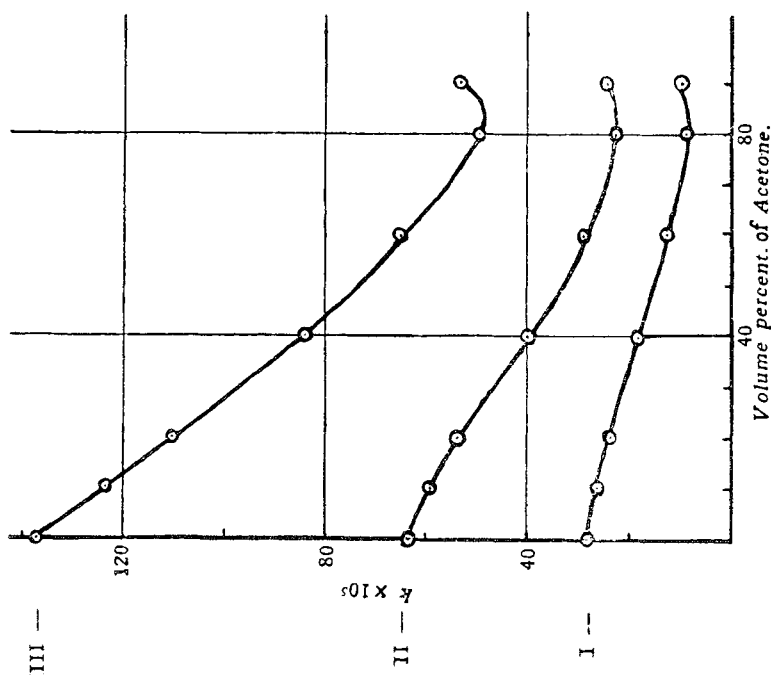
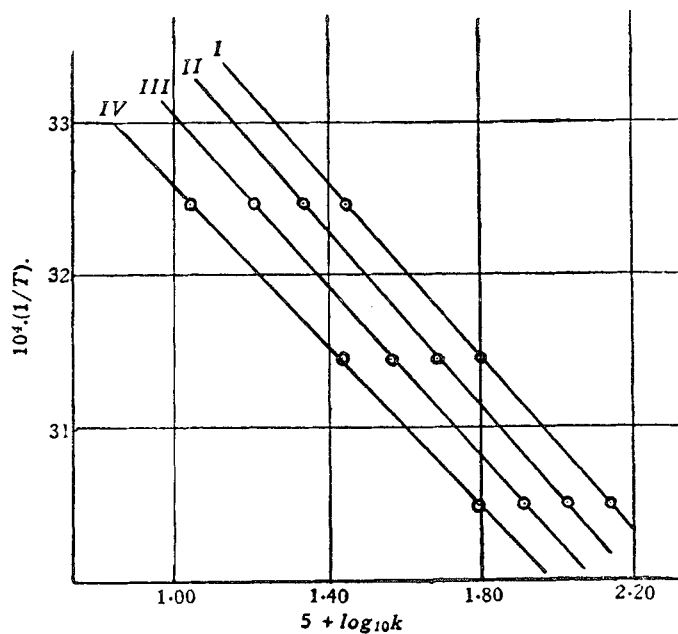
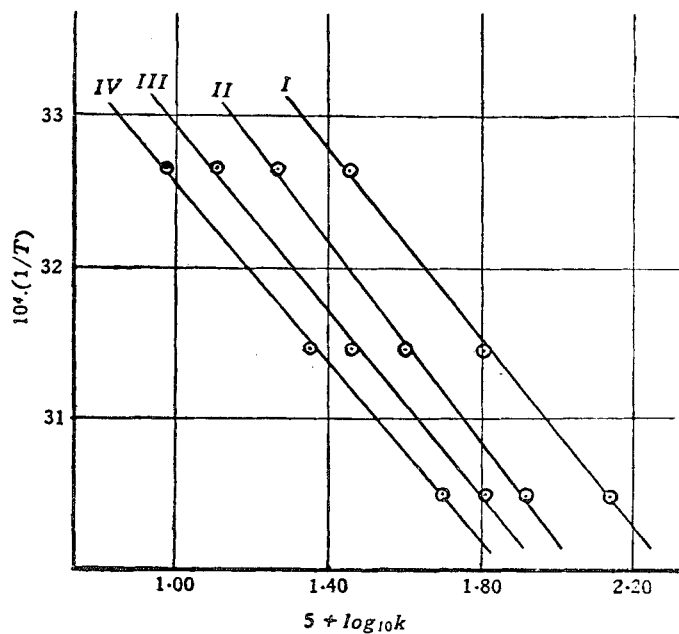


FIG. 1. Velocity-composition curves for Acetone-water mixtures.  
 Curve no. I II III  
 Temp. 35° C. 45° C. 50° C.

FIG. 3.  $\text{Log}_{10}k-1/T$  curves for Dioxane-water mixtures.

Curve no.	I	II	III	IV
Vol.% of Dioxane	0	40	60	80

FIG. 4.  $\text{Log}_{10}k-1/T$  curves for Acetone-water mixtures.

Curve no.	I	II	III	IV
Vol.% of Acetone	0	40	60	80

A remarkable feature of the reaction is the strict linearity observed in the  $\log k - 1/T$  curves (Figs. 3 and 4) for all the solvent compositions and it is interesting here to recall the objections raised by Svirbely and Warner<sup>6</sup> against the conventional method of evaluating activation energies in reactions that are affected by dielectric constant of the solvent. The observed behaviour proves that there is no change in the energy of activation within the temperature range studied and that the correction factor in the expression for iso-dielectric activation energy

$$E_D = E_{app} + R \left( \frac{\partial \ln k}{\partial D} \right)_T \frac{dD}{d(1/T)}$$

is small in comparison with  $E_{app}$  (apparent, *i.e.*, experimental activation energy).

The experimental activation energies and frequency factors are given in Table III.

TABLE III

Solvent composition % of organic solvent by volume	Acetone-water		Dioxan-water	
	Energy of activation in kilocalories per mole	Log of frequency factor	Energy of activation in kilocalories per mole	Log of frequency factor
0	16.000	7.77	16.000	7.77
10	15.700	7.55	16.400	8.05
20	15.600	7.43	16.100	7.86
40	15.300	7.14	16.000	7.71
60	16.400	7.77	16.300	7.78
80	16.800	7.87	17.200	8.23
90	17.200	8.18	17.200	8.27

While the activation energy in acetone-water mixtures shows a position of minimum at about 40% acetone and then progressively rises with increasing proportion of acetone, dioxane-water mixtures show only smaller changes with a possible maximum in the 10% region, minimum in the 40% region and reaches possibly a stationary value after 80% dioxan. However, the variations are too small to admit of any rigid conclusions being drawn from them. In the case of dioxane-water mixtures, this behaviour corroborates the observations of Harned and Ross<sup>4</sup> with methyl acetate that activation energies are not appreciably sensitive to changes in solvent composition and that changes in the values of the frequency factor are

primarily responsible for changes in reaction rate. It should also be mentioned here that the observed trends clearly show that as higher proportions of the organic solvents are used, one has to reckon with Van der Waals forces or a possible change of catalyst or both. Discussion on this aspect has to be deferred until velocity constants for alkaline hydrolysis in these solvents have also been considered.

#### EXPERIMENTAL

*Purification of materials.*—Ethyl acetate was purified by the usual method to free it from acid. It was then over calcium chloride for three days and distilled, large head and tail fractions being rejected. B.P.  $77.1^{\circ}\text{C}$ . 757.6 mm.

1:4-Dioxan was purified by the method of Eigenberger.<sup>3</sup> It was refluxed with dilute HCl (100 c.c. of 1 N HCl for every litre of dioxane) for about eight hours to hydrolyse any acetal present and the acetaldehyde formed was removed in a rapid current of air. It was then dried over sticks of pure potassium hydroxide for 48 hours and distilled. The distillate was further dried over analar sodium for three days and finally redistilled over the same. The middle fraction was collected for use. B.P.  $100.5^{\circ}$ – $101^{\circ}\text{C}$ ./754.35 mm.

Acetone was treated with potassium permanganate<sup>5</sup> to free it from easily oxidisable impurities, and left for a week. The manganese dioxide formed was filtered off and the filtrate distilled. The distillate was dried over pure anhydrous potassium carbonate and redistilled. Large head and tail fractions were rejected and the middle fraction coming over between  $56.1^{\circ}$  and  $56.3^{\circ}\text{C}$ . (under 756.4 mm. pressure) was collected.

The water used was twice distilled with potassium permanganate in a Pyrex all-glass distillation unit, only the middle fractions being used.

*Velocity Measurements.*—The reactions were carried out in an electrically operated water thermostat which maintained temperature constant within  $0.015^{\circ}\text{C}$ .

N/10 ester solutions were prepared by weighing the necessary amount of ester into a 100 ml. standard flask and adding the appropriate volume of acetone or dioxane from standard pipettes and water enough to bring the level a little below the neck. The flask was then allowed to stand with occasional shaking for about an hour for attainment of room temperature and was then filled up to the mark with water. (For lower percentages of organic solvent, there was very little heat evolved on mixing.) The concentration of each ester solution was determined by complete alkaline hydrolysis in sealed bulbs and back titration of the excess of alkali using bromo thymol blue as indicator,

An aqueous solution of analar HCl (Merck) of strength about 0.625 N was prepared and standardised gravimetrically. The standardisation was checked up with sodium carbonate standard. The required amount of this solution to make 100 c.c. of N/10 solution was pipetted out into a 100 c.c. flask and the preparation of the solution proceeded with as before. The strengths of the acid solutions were determined by titrations just before use.

5 c.c. portions of acid and ester solutions were mixed in bulbs (of 11 to 13 c.c. capacity) at the temperature of a mixture of ice and salt. The bulbs were sealed off and immersed in the thermostat, the time of immersion being taken as zero time. They were withdrawn at suitable intervals and chilled in a freezing mixture of ice and salt. The seals were then broken at the top and the contents of the bulbs poured into 20 c.c. of ice-water (previously boiled and cooled to expel carbon dioxide) in each case and bulbs rinsed carefully with ice-water. The total volume of water used was kept approximately constant at 60 c.c. The chilled mixture was then titrated against standard barium hydroxide (N/40), bromo thymol blue being used as indicator.

Plots of  $\log_{10} (a - x)$  against  $t$  (where  $a$  is the initial concentration and  $x$  the fraction of hydrolysed at time  $t$ ) gave very good straight lines (Fig. 5)

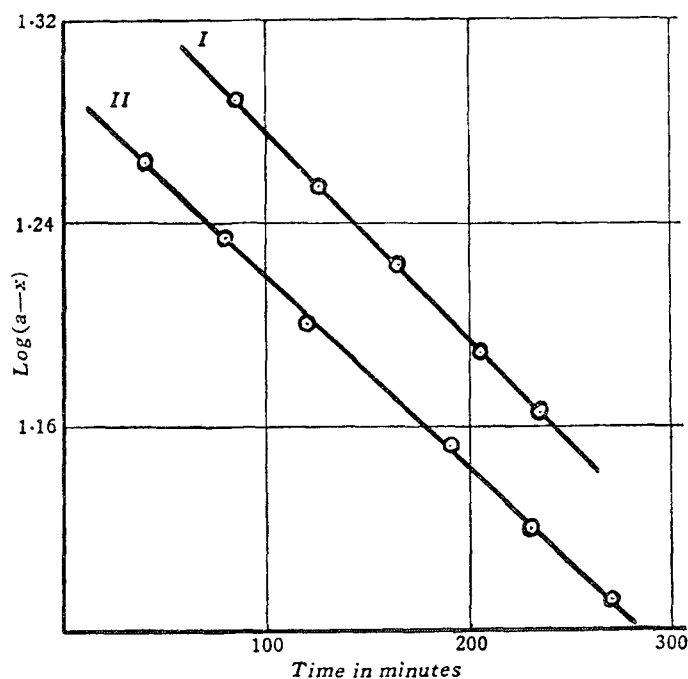


FIG. 5. Plot of  $\log (a-x)$  against time for acid hydrolysis at 55°C.  
No. 1 80% Dioxane, No. 2 60% Acetone.

indicating that the reaction was unimolecular and that there was no drift in the velocity constants within the limit to which the reaction was followed. The slope,

$$\frac{1}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2}$$

of each line was read for different intervals and the average value was used for calculation of the velocity constant.

$$(k [H^+] = k' = \frac{2 \cdot 303}{t_2 - t_1} \log_{10} \frac{a - x_1}{a - x_2})$$

Typical experimental runs are presented in Tables IV and V.

All the  $k$ -values were corrected for solvent expansion. The densities for different percentages of organic solvents at the particular temperatures

TABLE IV

*Acid hydrolysis of ethyl acetate in acetone-water mixtures at 35° C.*

Volume % Acetone	Strength of Hydrolysing Acid	Titre for 5 ml. of acid solution	Baryta equivalent to 5 ml. ester solution							
0	0.0489 N	19.05	20.01	Time in minutes	100.0	200.0	324.0	473.0	573.0	..
				Titre of 10 ml reaction mixture $V_t$	20.50	21.90	22.40	25.10	26.15	..
10	0.0491 N	20.45	21.35	$t$	100.0	200.0	300.0	400.0	500.0	700.0
				$V_t$	21.90	23.40	24.70	25.95	27.10	29.05
20	0.0491 N	20.45	21.65	$t$	100.0	200.0	300.0	400.0	500.0	600.0
				$V_t$	21.90	23.25	24.45	25.70	26.70	27.80
40	0.0492 N	20.50	22.00	$t$	100.0	200.0	300.0	400.0	500.0	600.0
				$V_t$	21.55	22.65	23.70	24.65	25.62	26.55
60	0.0491 N	21.50	23.77	$t$	100.0	200.0	300.0	400.0	500.0	601.0
				$V_t$	22.40	23.25	24.05	24.70	25.55	26.25
80	0.0492 N	21.50	24.05	$t$	100.0	200.0	300.0	425.0	500.0	600.0
				$V_t$	22.00	22.60	23.30	24.00	24.45	25.00
90	0.0440 N	18.45	22.60	$t$	125.0	300.0	415.0	500.0	..	..
				$V_t$	19.20	20.00	21.60	21.05	..	..



TABLE V  
Acid hydrolysis of ethyl acetate in dioxan-water mixtures at 35° C.

Volume % Dioxan	Strength of hydrolysing acid	Titre for 5 ml. of acid	Baryta equivalent to 5 ml. of ester							
0	0.0489 N	19.05	20.01	Time in minutes $t$	100.0	200.0	324.0	473.0	573.0	..
				Titre of 10 ml. reaction mixture $V_t$	20.50	21.90	22.40	25.10	26.15	..
10	0.0489 N	19.05	20.00	$t$	106.1	161.6	256.6	325.0	412.4	473.4
				$V_t$	20.60	21.40	22.70	23.50	24.50	25.13
20	0.0488 N	19.00	20.30	$t$	128.8	199.9	305.8	395.9	492.9	524.5
				$V_t$	20.85	21.85	23.20	24.23	25.25	27.70
40	0.0487 N	20.80	22.65	$t$	113.2	199.8	370.7	468.3	671.3	..
				$V_t$	22.43	23.60	25.60	26.65	28.70	..
60	0.0488 N	21.20	22.50	$t$	122.5	247.5	404.1	604.0	661.0	..
				$V_t$	22.00	23.30	24.60	26.30	26.70	..
80	0.0488 N	20.75	23.98	$t$	90.0	180.0	270.0	480.0	580.0	660.0
				$V_t$	21.38	22.05	22.65	24.10	24.83	25.25
90	0.0607 N	25.75	23.00	$t$	120.0	240.0	370.0	480.0	601.0	720.0
				$V_t$	26.68	27.90	28.86	29.70	30.65	31.55

were obtained by interpolation using the data given in Landolt and Bornstein's "Physikalisch Chemische Tabellen" (p. 459) in the case of acetone-water mixtures, and those given by F. Hovorka, R. A. Schaefer and D. Dreisbach<sup>7</sup> in the case of dioxane-water mixtures.

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#### SUMMARY

The kinetics of the hydrolysis of ethyl acetate in acetone-water and dioxane-water systems are reported. The rate constant passes through a minimum when the concentration of the organic solvent in the medium is in the neighbourhood of 80%. The temperature variation conforms strictly to the Arrhenius equation even for media containing extremely high

proportions of organic solvent. Even though the activation energy is affected by changes in solvent composition, the variations are not sufficiently marked for an analysis. The frequency factor has got a tendency to follow the trend of activation energies.

## REFERENCES

1. Akerlof .. *J. Am. Chem. Soc.*, 1932, 4129 ; 1936, 58, 1241.
2. Anantakrishnan and Krishnamoorthi, S. .. *Proc. Ind. Acad. Sci.*, 1941, 14 A, 279.
3. Eigenberger .. *J. Prakt. Chem.*, 1931, 130, 75.
4. Harned and Ross .. *J. Am. Chem. Soc.*, 1941, 63, 1993.
5. Norris and Psentiss .. *J. Chem. Soc.*, 1928, 129.
6. Svrbely and Warner .. *J. Am. Chem. Soc.*, 1935, 57, 1883.
7. Hovorka, Schæfer and Dreisbach .. *Ibid.*, 1936, 58, 2264.