SAPONIFICATION OF POLY(VINYL ACETATE) IN AQUEOUS ALCOHOLIC SOLUTIONS

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Saponification of poly(vinyl aceate) PV-OAc, in various methanol/H_2O and ethanol H_2O mixtures was studied using NaOH as catalyst. The rate of reaction was dependent upon temperature and solvent compositions and it followed second order kinetics in the initial stages of the reaction. In mixtures richer in water in ethanol/H_2O system, the rate was enhanced by a closer coiling of the macromolecules. Viscosity measurements of the polymer solutions revealed the state of coiling of the polymer molecules. Partially soluble polymers exhibited autocatalytic properties.

INTRODUCTION

Lee and Sakurada [1] studied the saponification of PV–OAc in methanol/H_2O mixtures and found it to be of the second order and of the first order with respect to each of the reactants PV–OAc and the catalyst, but independent of the polymer chain length. In acetone/H_2O mixtures, it was observed that the rate increased with increasing degree of hydrolysis which has been associated with the absorption of the alkali catalyst at the hydroxyl groups adjacent to the acetate groups [2-6].

The present work is an attempt to study the effect of temperature and the nature of solvent on the hydrolytic conversion of PV-OAc to poly(vinyl alcohol) PV-OH.

EXPERIMENTAL

Materials. The solvents, methanol and ethanol, were of A.R. grade. PV-OAc (BDH) (molecular weight approximately 45,000) was used as supplied. Alcohol/H_2O mixtures were prepared in the ratio of 80/20, v/v. Stock solutions of NaOH (0.3 mol dm^{-3}) and PV-OAc (0.3 mol dm^{-3} were in alcohol/H_2O, 80/20.

Procedure. The stock solutions of PV-OAc and NaOH were mixed in equal volumes. They were stirred at constant temperature in a thermostat. 5 ml of the reaction mixture were withdrawn at intervals and titrated with standard acid. The ultimate extent of the saponification of

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acetate unit was found to be equivalent to the amount of the NaOH used. Viscosity measurements of the polymer in different solvent mixtures were carried out in a Ubbelohde viscometer at 25°. The use of the polymer as supplied was justified by checking that reprecipitation of the polymer before use had no effect on the results described in this paper.

RESULTS AND DISCUSSION

A. Effect of Temperature on the Rate of Reaction: (a) Saponification in Methanol/H_2O, 70/30. Table 1 illustrates the effect of temperature on the course of the reaction in methanol/H_2O, 70/30. As expected, the initial rate increases with temperature, but in a polymer system of this kind the normal activation effect may be modified somewhat by the fact that the medium changes with temperature in the sense that the molecules will be rather less coiled at higher temperatures and the individual acetate groups thus become more liable to attack.

The relatively high initial rate decreases rapidly in the later stages. Although this will be principally due to decreasing concentrations, it has been suggested [7] that the reverse reaction may contribute as the concentration of methyl acetate increases. We find in Table 1 that equilibrium is reached at about 75% hydrolysis in methanol/H_2O, 70/30. This value is lower than 97% hydrolysis which Lee and Sakurada [1] report in the methanol/H_2O, 60/40 system. Methanol/H_2O, 70/30 is a good solvent for PV-OAc than methanol/H_2O, 60/40. The hydroxyl content of the polymer in the methanol/H_2O, 70/30 system may cause a change in the solvent solute relationship as the reaction

Table 1. Saponification of PV-OAc in methanol/H_2O, 70/30 at various temperatures

Temperature (°C)	Time (min)	% Saponification	Temperature (°C)	Time (min)	% Saponification
26	5	29.0	36	5	22.70
"	15	41.45	"	10	53.90
"	23	50.83	"	18	63.27
"	32	57.68	"	23	66.67
"	42	61.57	"	30	69.90
"	57	65.65	"	42	72.13
"	67	67.70	"	50	73.50
"	82	70.40	"	60	73.92
30	5	31.9	45	5	27.10
"	13	46.56	"	8	56.79
"	21	56.45	"	13	66.17
"	31	63.26	"	18	70.43
"	38	65.48	"	23	72.30
"	48	68.21	"	28	73.66
"	63	70.77	"	33	74.35
"	78	72.64			

progresses, (i.e. methanol/H_2O, 70/30 becoming poor and a poor solvent for the hydrolysed polymer as the reaction proceeds). This may affect the shape of the reaction curve and equilibrium value. Steric effects of this kind have been shown to be responsible for the changes which have been noted in other investigations of alcoholysis [8] and the hydrolysis of esters of poly basic acids [9]. A solvent mixture richer in water (i.e. methanol/H_2O, 60/40) acts as a good solvent for the hydrolysed polymer. Consequently, the changed situation with regard the solvent-solute relationship as reported earlier may not arise in this system. This may bring the equilibrium value higher as compared with our value.

The second-order plots shown in Fig. 1 were derived from the data in Table 1. They are not straight lines presumably due to the complicating factors mentioned above. Accepting Lee and Sakurada's finding [1] that the reaction is of the second order in the initial stages, the rate constants were calculated from the initial slopes of the curves in Fig. 1. The rate constants are given in Table 2. From the Arrhenius plot in Fig. 2, a value of 11.45 kcal mol^{-1} for the energy of activation may be calculated. This value is lower than 15.5 kcal mol^{-1} which Lee and Sakurada [1] give for methanol/H_2O, 60/40. The low value of activation energy in the methanol/H_2O, 70/30 system may be the result of increasing hydroxyl content of the polymer as the reaction progresses.
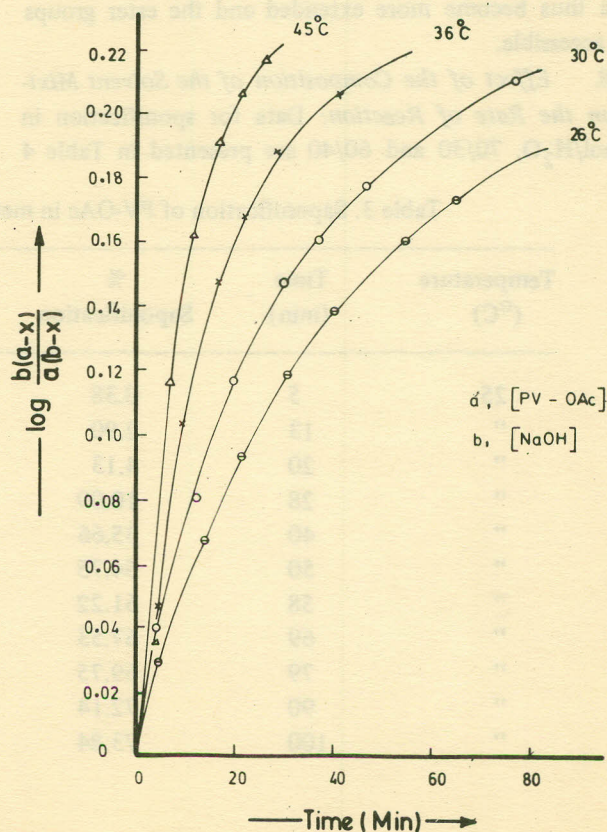

Fig. 1. Second order plots of saponification of PV-OAc in methanol/ H_2O, 70/30 at different temperatures.

Table 2. Rate constants, k, for the saponification of PV-OAc in methanol/H_2O, 70/30

Temperature (°C)	k $dm^3 \, mol^{-1} \, min^{-1}$
26	19.76 x 10^{-2}
30	24.75 x 10^{-2}
36	34.58 x 10^{-2}
45	44.24 x 10^{-2}

(b) *Saponification in Methanol/H_2O, 50/50:* PV-OAc is partially soluble in methanol/H_2O, 50/50 forming a cloudy solution. Fig. 3 derived from the data in Table 3 shows the progress of the reaction at different temperatures. The course of the reaction is clearly autocatalytic and temperature-dependent. The autocatalytic characteristics may be due to the fact that in the initial stages of the reaction the polymer molecule is in a state of tighter coiling, which hinders chemical reaction. As the reaction proceeds the polymer becomes more soluble. The polymer chains thus become more extended and the ester groups more accessible.

B. *Effect of the Composition of the Solvent Mixture on the Rate of Reaction:* Data for sponification in ethanol/H_2O, 70/30 and 60/40 are presented in Table 4

and illustrated in Fig. 4. For these solvent compositions the polymer was soluble. Rate constants reported in Table 5 are obviously dependent upon the composition of the solvent. In contrast with the acetone/H_2O system [6], however, the rate of the reaction increases rather than decrease with increase in the proportion of water in the
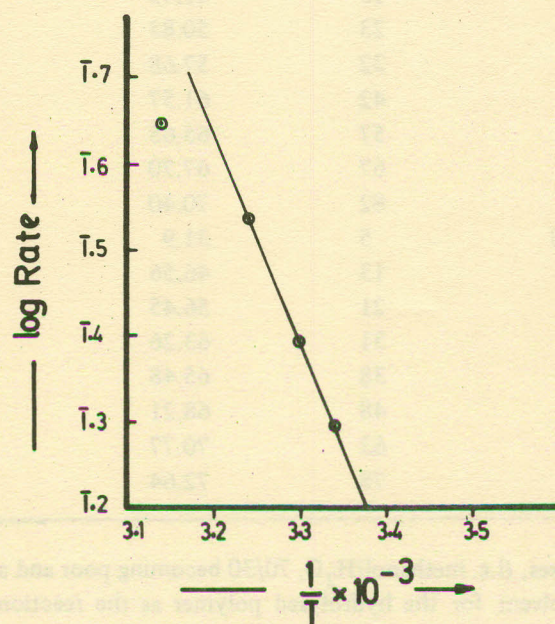

Fig. 2. Determination of activation energy for PV-OAc in methanol/H_2O 70/30 by plotting value of log rate vs 1/T °K (the Arrhenius plot).

Table 3. Saponification of PV-OAc in methanol/H_2O, 50/50 at various temperatures

Temperature (°C)	Time (min)	% Saponification	Temperature (°C)	Time (min)	% Saponification
25	5	0.38	30	5	0.38
”	13	2.90	”	12	2.93
”	20	4.13	”	21	21.34
”	28	10.09	”	25	55.94
”	40	35.66	”	30	66.50
”	50	54.75	”	36	70.94
”	58	61.22	”	42	72.98
”	69	67.53	”	55	74.68
”	79	69.75	45	5	1.57
”	90	72.14	”	10	34.13
”	100	73.84	”	17	57.64
			”	22	63.27
			”	28	70.60
			”	35	74.18
			”	40	74.86

solvent despite the fact that one would still expect,, in the ethanol/H_2O system, mixtures richer in water to be less good solvents. Thus some other effects must be overcoming the chain coiling factor in influencing the rate of reaction. This may be represented in terms of the generally accepted saponification mechanism [10] shown in Fig. 5. In this mechanism the last step in the formation of a hydroxyl group involves the release of the ion active in the first step of the process. If the chain is expanded, this ion may rapidly diffuse in the solvent, but if the chain is more coiled, it is trapped in the coil and may readily attack an adjacent carbonyl group. Thus the acceleration in the rate may be visualised as a progressive trapping of the catalyst ion by the coiled macromolecules.

C.   Viscosity Measurements of PV-OAc Solutions:
The state of coiling of the PV-OAc molecules in a solution which determines the main characteristics of their saponification or hydrolysis as suggested in a previous section is qualitatively related to the intrinsic viscosity of the solution. In general, the better the solvent, the less coiled are the molecules and the higher is the intrinsic viscosity of the solution. Thus it is relevant to make viscosity measurements on the solutions in which the reactions have been studied.

Fig. 6 and Table 5 show the plots $\eta sp/\tilde{C}$ against polymer concentration and the intrinsic viscosity data respectively. The higher intrinsic viscosity of the polymer in ethanol/H_2O 70/30 than ethanol/H_2O, 60/40 indicates that the former solvent is better for the polymer than the latter solvent in spite of the fact that the rate of reaction is higher in the latter as discussed in section B.
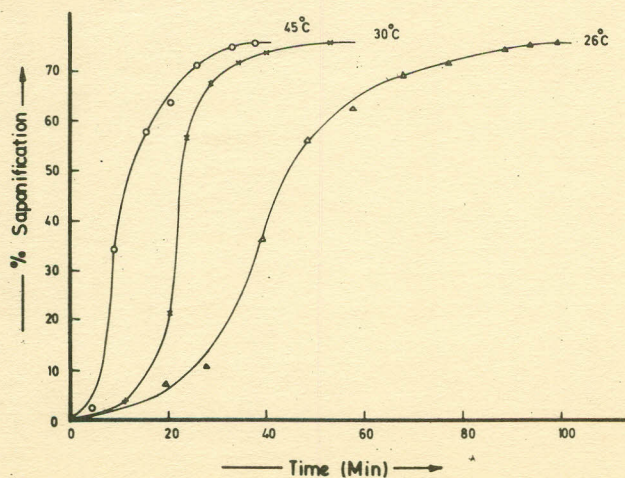
Table 4. Saponification of PV-OAc in Ethanol/H_2O at 25^{0}C.

Solvent Composition	Time (Min)	% Saponification
Ethanol/H_2O, 70/30	2	10.90
”	7	32.10
”	12	39.17
”	24	46.23
”	41	53.10
”	55	56.33
”	77	58.95
”	84	59.56
Ethanol/H_2O, 60/40	6	29.88
”	12	37.55
”	24	48.40
”	37	54.70
”	43	57.00
”	61	59.15
”	67	59.56
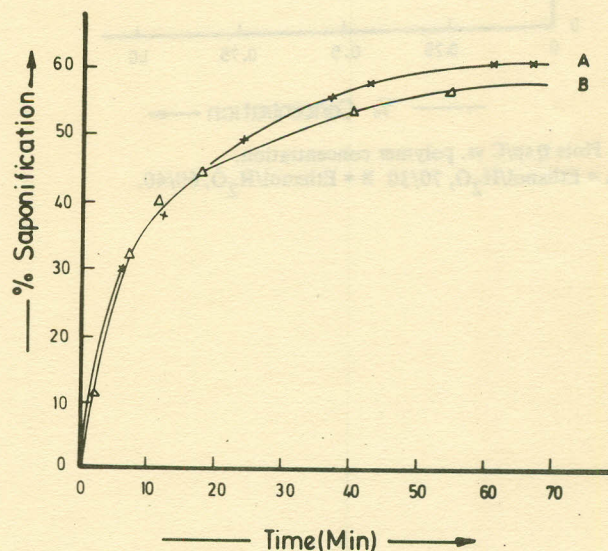
Fig. 4. Saponification of PV-OAc as a function of time at 25^0
A = Ethanol/H_2O, 60/40   B = Ethanol/H_2O, 70/30

Fig. 3. Saponification of PV-OAc in methanol/H_2O, 50/50 as a function of time at different temperatures.

Table 5. Rate constants, k, and intrinsic viscosity data for PV-OAc at 25°C

Solvent Composition	k dm^3 mol^{-1} min^{-1}	Instrinsic Viscosity (dl/g)
Ethanol /H_2O, 70/30	13.16 x 10^{-2}	0.29
Ethanol/H_2O, 60/40	16.45 x 10^{-2}	0.235

R = alkyl group
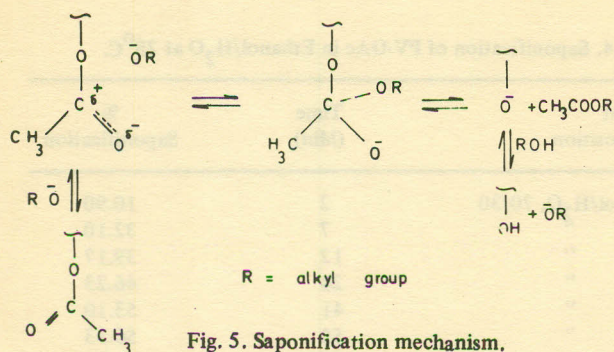
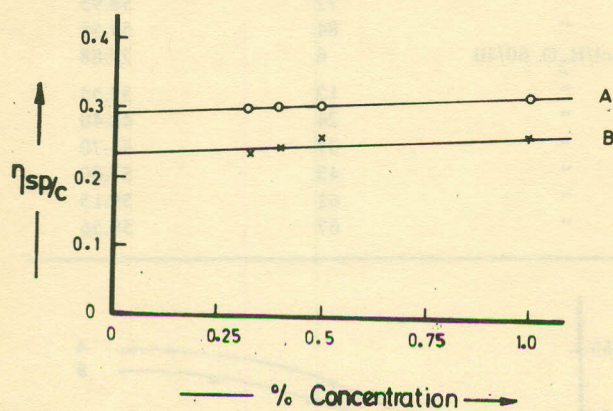Fig. 5. Saponification mechanism.

⟶ % Concentration ⟶

Fig. 6. Plots η sp/C vs. polymer concentration.
A = Ethanol/H_2O, 70/30   B = Ethanol/H_2O, 60/40.

REFERENCES

1. S. Lee and I.Z. Sakurada, Zert Physik. Chem., **A 184**, 268 (1939).
2. S. Sakaguchi, *"The Mechanism of Hydrolysis of PV-OAc in (poly vinyl alcohol)"* (ed. I. Sakurada The Society of Polymer Science, Tokyo p. 43. (1956).
3. I. Sakurada, K. Ohashi and S. Morikawa, Kogyo Kagaku Zasshi, **45**, 1287 (1942). C. A. 44, 8161 b(1950).
4. I. Sakurada, Gahsei Semi Kenkyn, **1-1**, 192(1942).
5. I. Sakurada, *et al.* Velocity of the Hydrolysis Reaction, in (Poly vinyl alcohol), (ed. C.A. Finch, pp. 90-101.
6. M. Feroze Bakht, Unpublished observations.
7. L M. Minsk, W J. Priest and W.O Kenyon, J. Am. Chem. Soc., **63**, 2715 (1941).
8. Z. Patel and H. Watson, J. Indian Inst. Sci. **16**, A, 55 (1933).
9. E.G. A. Skrabal and E. Singer, Monatsh, **40**, 363 (1919); 41, 339 (1920).
10. E.W. Eckery, *Ester, Tinterchange in "An Encyclopedia of Chemical* Technology" eds. R.E. Kirk and D.F. Othmer, (Inter-Science, New York 1950), 5, pp. 817-23.