

## THE SAPONIFICATION OF POLY(VINYL ACETATE)

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The saponification of poly(vinyl acetate) PV-OAc, in various acetone/H<sub>2</sub>O mixtures was studied using NaOH as a catalyst. Viscosity measurements of the polymer solutions revealed the state of coiling of the polymer molecules. Partially soluble polymers exhibited autocatalytic properties.

**Key words:** Poly (vinyl acetate), Saponification, Solvent composition effect.

### INTRODUCTION

The alcoholysis of PV-OAc in methanol/H<sub>2</sub>O and ethanol/H<sub>2</sub>O solutions have been reported in the literature [1-2]. It was found 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 [3-6]. It was also concluded that the initial rate constant,  $K_0$ , was independent of polymer concentration.

In the present study the effect of solvent composition on the saponification of PV-OAc and the measurement of its intrinsic viscosities have been investigated.

### EXPERIMENTAL

**Materials.** PV-OAc, (BDH), mol. wt. approximately 45,000, was used as supplied. The solvent, acetone, was of A.R. grade. Standard 0.3 mole dm<sup>-3</sup> solution of NaOH was prepared in acetone/H<sub>2</sub>O, (80/20).

**Procedure.** PV-OAc solution (0.23 mol dm<sup>-3</sup>) in acetone/H<sub>2</sub>O was mixed with NaOH solution (0.3 mol dm<sup>-3</sup>). The solutions were stirred continuously at constant temperature in a thermostat. 5 ml of the reaction mixture was withdrawn at intervals and titrated with standard acid. The ultimate extent of the saponification of acetate unit was found to be equivalent to the amount of NaOH used. Viscosity measurements of the polymer in different solvent mixtures were carried out in a Ubbelohde viscometer at 25<sup>o</sup>.

### RESULTS AND DISCUSSION

**A. Effect of the solvent mixture on the saponification reaction.** Fig. 1-2 show the effect of the composition of

the solvent mixture on the course of the saponification reaction. The polymer was soluble, forming clear solution in 90/10, 80/20, 70/30 and 65/35 solvent mixtures. It becomes progressively less soluble as the proportion of the water increases.

Autocatalytic properties appear when the polymer is partially soluble in the solvent mixture and it may be accounted for principally in terms of polymer chain coiling. The shape of the reaction curve may be affected by progressive increase in the hydroxyl content of the polymer,

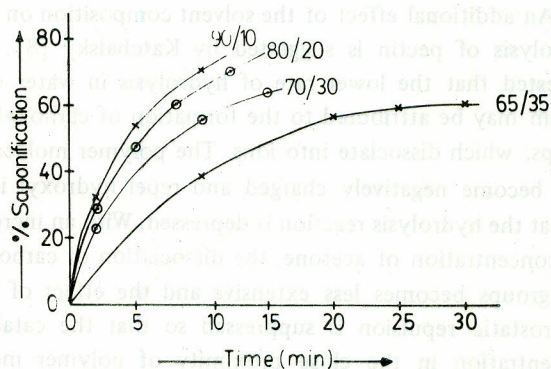


Fig. 1. Saponification of PV-OAc as a function of time for various Acetone/H<sub>2</sub>O mixtures.

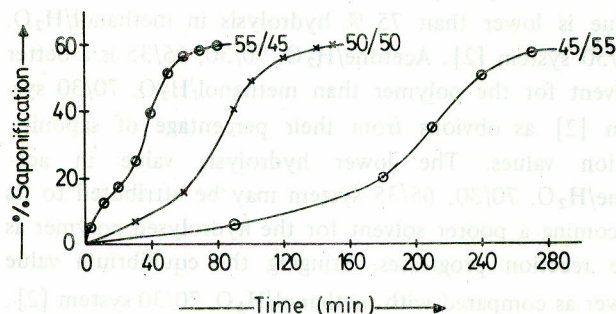


Fig. 2. Saponification of PV-OAc as a function of time for various Acetone/H<sub>2</sub>O mixtures.

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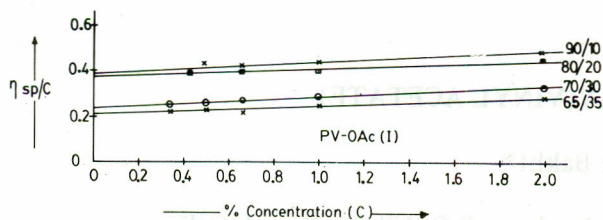


Fig. 3. Plots  $\eta_{sp}/C$  versus PV-OAc (I) concentration.

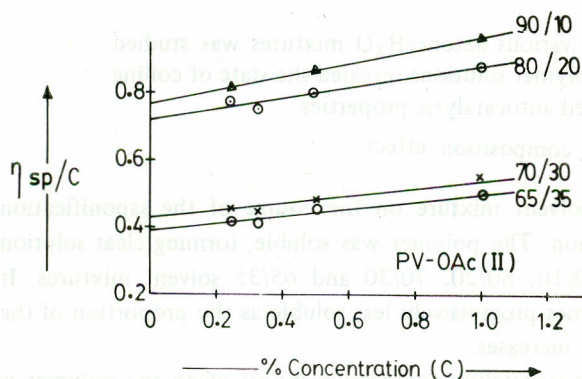


Fig. 4. Plots  $\eta_{sp}/C$  versus PV-OAc (II) concentration.

which may cause a change in the solvent-solute relationship as the reaction progresses [7].

An additional effect of the solvent composition on the hydrolysis of pectin is suggested by Katchalsky [8]. He suggested that the lower rate of hydrolysis in water rich system may be attributed to the formation of carboxylate groups, which dissociate into ions. The polymer molecules thus become negatively charged and repel hydroxyl ions so that the hydrolysis reaction is depressed. With an increasing concentration of acetone, the dissociation of carboxylate groups becomes less extensive and the effect of the electrostatic repulsion is suppressed so that the catalyst concentration in the close proximity of polymer molecules is higher.

We find from Fig. 1. that equilibrium is reached at about 60 % hydrolysis in acetone/ $H_2O$ , 70/30, 65/35. This value is lower than 75 % hydrolysis in methanol/ $H_2O$ , 70/30 system [2]. Acetone/ $H_2O$ , 70/30, 65/35 is a better solvent for the polymer than methanol/ $H_2O$ , 70/30 system [2] as obvious from their percentage of saponification values. The lower hydrolysis value in acetone/ $H_2O$ , 70/30, 65/35 system may be attributed to its becoming a poorer solvent for the hydrolysed polymer as the reaction progresses, bringing the equilibrium value lower as compared with methanol/ $H_2O$ , 70/30 system [2].

B. *Viscosity measurements of PV-OAc solutions.* The state of coiling of the polymer molecules in a solution

plays an important role in determining the main characteristic of their hydrolysis. It 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.

The specific viscosity,  $\eta_{sp}$ , of a solution is given by the relationship:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0}$$

Where

- $\eta$  = viscosity of the solution
- $\eta_0$  = viscosity of the solvent
- $t$  = flow time for the solution
- $t_0$  = flow time for the solvent

Plots of  $\eta_{sp}/C$  against polymer concentration for polymers I and II are reproduced in Fig. 3-4. The intrinsic viscosities  $[\eta] = \eta_{sp}/C$  at zero concentration derived from these plots are presented in Table 2. The constants  $K$  and  $\alpha$  calculated using the Mark - Houwink equation:

$$[\eta] = KM \text{ or } \log [\eta] = \log K + \alpha \log M$$

are given in Table 3. The value of  $\alpha$  is a measure of the extent of coiling of the long-chain molecule. When the

Table 1. Rate constants,  $K_0$ , of saponification of PV-OAc.

Temperature (oC)	Catalyst	Solvent composition	$K_0$ ( $1 \text{ mol}^{-1} \text{ min}^{-1}$ )
25	NaOH	Acetone/ $H_2O$ , 90/10	$53.10 \times 10^{-2}$
"	"	Acetone/ $H_2O$ , 80/20	$50.03 \times 10^{-2}$
"	"	Acetone/ $H_2O$ , 70/30	$46.06 \times 10^{-2}$
"	"	Acetone/ $H_2O$ , 65/35	$19.74 \times 10^{-2}$

Table 2. Intrinsic viscosity data for PV-OAc at 25°.

Solvent composition	Intrinsic viscosity (dl/g)	
	PV-OAc (I) M.W. 45,000	PV-OAc (II) M.W. 169,400
Acetone/ $H_2O$ , 90/10	0.380	0.770
Acetone/ $H_2O$ , 80/20	0.375	0.720
Acetone/ $H_2O$ , 70/30	0.240	0.430
Acetone/ $H_2O$ , 65/35	0.210	0.391

Table 3. Mark – Houwink constants K and  $\alpha$  at 25°.

Solvent composition (Acetone/H <sub>2</sub> O)	K x 10 <sup>3</sup>	$\alpha$
90/10	21.88	0.700
80/20	41.96	0.625
70/30	50.12	0.533
65/35	55.14	0.472

chain is tightly coiled into a sphere, the value of  $\alpha$  approaches zero. As the chain becomes more extended the value increases to unity. The value of K changes in different solvents in a way apposite to the intrinsic viscosity. Thus it is clear from the  $\alpha$  values in Table 3 that the PV-OAc molecules are more tightly coiled as the proportion of water in the acetone/H<sub>2</sub>O solvent mixture increases. This is in agreement with the observations discussed in section A.

REFERENCES

1. S. Lee and I.Z. Sakurada, *Physik, Chem.*, A 184, 268 (1939).
2. M. Feroze Bakht, *Pakistan, J. Sci. Ind. Res.*, 28, 92 (1985).
3. S. Sakaguchi, *The mechanism of hydrolysis of PV-OAc*, in *Poly (Vinyl Alcohol)*, I. Sakurada, (ed.) Soc. Polymer Sci. Tokyo, pp. 43 (1956).
4. I. Sakurada, K. Ohashi and S. Morikawa, *Kogyo kagaku, Zasshi*, 45, 1287 (1942) [C.A.; 44, 8161 b (1950)].
5. I. Sakurada, *Gohsei Semi Kenkyn*, 1, 192 (1942).
6. I. Sakurada, *Kogyo kagaku Zasshi*, 45, 1290 (1942).
7. E.g., A. Skrabal and E. Singer, *Monatsh*, 40, 363 (1919); 41, 339 (1920).
8. A. Katchalsky, N. Shavit and H. Eisenberg, *J. Polymer Sci.*, 13, 69 (1954).

MATERIALS AND METHODS

High molecular weight poly (vinyl acetate) was prepared from vinyl acetate and the whole film was cut into small pieces and dissolved

The saponification of poly (vinyl acetate) was carried out in a stirred reactor under nitrogen atmosphere. The reactor was equipped with a stirrer and a reflux condenser. The reaction mixture was prepared by dissolving a known amount of poly (vinyl acetate) in a known volume of acetone-water mixture. The reaction was carried out at 25°C for a known period of time. The reaction mixture was then cooled and stored under nitrogen atmosphere. The saponification was carried out in a stirred reactor under nitrogen atmosphere. The reactor was equipped with a stirrer and a reflux condenser. The reaction mixture was prepared by dissolving a known amount of poly (vinyl acetate) in a known volume of acetone-water mixture. The reaction was carried out at 25°C for a known period of time. The reaction mixture was then cooled and stored under nitrogen atmosphere.