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THE REACTION OF HIGH POLYMERS IN SOLUTION. THE ALKALINE SAPONIFICATION OF POLYVINYL ACETATE.

Preliminary Report.

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Introduction.

H. Staudinger[1] reported that when a methanol solution of sodium hydroxide was added to the equivalent quantity of polyvinyl acetate, a white precipitate was produced instantaneously which was left to stand for two hours in a water bath and polyvinyl alcohol was obtained. W. O. Herrmann proposes for this reaction the following equation[2]:

$$(CH_2:CHCOOCH_3)_n + nNaOH = (CH_2:CHOH)_n + nCH_3COONa. \qquad (1)$$

It is further reported that if potassium hydroxide is used in a quantity less than its equivalent amount, partially saponified products are obtained[3], which are distinguished from pure polyvinyl alcohol in being soluble in both water and dioxane and slightly in alcohol.

S. Lee and I. Sakurada[4] tried to saponify polyvinyl acetate of different polymerisation degrees and monovinyl acetate in methanol water solution with NaOH. By titrating NaOH in the reaction system, the reaction was recognized to be a bimolecular one. Then the velocity constant was calculated and found to have no relation to the polymerisation degree. It was therefore not proper, even from the standpoint of chemical kinetics, to think that the whole ground molecules of polyvinyl acetate at saponification with NaOH were restrained as a huge stiff macromolecule in the shape of a pole. On the contrary, each of them acts fairly freely. However, considering it as a misunderstanding of the experimental method, Skrabal said that the main reaction was

$$AR + CH_3OH \rightleftarrows ACH_3 + ROH. \qquad (2)$$

In this case NaOH acted as a catalist only, and on account of the large quantity

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[1] H. Staudinger, K. Frey and W. Stark, *Ber.*, 60, 1782 (1927).
[2] W. O. Herrmann and W. Haehnel, *Ber.*, 60, 1658 (1927).
[3] H. Staudinger and A. Schwalbach, *Ann. Chem.*, 488, 8 (1931).
[4] S. Lee and I. Sakurada, *Z. physik. Chem.* A 184, 268 (1939).

of CH_3OH the equilibrium moved to the right and in parallel with it the following side-reaction took place,

$$ACH_3 + NaOH \rightarrow ANa + CH_3OH, \qquad (3)$$

where A is the acetyl radical and R is the polyvinyl alcohol radical[5]. According to S. Lee who measured the side-reaction (3), it was natural that the velocity constant had no relation to the polymerisation degree. It has already been known that in this reaction fairly perfect saponification occurs with NaOH amounting to 2 or 4% of the amount calculated from Herrmann's formula[6] [7].

The author carried out the following preliminary experiments to verify whether the present reaction belonged to the Herrmann type as was assumed by S. Lee and I. Sakurada or to the type proposed by Skrabal (2), i.e. whether there existed any partially saponified product in the course of this reaction and whether the presence of equivalent quantity of NaOH was necessary.

Characters of the Saponified Product in Various Concentrations of Alkali.

If the reaction proceeds according to the equation,

$$(CH_2:CHCOOCH_3)_n + nNaOH = (CH_2:CHOH)_n + nCH_3COONa,$$

when less NaOH than the equivalent amount is used, either partially saponified product which Staudinger has reported or a mixture of polyvinyl alcohol and polyvinyl acetate must be produced. Before making the experiments on the reaction velocity, it was necessary to know the substance finally to be produced, and so experiments were made on saponified products with various concentrations of alkali.

a) Experimental method.

Polyvinyl acetate used was made in the Nippon Chisso Co. and its mean polymerisation degree was 440 ($K_m = 2.6 \times 10^{-4}$) according to the calculation from Staudinger's formula[7]. About 50 g. of polyvinyl acetate was dissolved in 500 c.c. of redistilled methanol. Each 100 g was added to a mixture of pure methanol and caustic soda methanol, 80.80 g/L in concentration; it was then tightly corked and kept in a thermostat at 20°C. for 24 hours. In each case white flocculent precipitate was recognized within 5 minutes.

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5) A. Skrabal, *Z. physik. Chem.*, A 185, 389 (1939).
6) Houwink, *Chem. und Tech. der Kunststoff.* S. 325.
7) W. H. McDowell and W. C. Kenyon, *J. Am. Chem. Soc.*, 62, 415 (1940).

After filtration the precipitate was washed with methanol and dissolved in water and made to a given volume. NaOH consumed was calculated from the analytical data of the solution and the filtrate.

When 20 c.c. of the above aqueous solution of the precipitate was poured into 60 c.c. acetone, white precipitate was again produced. It was filtered, washed with acetone, dried at 110°C. for 5 hours, and then weighed. It was denoted as " acetone precipitate ". At first the weights of the different lots of the " acetone precipitate " differed because of the adsorbed substances, but they became constant by washing with dioxane. Its acetyl value decreased remarkably by reprecipitation with acetone.

A given amount of the aqueous solution of " acetone precipitate " was dissolved in *n* NaOH, tightly corked, and left to stand for 24 hours. It was titrated with *n* H_2SO_4 with phenolphthalein as an indicator. By regarding the consumed NaOH as due to CH_3COOH, the acetyl values were calculated. Staudinger says that it is difficult to get the acetyl values given by the theory. The author desired to use a more accurate analytical method, but in the meantime he had to content himself with relative values.

Viscosity of the " acetone precipitate " was measured by the ordinary method by means of Ostwald's viscosimeter in a thermostat kept at 20°C.

b) Experimental Results.

Tables I and II show the products obtained by saponification with NaOH and Table III shows those obtained particularly with KOH according to Staudinger's report.

From the results it is seen that the amount of the product obtained is almost equal to the theoretical amount of polyvinyl alcohol nearly independent of that of the alkali used, and that the acetyl values agree generally with one another and are too small to be regarded as due to partially saponified products.

Staudinger says that partially saponified products are soluble in dioxane. In the above mentioned experiments a slight decrease in amount by washing with dioxane is observed, but it is considered to be due to the removal of adsorbed substances. The products, washed with dioxane always show the equal weight independent of the amounts of the alkali used and this weight almost agrees with the value calculated as polyvinyl alcohol.

When KOH was used, the decrease by washing with dioxane was remarkably small.

The viscosity-concentration curves of aqueous solutions of "acetone precipitate" nearly agreed with one another independent of the amounts of alkali used. Even when less alkali than the equivalent amount was used, anything that might be regarded as a partially saponified product could not be detected at the end of reaction; it was polyvinyl alcohol that was always obtained. Herrmann's formula was not sufficient to explain these facts.

Table I.

Saponification Products with NaOH of Various Concentrations.

Exp. 1.

Sample Number	1	2	3	4
Initial polyvinyl acetate (g)*	11.24	11.24	11.24	11.24
NaOH taken (g)	3.232	4.040	4.848	8.080
Conc. (g/L)	32.32	40.40	48.48	80.80
NaOH mol/gd. mol.	0.618	0.773	0.929	1.546
NaOH consumed (g)	2.140	2.570	3.069	5.150
Polyvinyl alcohol (Theo.) (g)	5.751	5.751	5.751	5.741
"Acetone precipitate" at first. (g)	5.664	6.548	6.413	6.570
"Acetone precipitate" washed with dioxane (g)	5.756	5.542	5.568	5.698
η_r of "acetone precipitate" (10 g/L)	1.59	1.60	1.70	1.69

* This sample was a commercial material, not specially purified. Therefore, the theoretical quantity of polyvinyl alcohol has not any absolute meaning.

Table II.

Products of Saponification by NaOH of Various Concentrations.

Exp. 2.

Sample Number	1	2	3	4
Initial polyvinyl acetate (g)	11.24	11.24	11.24	11.24
NaOH taken (g)	3.224	4.030	4.836	8.060
Conc. (g/L)	32.32	40.30	48.35	80.60
NaOH mol/gd.mol.	0.617	0.778	0.925	1.541
NaOH consumed (g)	2.300	2.813	4.108	3.889
Polyvinyl alcohol (Theo.) (g)	5.751	5.751	5.751	5.751
"Acetone precipitate" at first. (g)	6.125	5.333	5.417	6.068
"Acetone precipitate" washed with dioxane. (g)	4.745	4.745	4.985	4.980
Acetyl value as CH_3COOH of "acetone ppt." (%)*	7.96	8.72	7.89	7.03
Acetyl value of acetone re-ppt. (%)**	1.22	1.78	2.18	2.86

* This sample was crude acetone precipitate not washed with dioxane.

** The said crude acetone precipitate was dissolved in water and poured into acetone. The precipitate thus prepared was taken as the sample for analysis.

Table III.

Products of Saponification by KOH of Various Concentrations.

Exp. 3.

Sample Number	1	2	3	4
Initial polyvinyl acetate (g)	7.84	7.84	7.84	7.84
KOH taken (g)	4.774	5.967	7.160	11.934
Conc. (g/L)	47.47	59.67	71.60	119.34
KOH mol/gd.mol.	0.933	1.166	1.399	2.332
KOH consumed (g)	4.281	3.625	5.175	5.021
Polyvinyl alcohol (Theo.) (g)	4.011	4.011	4.011	4.011
"Acetone precipitate" (g)	4.050	4.015	4.150	4.295
"Acetone precipitate" washed with dioxane (g)	4.009	4.060	4.000	4.172
Acetyl value of "acetone ppt." (%)	2.52	2.99	2.17	2.34
Acetyl value of acetone re-ppt. (%)	2.23	2.60	2.20	2.62

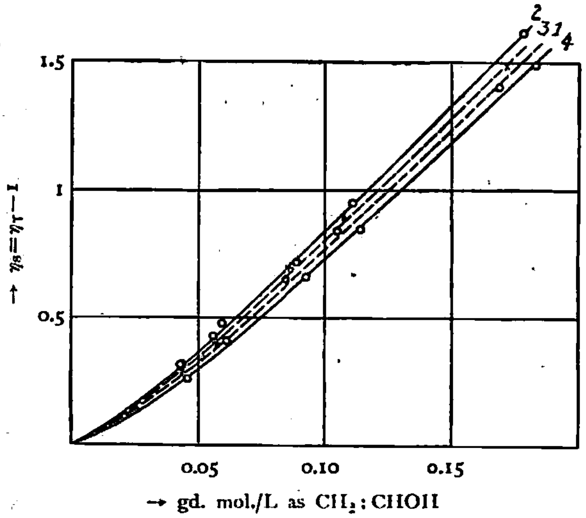

Fig. 1. Viscosity-Concentration Curve at 20°C of the Saponified Product (Exp. 3).

On the Change of the Concentration of NaOH During the Reaction.

If the reaction proceeds according to Herrmann's formula, the reaction velocity should be measured simply by determining the NaOH concentration in the reaction system. But the change of concentration of NaOH is not always in parallel with the formation of polyvinyl alcohol, and it is often recognized even after the separation of polyvinyl alcohol. This phenomenon was ascertained by the following experiments.

a) Experimental Method.

50 g. of the above-mentioned commercial polyvinyl acetate was dissolved in 500 c.c. of methanol. 400 c.c. of the solution was mixed at 0°C. with 240 c.c. of methanol and 160 c.c. of 83.4 g/L NaOH methanol solution and then placed in a thermostat kept at 0°C. The concentration of NaOH after the mixing was 16.68 g/L. About 5 minutes after the mixing the whole turned into gel and then syneresis occurred; this was broken with a glass rod, quickly taken out, and pressed on a Buchner funnel. The solution obtained by pressing was held again in a thermostat kept at 0°C. This procedure required about 3 minutes. The change of concentration of alkali in that case is shown in Fig. 2, curve 1; curve 2 shows the case when the upper layer of unseparated system was taken out and analysed. Both curves indicate much the same tendency.

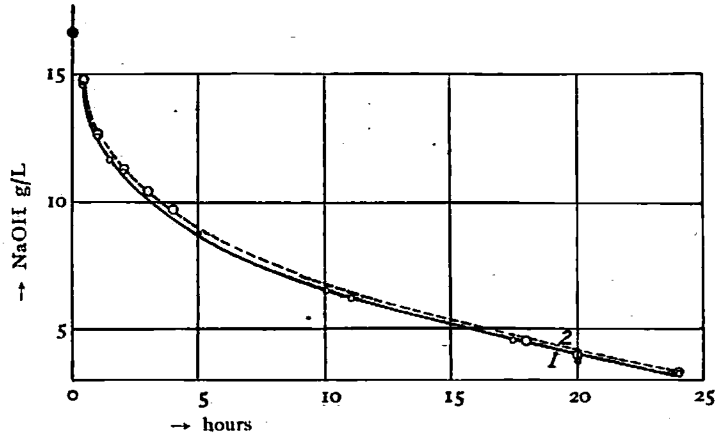

Fig. 2. Decrease of NaOH Conc. after the Polyvinyl Alcohol Separation (0°C).

b) Experimental Results.

Fig. 2 clearly shows that NaOH is being consumed for many hours after the precipitation of saponified high polymers. Let the precipitate corresponding to curve 1 be diluted with water up to 500 c.c. and let "acetone precipitate" be made from a portion of it; the acetyl value is found to be 8.12% as CH_3COOH. But when the acetone re-precipitated substance is used, the acetyl value is found to be 3.01%. Comparing these values with that mentioned in the previous chapter, it is seen that a substance to be considered as polyvinyl alcohol has already been generated before the large portion of NaOH begins to be consumed.

Conclusion.

From the present experiments, it is made clear that the saponification of

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polyvinyl acetate with alkali cannot be explained by Herrmann's formula (1) and that accordingly it is inappropriate to study the reaction velocity from the change of the concentration of NaOH on such an assumption.

It is, however, not yet clear whether Skrabal's formulae (2) and (3) hold good or not. The author will treat this problem in the next report.

Summary.

On the saponification of polyvinyl acetate in methanol solution by NaOH, the author has perceived the difference between the explanations of Staudinger, Herrmann and Skrabal. By ascertaining the following facts, he has got the preliminary knowledge for the study of the reaction velocity.

(1) A partially saponified product cannot be detected in spite of the use of the same procedures as Staudinger's report.

(2) The perfect saponification does not always require the same equivalent quantity of NaOH or KOH for the ground molecule of polyvinyl acetate. Therefore, the reaction is not to be considered as a simple bimolecular reaction of the ground molecule with NaOH.

(3) After the completion of saponification, the concentration of NaOH continues to change for many hours. This shows that Skrabal's explanation in which NaOH is consumed in the side reaction is more appropriate.

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