

PREPARATION AND PROPERTIES OF PHOSPHORYLATED JUTE CELLULOSE

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Different methods were examined for phosphorylation of jute cellulose. Best results were obtained with urea-phosphoric acid method with slight modification of the procedure. The effects of reagent/cellulose ratio, temperature and period of reaction were studied. Under optimum conditions, the product contained about 11% phosphorus and had a cation exchange capacity of over 3.5 m. equiv/g. The ion-exchange behaviour has been characterized and evaluated by pH-titration and conductometric methods. The product has good flow characteristics and can be conveniently used in a column.

It was earlier reported,^{1,2} that purified jute cellulose can be conveniently used for the preparation of carboxymethylcellulose. As it was noted that jute cellulose responded equally well (and sometimes even better) towards substitution, compared to cotton or pulp, it was thought that the preparation of cellulose phosphate from jute should also be explored. And, although indications of useful applications of phosphorylated cellulose as flame-resistant fabric³ and as cation exchanger⁴ are available, no reference has yet been made regarding the use of jute as the source material.

Champetier⁵ in 1933 first reported the formation of a phosphoric acid ester of cellulose containing one phosphate group per three glucose units; but this decomposed readily in water. Tanner⁶ used 85% phosphoric acid in presence of sulphuric and acetic acids for phosphorylation but their results could not be reproduced.⁷ Other reagents used for phosphorylation of cellulose were a mixture of phosphoric acid and phosphorus oxychloride⁸⁻¹⁰ phosphorus trichloride and monophenyl phosphate,¹¹ phosphorus pentoxide¹² and chlorides of partially esterified polybasic acids.¹³ Other processes utilized pyridine as a solvent,^{14,15} for phosphorylation with phosphoric acid, but in these preparations, cellulose suffered considerable loss of strength.

The most satisfactory reagent so far used appears to be a mixture of phosphoric acid and urea originally due to Coppick and Hall,¹⁶ but later modified by Hoffpaur and Guthrie.¹⁷ In the present investigation, the authors studied the phosphorylation of purified jute cellulose with phosphoric acid and urea mixtures, with some modifications. The cation exchange properties were also studied.

Experimental

Materials.—Cotton, pulp or jute cellulose used for the different experiments were prepared by following the procedure mentioned earlier.¹

All chemicals were laboratory grade reagents.

Methods.—In the preliminary experiments, the method of Coppick and Hall¹⁶ was followed, with modification in conditions and procedure as mentioned:

10 g. of the desired cellulose was steeped at room temperature (28-30°) in a mixture containing 13.8 g. H₃PO₄, 21.6 g. urea and 24.0 g. water. After one hour, the excess liquor was pressed out to leave a mass of 50 g. This was now heated in a beaker on an oil bath for ½ hour at 100°, followed by another ½ hour at 150°. These conditions gave a reagent/cellulose ratio of 6:1 during steeping and 4:1 during heating. The product was thoroughly washed with water and dried *in vacuo* at 50-60°. The dried sample was treated with HCl, washed again with water and dried. The whole procedure took 4-5 days.

Final Procedure for Phosphorylation.—In the final procedure, the modification of Guthrie *et al.*¹⁷ was followed. But instead of passing a current of hot air, the experiments were conducted in an open vessel with constant stirring. It may be briefly stated as follows:

10 g. of cellulose was soaked in a solution containing 14.9 g. urea, 5.3 g. H₃PO₄ (89%) (molar ratio 4:1) and 9.5 g. water for 2 hours at room temperature (28-30°). The mixture was then heated in a beaker on an oil bath for about an hour while the temperature was raised gradually to 130°, and maintained at this temperature for another hour with constant stirring. After the reaction, the product was washed thoroughly with water, filtered and dried in a steam oven.

Determination of Total Cation Exchange Capacity.—This was determined for the ester (CP) by calcium acetate method. 1 g. of the sample was converted to the H-form and to it 4% Ca-acetate solution added. The material was mechanically shaken for 48 hours and subsequently washed free of acid.

The filtrate was titrated with standard 0.1(N) NaOH. The amount of Ca^{++} adsorbed was calculated from a blank experiment.

pH and Conductometric Titration Curves.—For the pH titration curve, standard procedure was followed using 0.3 g. of the ester (CP) in the H-form in 50 ml. 1% KCl. Several samples, specially those with longer curing time were titrated after seven days' conditioning in H-form in water.

For conductance measurement 0.3 g. of the NH_4 -salt was converted to the H-form and suspended in 50 ml. of re-distilled water. A Mullard Bridge was employed for measurement.

Results and Discussion

Results obtained by phosphorylation of cotton and jute cellulose by Coppick and Hall method are presented in Table 1. It will be noted that with

cotton, phosphorylation was poor, even with some variation in the procedure. With jute cellulose, results were only somewhat better. When both the dryings were done at room temperature, with jute cellulose the phosphorus content increased to 2.01%, but about a fortnight was required for the purpose. The products with about 2% phosphorus was flame-resistant, but unsatisfactory for use as cation-exchanger. Need for use of a relatively large proportion of reagents is also a point against it.

In the final procedure adopted, the reagent/cellulose ratio(w/w) was kept at 3.0. Although jute was the main point of interest, experiments were carried out with cotton and pulp for comparison. It will be seen from Table 2 that under identical conditions, pulp and jute gave more or less similar products. Although the phosphorus content was a bit higher in the products from pulp, cation-exchange capacities were nearly the same.

TABLE 1.—PREPARATION OF CELLULOSE PHOSPHATE FOLLOWING COPPICK AND HALL METHOD IN PRINCIPLE.

Expt. No.	Source of cellulose	Method of preparation	P content % product	Remarks and properties
B _{3a}	Cotton	Coppick method, first drying step avoided	0.79	Fibrous
B _{3b}	"	HCl treatment avoided	0.59	Fibrous, no change in the product
B _{3c}	"	Coppick method followed	0.74	Fibrous
B ₁	Jute	"	1.93	Fibrous product
B ₄	"	Both the drying was at room temp. (28-30°C.)	2.01	Fibrous product

TABLE 2.—PREPARATION OF CELLULOSE PHOSPHATE FROM DIFFERENT RAW MATERIALS.

Expt. No.	Source of cellulose	Temp. of reaction °C.	P content % product	Total capacity m. equiv./g.	Physical properties
P ₃	Cotton	100-110	2.3	1.01	Lumps
P ₂	Pulp	100-110	3.3	1.63	Lumps
P ₁	Jute	100-110	3.2	1.62	Lumps
P ₉	Cotton	130-135	7.6	3.19	Fibrous Lumps
P ₈	Pulp	130-135	9.0	3.32	Fibrous
P ₇	Jute	130-135	8.3	3.24	Fibrous

The physical properties and flow characteristics were also similar. Cotton, however, was found to give less satisfactory results.

High temperature facilitates the reaction considerably. By increase of temperature of about 20-25° (100-110°C. to 130-135°C.) the phosphorus content increased almost three-fold and the ion-exchange capacities in a like manner. Temperature higher than 130-135°C. tended to char the cellulosic material, specially when the reagent/cellulose ratio is lower and for higher reagent/cellulose ratio longer reaction periods were necessary. So a temperature range of 130-135°C. was maintained for further experiments.

Effect of Reagent/Cellulose Ratio and Time.—In the preceding experiments with the reagent/cellulose ratio of 3:1, good results were obtained. But with this quantity of reagent, the H_3PO_4 was sufficient only for a degree of substitution of 0.9 (theoretically possible D.S. being taken as 3.0). As the ion-exchange capacity of cellulose phosphate was expected to increase with increasing phosphorus content, the effect of reagent/cellulose ratio was studied next (Table 3). Longer

time taken to vapourize the liquid before the actual reaction takes place, or due to the melting of excess urea.

Evaluation of Cellulose Phosphate as Ion Exchanger.—The physical form, flow characteristics and cation exchange capacity of the cellulose phosphate (CP) obtained from jute were carefully studied. All the above mentioned properties improved with increase of phosphorus content of the product. Handling of the mass during and after reaction is also important.

With the increase of phosphorus content the physical form changes from lumps (most unsatisfactory as ion-exchanger) to fibrous lumps and finally fibrous powder (most desirable as ion-exchanger). The last form is best obtained with longer time of reaction, but it tends to decrease the ion-exchange capacity slightly.

The ion-exchange capacity has been determined by pH titration and the characterization curve has been worked out (Fig. 1). The cellulose phosphate (as prepared by urea-phosphoric acid

TABLE 3.—PREPARATION OF CELLULOSE PHOSPHATE FROM PURIFIED JUTE (EFFECT OF REAGENT/CELLULOSE RATIO AND TIME OF REACTION).

Expt. No.	Reagent/cellulose ratio.	Time of reaction (hrs.)	P-content % product	Total capacity (m. equiv./g.)	Physical appearance
P ₇	3.0	1.0	8.30	3.24	Fibrous
P ₁₂	3.0	2.5	9.30	3.33	Fibrous powder
P ₁₆	3.0	3.5	10.25	3.25	powder Fibrous
P ₁₁	4.5	1.0	8.55	3.30	Lumps
P ₁₄	4.5	2.5	10.57	3.79	Fibrous
P ₁₅	4.5	3.5	11.17	3.50	Fibrous

period of reaction increases the phosphorus content (with the same reagent/cellulose ratio), but obviously cannot go beyond the calculated value. By increasing the reagent/cellulose ratio to 4.5, the phosphorus content of the product increased to some extent.

It was found that the time of reaction was more important when the reagent/cellulose ratio was higher. This is due most probably to the longer

method) being in the NH_4 -form had to be converted to the H-form. The curve in Fig. 1 represents the titration in presence of KCl. Titration without addition of KCl gave almost identical curves. Curves with products obtained with longer curving and conditioning showed some difference. The curve shows two changes indicating the presence of $-PO_3H_2$ group which has two ionizable hydrogen atoms ionizing at about pH of 4.5 and 8.5, respectively.

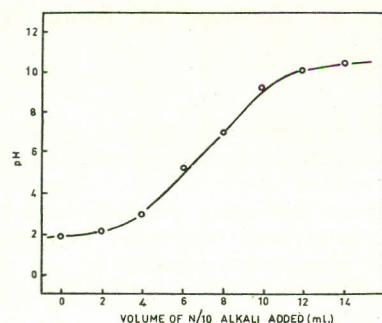


Fig. 1.—Showing pH. titration curve of phosphorylated jute cellulose.

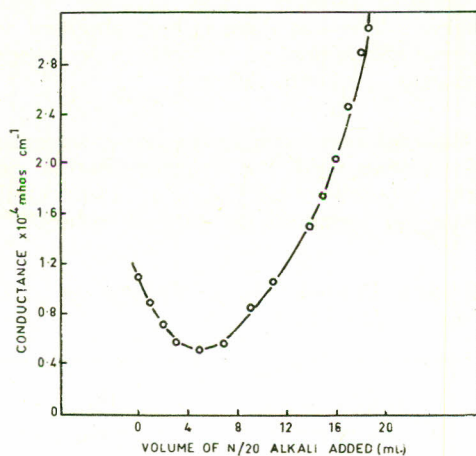


Fig. 2.—Conductivity titration curve of phosphorylated jute cellulose.

A typical curve obtained by conductometric titration of the product (which behaves like an acid when suspended in water) with standard N/20 NaOH solution is shown in Fig. 2. There are two distinct end points, indicating the presence of two ionizable hydrogen atoms in the polyelectrolyte. Near the first neutralization point, change of conductance was very slow (which necessitated the extrapolation of the straight lines), it is evident that this ester of cellulose behaves as a weak acid in water suspension.

The observation, from both pH and conductometric titrations, of the presence of $-\text{PO}_3\text{H}_2$ in the cellulose phosphate prepared in the present work is in conformity with the work of Head *et al.*¹⁸

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