# Phosphorylation of Cellulose with *cyclo*-Triphosphate

Hideko INOUE, Yoshinobu BABA, and Mitsutomo TSUHAKO*

*Department of Chemistry, Kobe Pharmaceutical University, Kitamachi, Motoyama, Higashinada-ku, Kobe 658, Japan.*
Received November 2, 1994; accepted December 27, 1994

**The phosphorylation of cellulose with inorganic *cyclo*-triphosphate ($P_{3m}$) was studied in aqueous solutions under various conditions. One glucose unit per thirty glucose units of cellulose molecule was phosphorylated under the optimum conditions (25% $P_{3m}$, pH 12, and 50 °C). Phosphorylated cellulose is characterized by its adsorption of metal ions and noncombustibility.**

**Key words** phosphorylation; cellulose; *cyclo*-triphosphate

Inorganic sodium *cyclo*-triphosphate ($P_{3m}$) is a very useful phosphorylating agent which produces phosphorylated products of alcohols,[1] amines,[2] amino acids,[3-6] phenols,[7] and sugar[8] in aqueous solutions without complicated handling. The phosphorylated products of a polysaccharide are expected as a chiral selector, a masking agent of metal ions, water treating agent, and drug delivery system (DDS) material.[9]

Feldmann reported in 1967 that $P_{3m}$ reacts with alcohols to form their mono- and triphosphate derivatives.[1] On the other hand, the present authors[8] demonstrated that the reaction of α-D-glucose with $P_{3m}$ afforded good yields of phosphorylated products of α-D-glucose. The main product in the reaction of glucose with $P_{3m}$ was a glucose triphosphate. Also, disaccharides such as maltose, lactose, sucrose, and cellobiose were easily phosphorylated by $P_{3m}$. More recently, we found that cyclodextrin and starch are phosphorylated with $P_{3m}$ in aqueous solutions by a one-step reaction.[10] However, the phosphorylation of cellulose with $P_{3m}$ has not yet been reported. Thus, in the present paper, for the purpose of examining the effective use of cellulose, we have studied the phosphorylation of cellulose with $P_{3m}$, and the phosphorylated cellulose was characterized by the adsorption of metal ions.

## Results and Discussion

Table 1 shows the phosphorus content in cellulose papers phosphorylated under various reaction conditions. As can be seen, the phosphorus content in the cellulose phosphates increased with an increase in concentration of $P_{3m}$. The treatment of cellulose with 25% $P_{3m}$ solution yielded more a five-fold increase in phosphorus content than that with 10% $P_{3m}$ solution.

The effect of temperature on the phosphorylation of cellulose paper was investigated in the range of room temperature to 50 °C. At 50 °C, the rate of phosphorylation was constant after two weeks of incubation, whereas four weeks were required at room temperature. The effect of stirring on the phosphorylation reaction was not observed because of the high $P_{3m}$ concentration. Therefore, optimum conditions in the phosphorylation of cellulose paper were established to be a reaction with 25% $P_{3m}$ solution at 50 °C for 14 d without stirring. From the analysis of phosphorus in the phosphorylated cellulose paper, one glucose unit per thirty glucose units of cellulose molecule was estimated to be phosphorylated under the optimum conditions.

Table 2 shows the amounts of adsorption of metal ions per a phosphorylated cellulose paper produced by the reaction with 10% $P_{3m}$ solution at pH 12 and 50 °C. The phosphorylated cellulose paper was found to adsorb significant amounts of certain metal ions ($Fe^{2+}$, $Fe^{3+}$, $Ag^{+}$, and $Bi^{3+}$). Especially, of all the metal ions, $Fe^{2+}$ and $Fe^{3+}$ ions were exceedingly adsorbed by cellulose

Table 1. Phosphorylation of Cellulose with $P_{3m}$

| No. | Reaction condition[a] | | | | P content |
|---|---|---|---|---|---|
| | Conc. of $P_{3m}$ | Temp. (°C) | Stirring | Time | (μg/paper[b]) |
| 1 | 10% | R.T. | No stirring | 4 weeks | 435 (0.17%) |
| 2 | 10% | 50 | No stirring | 2 weeks | 424 (0.15%) |
| 3 | 10% | 50 | No stirring | 2 weeks (two times) | 518 (0.19%) |
| 4 | 20% | 50 | No stirring | 2 weeks | 686 (0.25%) |
| 5 | 10% | R.T. | Urtrasonic | 4 weeks | 483 (0.18%) |
| 6 | 10% | 50 | Stirring | 2 weeks | 403 (0.14%) |
| 7 | 25% | 50 | Stirring | 2 weeks | 1752 (0.63%) |

*a)* Phosphorylation was carried out with 10 papers in 500 ml of $P_{3m}$ solution (10, 20, and 25%) at pH 12. *b)* Paper size: 100×210 mm/paper, paper weight: 0.283 g/paper. R.T. = room temperature.

Table 2. The Amount of Adsorption of Metal Ions by Cellulose Paper Phosphorylated with 10% $P_{3m}$ Solution at pH 12 and 50 °C

| Metal ion[a] | Adsorption (μg/paper[b]) |
|---|---|
| $Fe^{2+}$ | 1500—5627 |
| $Fe^{3+}$ | 1800 |
| $Co^{2+}$ | 30 |
| $Ni^{2+}$ | 270 |
| $Cu^{2+}$ | 360 |
| $Ag^{+}$ | 1250 |
| $Sn^{2+}$ | 356 |
| $Pb^{2+}$ | 119 |
| $Sb^{3+}$ | 270 |
| $Bi^{3+}$ | 2106 |
| $Zn^{2+}$ | 450 |
| $Al^{3+}$ | 93 |
| $La^{3+}$ | 253 |
| $Ce^{3+}$ | 257 |

*a)* 50 ml of the reaction solution (100 ppm) was used for the adsorption of metal ions by a phosphorylated cellulose paper. *b)* Paper size: 100×210 mm/paper, paper weight: 0.290 g.

* To whom correspondence should be addressed.

phosphate: 5.6 mg of $Fe^{2+}$ ion (data in Table 2) was adsorbed by the cellulose paper phosphorylated with 25% $P_{3m}$ solution at pH 12 and 50 °C.

The phosphorylated cellulose paper was also able to adsorb $Fe^{2+}$ and $Fe^{3+}$ ions in tap water. Slightly colored tap water, which included 42 $\mu$g of $Fe^{2+}$ and $Fe^{3+}$ ions in 50 ml, became colorless after the treatment with phosphorylated cellulose paper (25% $P_{3m}$ solution at pH 12 and 50 °C), showing that the phosphorylated cellulose paper completely adsorbed $Fe^{2+}$ and $Fe^{3+}$ ions in tap water. Therefore, the phosphorylated cellulose paper would be useful for the removal of $Fe^{2+}$ and $Fe^{3+}$ ions in aqueous solutions.

Lanthanum and cerium ions, that is lanthanoid, were also adsorbed by the phosphorylated cellulose paper, as shown in Table 2. Therefore cellulose phosphate would be applicable to the recovery of $La^{3+}$ and $Ce^{3+}$ ions from waste and sea water.

$Mg^{2+}$ and $Hg^{2+}$ ions were not adsorbed by the phosphorylated cellulose paper under acidic conditions, even though they are strongly bound to the $PO_4^{2-}$ group. This would be caused by the protonation of $PO_4^{2-}$ groups on cellulose phosphate in acidic solutions. The solution including phosphorylated cellulose paper and $Mg^{2+}$ or $Hg^{2+}$ ion was adjusted to a pH of 10 by the addition of 1% $NH_3$ solution in order to accelerate the adsorption of the metal ions. Table 3 lists the amounts of adsorption of $Mg^{2+}$ and $Hg^{2+}$ ions in the mixed solution by phosphorylated cellulose paper. $Mg^{2+}$ and $Hg^{2+}$ ions were completely removed from the mixed solution. The adsorption of metal ions by phosphorylated cellulose paper was strongly influenced by the pH of the solution. Metal ions adsorbed on the phosphorylated cellulose paper were almost excluded when the paper was washed by 0.1 mol dm$^{-3}$ hydrochloric acid solution. Thus, the phosphorylated cellulose paper can be reused many times as an ion-exchanger.

The phosphorylated cellulose paper and cellulose paper were tested for combustion. The phosphorylated paper was more stable against combustion compared to the cellulose only paper. Thus, phosphorylated cellulose paper can be used as a noncombustible paper.

Table 3. Adsorption of $Mg^{2+}$ and $Hg^{2+}$ in Mixed Solution by Phosphorylated Cellulose Paper

| Metal ion[a] | pH | Adsorption ($\mu$g/paper[a]) |
|---|---|---|
| $Mg^{2+}$ | 1.68 | 0 |
| | 10.03 | 1200 |
| $Hg^{2+}$ | 1.76 | 0 |
| | 8.93 | 765 |

*a*) Conditions are as in Table 2.

## Materials and Methods

**Chemicals** Sodium *cyclo*-triphosphate hexahydrate ($P_{3m}$), $Na_3P_3O_9 \cdot 6H_2O$, was obtained by recrystallizing it three times from an aqueous solution of industrial grade anhydrous sodium *cyclo*-triphosphate (98%) from Rasa Kogyo, Ltd. (Osaka, Japan). Cellulose paper was Clean Wipe-P (100 × 210 mm; 0.283 g/paper), purchased from Asahi Kasei (Osaka, Japan). Other chemicals were analytical grade regents from Wako (Osaka, Japan) and were used without further purification.

**Preparation of Cellulose Phosphate** The phosphorylation of cellulose paper with $P_{3m}$ was carried out under various conditions (concentration of $P_{3m}$, reaction temperature, time, and stirring method). Since the pH of the reaction solution gradually decreased with the progress of the reaction, the pH of the reaction solution was constantly adjusted to pH 12 by adding 6 mol dm$^{-3}$ sodium hydroxide aqueous solution. After the reaction, the phosphorylated cellulose paper was sufficiently washed with distilled water and dried in air. The degree of phosphorylation was measured as follows: the phosphorylated cellulose paper was ignited and the residue was decomposed by boiling it in an alkaline solution. Then, the solution was neutralized by 1 mol dm$^{-3}$ hydrochloric acid solution. Determination of phosphorus was carried out by spectrophotometry of phosphorus-molybdenum heteropoly blue complex at 830 nm.

**Characterization of Cellulose Phosphate** Phosphorylated cellulose papers were soaked in 100 ppm metal ion aqueous solutions and incubated at room temperature for 5 h. The residual metal ions after the reaction were determined by atomic absorption spectrophotometry (Hitachi 180-80). In addition, a control experiment was done with untreated cellulose paper, which did not adsorb any metal ions.

## References

1) Feldmann W., *Chem. Ber.*, **100**, 3850 (1967).
2) Tsuhako M., Nakahama A., Ohashi S., Nariai H., Motooka I., *Bull. Chem. Soc. Jpn.*, **56**, 1372 (1983).
3) Tsuhako M., Ohashi S., Nariai H., Motooka I., *Chem. Pharm. Bull.*, **30**, 3882 (1982).
4) Tsuhako M., Fujita N., Nakahama A., Matsuo T., Kobayashi M., Ohashi S., *Bull. Chem. Soc. Jpn.*, **53**, 1968 (1980).
5) Tsuhako M., Nakajima A., Miyajima T., Ohashi S., Nariai H., Motooka I., *Bull. Chem. Soc. Jpn.*, **58**, 3092 (1985).
6) Inoue H., Baba Y., Furukawa T., Maeda Y., Tsuhako M., *Chem. Pharm. Bull.*, **41**, 1895 (1993).
7) Inoue H., Baba Y., Miyajima T., Tsuhako M., *Chem. Pharm. Bull.*, **40**, 3127 (1992).
8) Tsuhako M., Sueyoshi C., Baba Y., Miyajima T., Ohashi S., Nariai H., Motooka I., *Chem. Lett.*, **1987**, 1431.
9) Uekama K., *Yakugaku Zasshi*, **101**, 857 (1981).
10) Inoue H., Baba Y., Miyajima T., Tsuhako M., *Phosphorus Research Bulletin*, **3**, 61 (1993).