

# Properties of 2,3-Dicarboxy Cellulose Combined with Various Metallic Ions

EIICHI MAEKAWA and TETSUO KOSHIJIMA, *Research Section of Wood Chemistry, Wood Research Institute, Kyoto University, Uji, Kyoto, Japan*

## Synopsis

2,3-Dicarboxy cellulose and partially oxidized 2,3-dicarboxy cellulose were prepared in good yields from the corresponding dialdehyde cellulose obtained by periodate oxidation of cellulose according to a modification of the method described by Hofreiter, Wolff, and Mehlretter [*J. Am. Chem. Soc.*, **79**, 6457 (1957)]. The 2,3-dicarboxy cellulose oxidized to nearly 100% oxidation level was completely soluble in water, but the 2,3-dicarboxy cellulose of 70% oxidation level was not. The former 2,3-dicarboxy cellulose took up various metallic ions other than alkali metals to form a precipitate or solid. The metal contents taken up corresponded to the theoretical values calculated as combined in the form of metallic salt of the carboxylic acid group. 2,3-Dicarboxy cellulose combined with metallic ions such as copper, cobalt, and nickel ions gave viscous, gel-like products, which solidified when exposed to air. The properties of products combined with such metallic ions are discussed.

## INTRODUCTION

The oxidation of cellulose by periodic acid and its salts leads to a product containing dialdehyde units formed by oxidative cleavage at the C-2 and C-3 of the anhydro D-glucopyranose residues.<sup>1,2</sup> The periodate oxidation is generally characterized by its selective cleavage of the carbon-carbon bond with vicinal hydroxyl groups without the simultaneous occurrence of side reaction to any great extent. By the amount of oxidant used, a variable degree of oxidized product is obtainable from cellulose composed of a large number of potentially oxidizable units. Since the completely oxidized so-called 2,3-dialdehyde cellulose no longer has the anhydro glucopyranose units which constitute the cellulose chain, it may be expected to give a novel polymer having no cellulosic properties.<sup>3</sup> Further mild oxidation of the periodate oxycellulose with oxidants such as bromine water or chlorous acid gives a product corresponding to 2,3-dicarboxy cellulose.<sup>1,3</sup> Oxidized products thus prepared are reactive polymers which may be regarded as derivatives of polycarboxylic acid, although they have many acetal linkages formed by opening the pyranose ring in the backbone chain. Therefore, the aim of this study is to prepare the 2,3-dicarboxy cellulose from cellulose and to convert it to the functional polymers by introduction of functional groups under mild conditions.

An attempt at oxidation using chlorous acid of the aldehyde groups in periodate oxycellulose was first made by Rutherford et al.,<sup>4</sup> and oxidation conditions using chlorous acid were subsequently studied in detail by Davidson and Nevell.<sup>5</sup> As a result, they showed the effective conditions for oxidation of aldehyde groups to carboxy groups with acidified sodium chlor-

ite solution. Afterward, Hofreiter et al.,<sup>6</sup> by the use of chlorous acid for oxidation of periodate oxidized corn starch, determined the preferred conditions for quantitative conversion to the corresponding dicarboxy derivatives in an aqueous acid medium. In recent years, 2,3-dicarboxy cellulose prepared by oxidation of periodate-oxidized cellulose has been used to study<sup>7</sup> changes in the fine structure of cellulose caused by the replacement of alcoholic groups by carbonyl, or carboxyl groups, or as a material of photoinduced graft copolymerization of methyl methacrylate.<sup>8</sup>

This report is concerned with the preparation of 2,3-dicarboxy cellulose by a modification of the method of Hofreiter et al.<sup>6</sup> and the characteristic properties of its products combined with various metallic ions.

## EXPERIMENTAL

**Materials.** Whatman CF 1 cellulose powder, Toyo Roshi cellulose powder made from cotton cellulose, and Schleicher and Schüll cellulose powder from beech wood pulp were used. These commercial cellulose powders for column chromatography were made in the size of 100–200 mesh using a sieve.

**Preparation of 2,3-Dialdehyde Cellulose.** Periodate-oxidized celluloses were prepared by oxidizing 20 g of cellulose powder suspended in water (1 L) with sodium metaperiodate at ambient temperature in the dark. The amount of sodium metaperiodate used was 1.3 times as much as the theoretical amount (26.4 g) for cellulose powder (20 g). Partially periodate-oxidized cellulose was also prepared by addition of sodium metaperiodate 0.75 times the theoretical amount (26.4 g). The initial pH values of the reaction medium were 4.45 in the former and 4.65 in the latter. Periodate oxidation was performed by shaking until periodate consumption reached a constant value. The amount of periodate consumed was determined by measuring the absorbance at 290 nm of the supernatant liquid. The relationship between the value of the absorbance of periodate ion at 290 nm and the amount of periodate was linear (Fig. 1) over a wide range of periodate, compared with the case of the determination at 223 nm (Fig. 2). Accordingly, this calibration curve (Fig. 1) was favorable for the determination of periodate consumed.

The reaction medium which reached a theoretical value of periodate consumption indicated a pH of 3.2. After the excess periodate was decomposed with ethylene glycol, oxidized products were separated by centrifugation as a water-insoluble precipitate and the supernatant liquid. The precipitate was an agar-like solid mass having a somewhat pasty property. The solid mass was recovered in the form of colorless powder (DAC-I) by washing with water, 50% EtOH, and ethanol, successively, and drying in a vacuum. The supernatant and the washings were desalted by dialysis using running water and then recovered as colorless or somewhat pale, brownish powder (DAC-II) through concentration to 100 mL and freeze-drying.

**Preparation of 2,3-Dicarboxy Cellulose Na Salt (DCC Na Salt).** DAC-I was used for the preparation of 2,3-dicarboxy cellulose and partial 2,3-dicarboxy cellulose. An aqueous suspension (300 mL) containing DAC-I (15

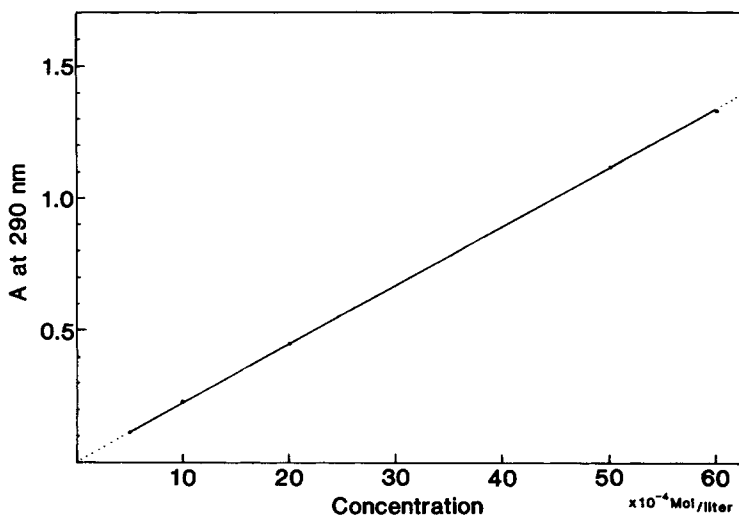


Fig. 1. Calibration curve for the determination of periodate consumed.

g) was further oxidized with sodium chlorite and acetic acid in a reaction vessel kept at 20–25°C with vigorous stirring. For oxidation of 1 mol of aldehyde group to carboxyl group, 4 mol of chlorite ( $\text{ClO}_2^-$ ) and 2 mol of acetic acid were used according to the oxidation conditions described by Hofreiter et al. The required amount of sodium chlorite was dissolved in an aqueous medium, and then acetic acid was added dropwise from a separatory funnel for 1 h. The reaction mixture turned from a black brown to a deep orange color with evolution of a considerable quantity of chlorine dioxide, and finally became a transparent, homogeneous solution during the progress of reaction, but partially oxidized products did not completely dissolve. The reaction mixture was allowed to react for more than 6 h, and was then immersed in ice water and adjusted to pH 8.5 with 10N NaOH.

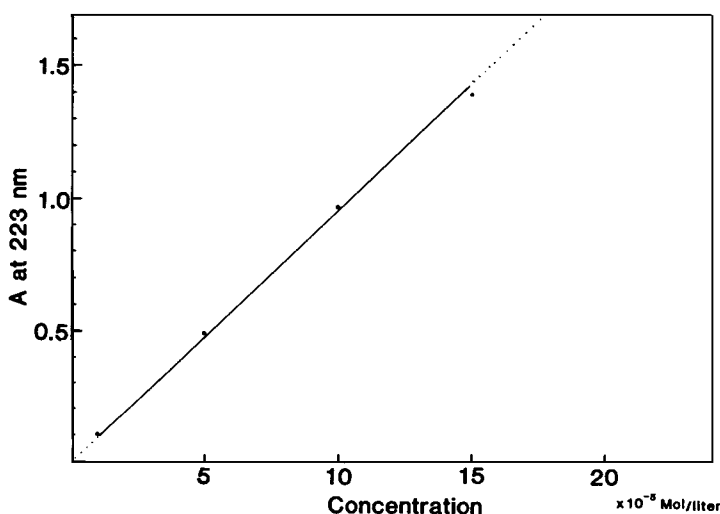


Fig. 2. Calibration curve for the determination of periodate consumed.

Oxidized products were precipitated by pouring into 3 volumes of ethanol and were allowed to stand in a refrigerator for a few days. After removal of the supernatant liquid from the settled product by decantation, the gummy sediment adhering to the bottom of the vessel was scraped out with a spatula and suspended in 50% EtOH. The sediment was separated by repeated decantation of the supernatant liquid and suspended in ethanol. The solidified solid in ethanol was collected by filtration, and then the small massive, colorless products were obtained in the form of Na salt by washing with ethanol and drying in a vacuum.

**Preparation of 2,3-Dicarboxy Cellulose.** Dicarboxy cellulose Na salt (15 g) was dissolved in water (100 mL), and then applied on a column of ion exchange resin (DOWEX 50  $\times$  8, H<sup>+</sup> form, 50–100 mesh). The column was eluted with distilled water until the eluate indicated no acidity, and then the eluate was neutralized with concentrated ammonia water to pH 6.8, concentrated to 50 mL, and freeze-dried to yield a colorless or pale creamy, fluffy powder. The powder was strongly hygroscopic and was sticky because of moisture absorption upon exposure to air.

**Preparation of Partial 2,3-Dicarboxy Cellulose.** Partial 2,3-dicarboxy cellulose Na salt (15 g) was suspended in water (100 mL) and adjusted to pH 3.5–3.8 by addition of 0.2*N* HCl. The total aqueous suspension (200 mL) was stirred overnight at room temperature and then was combined with 3 volumes of ethanol. The precipitate was collected in a glass filter, washed with 70% EtOH until the washings indicated neutrality. The powder was washed in ethanol and petroleum ether, and dried in a vacuum.

**Preparation of 2,3-Dicarboxy Cellulose Combined with Metallic Ions.** An aqueous solution (25 mL) containing 2,3-dicarboxy cellulose (1 g) was mixed with 0.1*M* acetate buffer solution (pH 4.6, 25 mL) containing 0.2*M* of metallic salts, and then stirred overnight at room temperature. Only silver salt was dissolved in water. As metallic salts, AgNO<sub>3</sub>, Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Ba(CH<sub>3</sub>COO)<sub>2</sub>, Ca(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, SrCl<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, ZnCl<sub>2</sub>, NiCl<sub>2</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, and FeCl<sub>3</sub>·6H<sub>2</sub>O were used. Precipitates of metallic salts produced by mixing were collected by centrifugation and recovered as glassy massive solids or powders after washing with 50% EtOH and drying in a vacuum at 60°C.

## RESULTS AND DISCUSSION

The time course for periodate consumption per anhydro D-glucose unit (162) on periodate oxidation of several commercial powders used in this experiment are shown in Figures 3 and 4. The results indicate that the difference in periodate oxidation depends on the degree of noncrystallinity of cellulose powder. Therefore, Schleicher and Schüll cellulose powder made from wood pulp is more easily subjected to periodate oxidation, compared with Toyo Roshi cellulose powder and Whatman cellulose powder prepared from cotton.

Since periodate oxidation of cellulose can be regarded as proceeding gradually from the amorphous to the crystalline portion without resulting in marked degradation, prolonged reaction time may be necessary to gain access into the inner microfibril region of cellulose. In order to promote the penetration and attack of periodate ions, the form of cellulose material

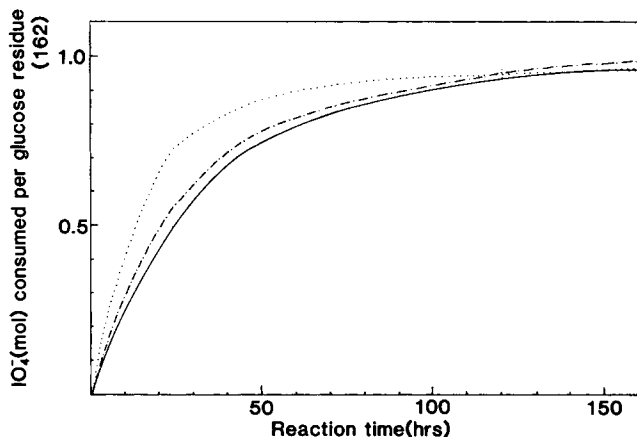


Fig. 3. Periodate oxidation of commercial cellulose powders: ( . . . ) Schleicher and Schüll; (- . -) Whatman CF 1; (—) Toyo Roshi.

such as fiber, particle, film, and powder may be an important factor regulating reactivity. In this experiment, by the use of commercial cellulose powder of 100–200 mesh, dialdehyde celluloses oxidized to nearly 100% oxidation level and those partially oxidized to 70% oxidation were prepared in good yields.

The yields, recoveries, and oxidation ratios of DAC-I and DAC-II thus prepared are summarized in Table I. The result shows that DAC-I is obtained in more than 90% as the major oxidized product. The yields and recoveries of 2,3-dicarboxy cellulose Na salt prepared from dialdehyde cellulose are shown in Table II. The product indicates a good recovery of nearly 90%. The preparation of 2,3-dicarboxy cellulose from the Na salt is shown in Table III. This result also indicates a good recovery of more than 90%.

Dialdehyde cellulose obtained was insoluble in water, but 2,3-dicarboxy cellulose of nearly 100% oxidation ratio was completely soluble in water, although partially oxidized products of 70% oxidation ratio were not. Also,

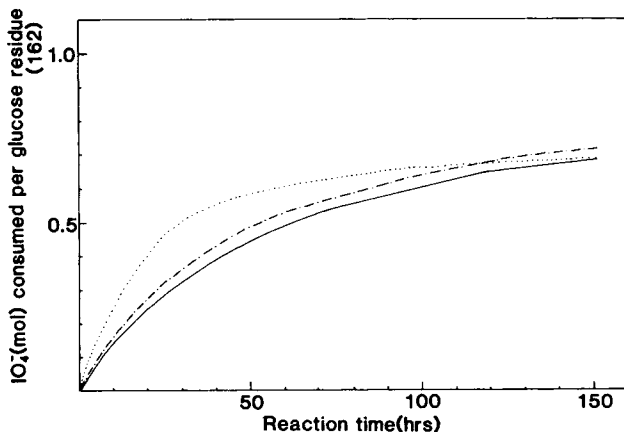


Fig. 4. Partial periodate oxidation of commercial cellulose powders: ( . . . ) Schleicher and Schüll; (- . -) Whatman CF 1; (—) Toyo Roshi.

TABLE I  
Yields and Recoveries of Dialdehyde Celluloses Prepared from Commercial Cellulose Powders

Cellulose powder used	Amount of sample (g)	DAC-I		DAC-II		Oxidation ratio (%) <sup>b</sup>
		Yield (g)	Recovery (%) <sup>a</sup>	Yield (g)	Recovery (%) <sup>a</sup>	
Whatman cellulose						
C-1	20	18.64	94.4	1.34	6.8	98.5
C-2	20	18.63	94.3	1.65	8.4	97.8
C-3	20	19.04	96.4	1.12	5.7	99.6
C-4	20	19.12	96.8	1.10	5.6	96.4
C-5	20	18.18	91.7	0.42	2.1	68.2
C-6	20	17.91	90.3	0.61	3.1	69.9
Schleicher and Schüll cellulose						
C-1	20	18.39	93.1	0.57	2.9	92.3
C-2	20	18.50	93.7	0.86	4.4	92.9
C-3	20	19.08	96.6	0.74	3.7	95.6
C-4	20	19.09	96.7	0.92	4.7	95.7
C-5	20	18.44	93.0	0.98	5.0	69.9
C-6	20	18.77	94.7	1.52	7.7	71.3

<sup>a</sup> Recovery (%) =  $(B/A) \times 100$ , where  $A$  = theoretical yield (g) and  $B$  = actual yield (g). Theoretical yield (19.75 g) in 100% oxidation was used in the case of cellulose samples C-1, C-2, C-3, and C-4, and theoretical yield (19.83 g) in 70% oxidation was used in the case of cellulose samples C-5 and C-6.

<sup>b</sup> Oxidation ratio (%) =  $B/A \times 100$ , where  $A$  = mole number (1.00) of periodate consumed per anhydro glucose unit (162) and  $B$  = mole number of periodate actually consumed per anhydro glucose unit (162).

TABLE II  
Yields and Recoveries of 2,3-Dicarboxy Cellulose Na Salts

DAC-I used	Amount of sample (g)	Yield (g)	Recovery <sup>a</sup> (%)
Whatman cellulose			
C-1	15.0	19.52	88.2
C-2	15.0	18.40	86.0
C-3	15.0	20.84	94.2
C-4	15.0	20.28	91.6
C-5	15.0	19.28	96.5
C-6	15.0	18.71	93.7
Schleicher and Schüll cellulose			
C-1	15.0	20.18	91.2
C-2	15.0	19.88	89.8
C-3	15.0	20.12	90.9
C-4	15.0	20.28	91.6
C-5	15.0	19.18	96.0
C-6	15.0	20.03	100.3

<sup>a</sup> Recovery (%) =  $(B/A) \times 100$ , where  $A$  = theoretical yield (g) and  $B$  = actual yield (g). Theoretical yield (22.13 g) in 100% oxidation was used in the case of cellulose samples C-1, C-2, C-3, and C-4, and theoretical yield (19.97 g) in 70% oxidation was used in the case of cellulose samples C-4 and C-5.

TABLE III  
Yields and Recoveries of 2,3-Dicarboxy Cellulose (DCC) Prepared by Desalting Na Salts

DCC Na salt	Amount of sample (g)	Yield (g)	Recovery <sup>a</sup> (%)
Whatman cellulose			
C-1	15.0	12.22	100.3
C-2	15.0	11.46	93.9
C-3	15.0	12.19	94.9
C-4	15.0	12.20	95.0
Schleicher and Schüll cellulose			
C-1	15.0	11.39	93.4
C-2	15.0	11.81	96.8
C-3	15.0	11.92	92.8
C-4	15.0	12.40	96.6

<sup>a</sup> Recovery (%) =  $(B/A) \times 100$ , where  $A$  = theoretical yield (g) and  $B$  = actual yield (g). Theoretical yield (12.20 g) in 100% oxidation was used in the case of cellulose samples C-1 and C-2, and theoretical yield (12.84 g) in 70% oxidation was used in the case of cellulose samples C-3 and C-4.

2,3-dicarboxycellulose was insoluble in solvents such as dimethyl sulfoxide or *N,N*-dimethyl formamide, but yielded a jellylike product.

Aldehyde groups at the C-2 and C-3 of dialdehyde cellulose obtained by periodate oxidation of cellulose form intermolecular and/or intramolecular hemiacetals with the hydroxyl group at the C-6.<sup>1</sup> This fact influences the mechanical properties of cellulose.<sup>7</sup> Actually, dialdehyde cellulose revealed better mechanical properties in the dry and wet state, containing resistant intermolecular linkages, compared with dialcohol cellulose.

Dialdehyde cellulose may be useful for the synthesis of various types of cellulose derivatives. One of the first reports devoted to this subject was made by Rogovin and his co-workers,<sup>9</sup> who synthesized the addition products of Schiff bases from dialdehyde cellulose. Kozlova and Rogovin<sup>10</sup> reported that treatment of dialdehyde cellulose with a solution of hydroxylamine (pH 5–6) at room temperature gave the dioxime derivatives in 94–96% yield.

“Diamino cellulose” can be prepared by reduction of the dioxime with sodium borohydride or sodium amalgam.<sup>1</sup> Also, dehydration of the dioxime with acetic anhydride in the presence of sodium acetate leads to the dinitrile derivative.<sup>3</sup> The condensation of dialdehyde cellulose with nitromethane results in the formation of a new ring with a number of members greater than six.<sup>3</sup> Koshijima et al.<sup>11</sup> indicated that the products prepared by condensation of 2,3-dialdehyde cellulose with thiosemicarbazide or isonicotinic acid hydrazide had the same properties as chelating polymers for specific metallic ions. These products are of interest as chelating polymers derived from natural polysaccharides such as cellulose. Recently, Nishiguchi and Segawa<sup>12</sup> reported that the diamino cellulose prepared by reduction of dialdehyde cellulose with sodium borohydride showed selective sorption (chelation) of metallic ions. This suggests that the product derived from dialdehyde cellulose can be useful for recovery of specific metals.

2,3-Dicarboxy cellulose prepared by further mild oxidation of dialdehyde cellulose was useful for recovery of heavy metals from an aqueous mixture

TABLE IV  
Properties of Dicarboxy Cellulose (DCC) Combined with Metallic Ions<sup>a</sup>

DCC metallic salts	Color	State after heating	Ionic radii <sup>b</sup> of metal ions in water (Å)
DCC-Na	White	S	4.0
DCC-Mg	Pale brown	S	8.0
DCC-Li	Pale brown	S	
DCC-Ni	Green	G	
DCC-Co	Purple	G	
DCC-Mn	Pale brown	G	6.0
DCC-Zn	Pale brown	G	
DCC-Cu	Blue	G	
DCC-Ca	White	NG	
DCC-Ag	Black brown	NG	2.0
DCC-Ba	White	NG	
DCC-Sr	White	NG	5.0
DCC-Cr	Deep blue	NG	
DCC-Fe	Brown	NG	9.0

<sup>a</sup> Each (0.5 g) of DCC metallic salts was heated in an oil bath of 100°C with water (3 mL). S: solution; G: gel; NG: no change.

<sup>b</sup> Approximate effective ionic radii of metal ions in aqueous solution at 25°C. Cited from Lange's *Handbook of Chemistry*, McGraw-Hill, New York, 1973.

TABLE V  
Yields and Metal Contents of Dicarboxy Cellulose (DCC) Combined with Metallic Ions

DCC metallic salts	Yield (g)	Recovery <sup>a</sup> (%)	Metal contents (mmol/g)			
			I	II	III	IV
DCC-Na			8.31 8.76			8.48
DCC-Ag	1.734	82.0	3.57			4.93
DCC-Mg	0.552	49.4		3.65		4.67
DCC-Ca	1.161	96.9		3.63		4.35
DCC-Sr	1.345	93.0	2.74	3.15		3.60
DCC-Ba	1.511	88.6	2.17	2.54		3.05
DCC-Mn	1.118	87.6	4.33	3.32	3.63	4.08
DCC-Co	1.131	87.3	4.82	3.26	3.54	4.02
DCC-Ni	1.090	84.5		3.22	3.14	4.02
DCC-Cu	1.131	85.7	2.24	3.84	3.71	3.94
DCC-Zn	1.079	80.4	2.88	3.32	3.08	3.92
DCC-Fe	1.301	109.9	4.92	4.06		2.93
DCC-Cr	0.892	76.4	2.90	2.61		2.97

<sup>a</sup> Recovery (%) =  $(B/A) \times 100$ , where  $A$  = theoretical yield (g) calculated as metallic salts of dicarboxy cellulose (1 g) combined with metal ions and  $B$  = actual yield (g). Analytical methods for metal contents: (I): determined by fluorescent X-ray<sup>13</sup>; (II): determined from the ash weight obtained by an incineration method<sup>13</sup>; (III): determined from the ash weight after pyrolysis using a thermobalance of a thermal analysis<sup>13</sup>; (IV) theoretical values for metal content calculated as DCC metallic salts.



of metallic ions. The 2,3-dicarboxy celluloses prepared in this experiment absorbed various metals through the formation of precipitate or massive solid with most metallic ions other than alkali metals.<sup>13</sup> 2,3-Dicarboxy cellulose was regenerated by treatment with aqueous dilute acids. The 2,3-dicarboxy cellulose combined with metallic ions such as cobalt, nickel, manganese, zinc and copper ions gave viscous, gel-like products (Table IV), which solidified when exposed to air. These products were mainly restricted to metallic ions having 6-Å effective ionic radii in an aqueous medium, although there was an exception, such as the calcium ion.<sup>13</sup> The products containing the other metallic ions were obtained as powder or solution. 2,3-Dicarboxy cellulose combined with metal yields different products depending on the kind of metallic ion. From the analytical data of metal contents taken up in dicarboxy cellulose (Table V), the metal contents were compatible with the theoretical values calculated as combined in the form of metal salts of carboxylic acids. Accordingly, the metals in 2,3-dicarboxy cellulose are taken up in the form of metallic salts of carboxylic acids. Only iron contents gave fairly higher values than theoretical owing to absorption of colloidal iron.

Thus, 2,3-dicarboxy cellulose would be useful as the intermediate for the introduction of functional groups or as the scavenger for the recovery of heavy metallic ions under comparatively mild conditions, although the breakdown of some acetal linkages may occur.

### References

1. R. D. Guthrie, *Advances in Carbohydrate Chemistry*, M. L. Wolfrom, Ed., Academic, New York, 1961, Vol. 16, p. 105.
2. T. P. Nevell, *Methods in Carbohydrate Chemistry*, R. L. Whistler, Ed., Academic, New York, 1963, Vol. III, p. 164.
3. L. S. Gal'braikh and Z. A. Rogovin, *Cellulose and Cellulose Derivatives*, N. M. Bikales and L. Segal, Eds., Wiley-Interscience, New York, 1971, Part V, p. 893.
4. H. A. Rutherford, F. W. Minor, A. R. Martin, and M. Harris, *J. Res. Nat. Bur. Stand.*, **29**, 131 (1942).
5. G. F. Davidson and T. P. Nevell, *J. Text. Inst.*, **46**, T-407 (1955).
6. B. T. Hofreiter, I. A. Wolff, and L. Mehlretter, *J. Am. Chem. Soc.*, **79**, 6457 (1957).
7. L. Kuniak, B. Alinca, V. Masura, and J. Alföldi, *Sven. Papperstidn.*, **72**, 205 (1969).
8. A. Takahashi and S. Takahashi, *Sen-I-Gakkaishi*, **36**, T-397 (1980).
9. Z. A. Rogovin, A. G. Yashunskya, and B. M. Bogoslovskii, *Zh. Prikl. Khim.*, **23**, 631 (1950).
10. Yu. S. Kozlova and Z. A. Rogovin, *Vysokomol. Soedin.*, **2**, 614 (1960).
11. T. Koshijima, R. Tanaka, E. Muraki, A. Yamada, and F. Yaku, *Cellulose Chem. Technol.*, **7**, 197 (1973).
12. T. Nishiuchi and S. Segawa, *Nippon Kagaku Kaishi*, **9**, 1256 (1979).
13. E. Maekawa, I. Ueno, and T. Koshijima, *Sen-I-Gakkaishi*, **37**, T-509 (1981).

Received September 12, 1983

Accepted December 9, 1983