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SHORT COMMUNICATIONS

Dissolution of Cellulose in Dimethyl Sulfoxide. Effect of Thiamine Hydrochloride

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Dissolution of cellulose has long been of interest to investigators concerned with either utilization of cellulose as a renewable resource or effective methods to functionalize the polysaccharide. Although cellulose is insoluble in neutral water and common organic solvent, utilization in manufacture has shown that the polysaccharide is soluble in sulfuric acid, aqueous solutions of zinc chloride, sodium hydroxide, tetraalkylammonium hydroxide, and cupric ammonium hydroxide. As an organic solvent, dimethyl sulfoxide containing paraformaldehyde (DMSO/PF system) has been found to be an excellent nondegrading solvent for cellulose.[1-3] In addition, studies have been reported on cellulose solvents containing sulfur dioxide and diethylamine in either acetonitrile or DMSO.[4,5] In these systems, however, high amount of PF and high temperature were required to dissolve cellulose in DMSO/PF system. In this study, we would like to report remarkable effects of thiamin hydrochloride (thiamin·HCl) on the dissolution of cellulose in DMSO/PF system.

EXPERIMENTAL

Avicel, microcrystalline cellulose, for column chromatography (Asahi Chem. Ind. Co., Ltd.), paraformaldehyde (Merck Co.), and thiamin·HCl (Nakarai Tesque, Inc.) were used without further purification.

In a typical experiment, avicel (1.0 g, 6.2 mmol per glucose residue), PF powder (3.16 g, 0.1 mol as HCHO), and thiamin·HCl (0.34 g, 1 mmol) were dispersed in DMSO (100 ml) at room temperature. The mixture was then heated with rapid stirring at 90°C for 3 h. Undissolved materials were removed by centrifugation (3,500 rpm, 5 min), followed by washing with DMSO, methanol, and hot H_2O to remove methylol groups.

The amounts of dissolved cellulose were estimated on the basis of the amounts of undissolved cellulose. The amount of dissolved HCHO in DMSO was determined by a chromotoropic acid method.[6]

RESULTS AND DISCUSSION

Figure 1 shows a dramatic effect of thiamin·HCl on the dissolution of cellulose in DMSO/PF system. By addition of 0.01 M thiamin·HCl, cellulose dissolved in DMSO/PF system at low amount of PF and low temperature (70°C). As shown in Table I, cellulose did not dissolve in DMSO/PF system in the absence of thiamin·HCl at 70°C. On the

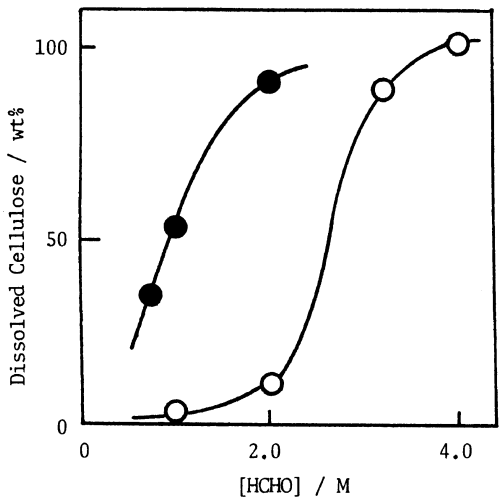

Figure 1. Effect of thiamin·HCl addition on the dissolution of cellulose in DMSO/PF system: cellulose, 1.0 g; DMSO, 100 ml; time, 3 h; ○, in the absence of thiamin·HCl at 130°C; ●, in the presence of 0.01 M of thiamin·HCl at 70°C.

Table I. Dissolution of cellulose in DMSO/PF system in the presence of various amounts of HCHO and thiamin·HCl[a]

Run	[HCHO]	[Thiamin·HCl]	Dissolved cellulose[b]
	M	M	wt%
1	0.55	0	2
2	0.55	0.01	34
3	0.55	0.03	17
4	1.00	0	3
5	1.00	0.01	52
6	1.00	0.03	73
7	2.00	0	6
8	2.00	0.01	90
9	2.00	0.03	100

[a] Celllose, 1.0 g; DMSO, 100 ml; temp. 70°C; time, 3 h.
[b] Dissolved material (g) per added cellulose (g).

Table II. Effect of temperature and thiamin·HCl concentration on the dissolution of cellulose[a]

Run	Temperature	[Thiamin·HCl]	Dissolved cellulose[b]
	°C	M	wt%
1	50	0	2
2	50	0.01	9
3	50	0.03	12
4	70	0	3
5	70	0.01	52
6	70	0.03	73
7	90	0	4
8	90	0.01	99
9	90	0.03	96
10	110	0.01	76
11	130	0.01	39

[a] Cellulose, 1.0 g; DMSO, 100 ml; [HCHO], 1.0 M; time, 3 h.
[b] Dissolved material (g) per added cellulose (g).

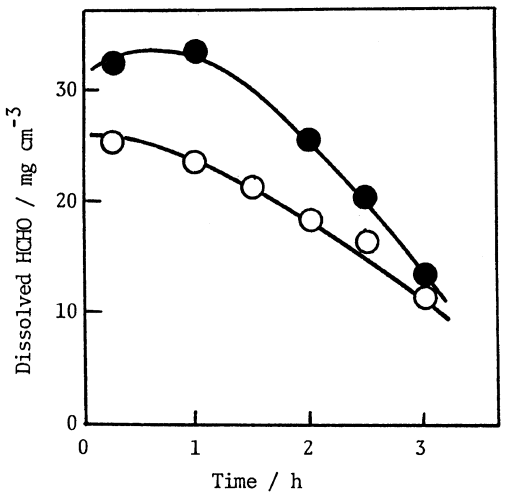

Figure 2. Effect of thiamin·HCl addition on the amount of HCHO dissolved in DMSO: [HCHO], 1.0 M; DMSO, 50 ml; temp. 90°C; ○, in the absence of thiamin·HCl; ●, in the presence of 0.01 M of thiamin·HCl.

other hand, the amount of dissolved cellulose was increased with increasing the amount of HCHO in the presence of 0.01—0.03 M of thiamin·HCl.

Table II shows the effect of temperature and thiamin·HCl concentration on the dissolution of cellulose in DMSO in the presence of 1 M HCHO. In the absence of thiamin·HCl, cellulose did not dissolve below 90°C. In the presence of 0.01—0.03 M of thiamin·HCl, the amount of dissolved cellulose increased with increasing temperature. However, the amount of dissolved cellulose decreased at high tem-

perature (110 and 130°C).

In order to give insight into the effect of thiamin·HCl, the amount of dissolved HCHO was investigated in the presence and absence of thiamin·HCl (Figure 2). Especially at the first stage of dissolution, the addition of thiamin·HCl gave higher amount of dissolved HCHO than no addition of thiamin·HCl. These results would suggest that thiamin·HCl affects the proportion of vaporized HCHO, dissolved, and undissolved paraformaldehyde which is an important factor controlling the dissolution of cellulose in DMSO.

Further studies will be published in near future.

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