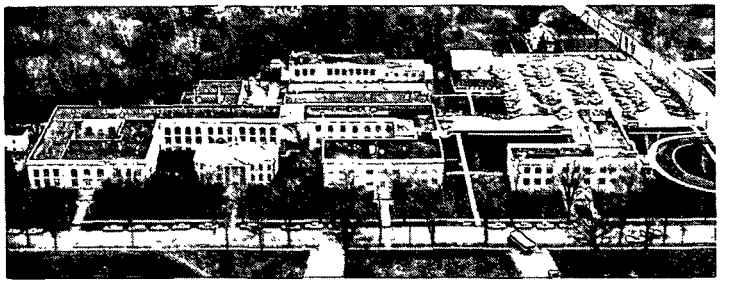

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DISSOLUTION OF CELLULOSE IN POLAR APROTIC SOLVENTS VIA FORMATION OF METHYLOL CELLULOSE

TIMOTHY J. BAKER, LELAND R. SCHROEDER, AND
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INTRODUCTION

Recently, the discovery of a new solvent system which dissolves cellulose without degradation was reported (IPC Technical Paper Number 5). The solvent system, dimethyl sulfoxide-paraformaldehyde (DMSO-PF) has been used in viscosity studies (IPC Technical Paper Number 8) and for homogeneous preparation of cellulose derivatives (IPC Technical Paper Number 36).

The present paper is the result of the doctoral thesis research of Timothy J. Baker. The work has demonstrated that cellulose can also be dissolved by the action of formaldehyde in pyridine, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, and tetramethylene sulfoxide. The peracetates of the resultant methylol celluloses can be prepared and used to determine the molar substitution of formaldehyde.

These new cellulose solvents clearly provide new versatility in the preparation of regenerated fibers and films and in the production of cellulose derivatives.

This paper will be submitted for publication in Carbohydrate Research.

Preliminary Communication

Dissolution of Cellulose in Polar Aprotic Solvents via Formation of Methylol Cellulose

Timothy J. Baker, Leland R. Schroeder*, and Donald C. Johnson+

The Institute of Paper Chemistry, Appleton, Wisconsin 54912 (U.S.A.)

Recently a new solvent system for cellulose, utilizing dimethyl sulfoxide (DMSO) and paraformaldehyde (PF), was discovered at The Institute of Paper Chemistry[1,2]. It has been demonstrated that the mechanism by which cellulose dissolves in the DMSO-PF system is dependent, in part, on the formation of a hemiacetal derivative, methylol cellulose[1,2]. As formaldehyde is generated by the thermal decomposition of PF, a portion of it reacts with cellulose hydroxyl groups, with the primary hydroxyl group at C-6 being the favored reaction site[1,3]. Previous indications have been that DMSO is the only solvent in which the methylol cellulose could be dissolved[4-6]. However, further investigation of the mechanism of methylol cellulose formation has led us to the discovery that methylol cellulose can also be prepared and dissolved in dipolar aprotic solvents other than DMSO.

We now report that cellulose can be dissolved by the action of formaldehyde in pyridine, N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N-methyl-2-pyrrolidinone (NMP), and tetramethylene sulfoxide (TMSO). These solvents have the common characteristics of being dipolar, aprotic, and good hydrogen bond acceptors. The aprotic nature of the solvents is essential since formaldehyde will undergo addition reactions with most protic solvents[7]. The dipolar nature of the solvents is important in the dissolution process.

*Author to whom correspondence should be addressed.
+Current address: Weyerhaeuser Company, Seattle, Washington 98134 (U.S.A.)

In order for cellulose to dissolve, the solvent must penetrate and swell the cellulose structure, even the highly ordered crystalline regions. Primarily because of their dipoles, the above solvents are good hydrogen bond acceptors. Therefore, they are able to effectively interact with the cellulose hydroxyls and thereby disrupt the cellulosic intermolecular hydrogen bonding. In addition, these solvents are relatively small and can penetrate the cellulose structure more readily than bulky molecules.

Interaction of the solvent with the formaldehyde also appears to be very important in these systems. The dipolar nature of monomeric formaldehyde presents the possibility for dipole-dipole interaction between the organic solvent and formaldehyde. Such interactions would be expected to enhance retention of formaldehyde in solution and would maintain it in a highly reactive state. A 1:1 complex of formaldehyde with pyridine has previously been isolated[8]. Similar interactions have been postulated to be important in other cellulose solvent systems as well[9].

Solutions of methylol cellulose in the new solvents have been prepared by two slightly different experimental techniques. Solutions of methylol cellulose can be prepared in all of the solvents by bubbling formaldehyde gas into a stirring slurry of cellulose in the organic solvent. The slurry is kept at the desired temperature, generally 80-90°, in an oil bath, and the formaldehyde gas is generated by thermal decomposition of PF in an external flask. In this temperature range solutions are generally limited to a maximum concentration of 1-2% cellulose. Alternately, in DMA, NMP, and TMSO, methylol cellulose solutions can also be prepared as previously described for DMSO[1,2]. Paraformaldehyde, with a suitably low decomposition temperature, is added directly to the stirring slurry of cellulose which is heated to a temperature of 120-125°. With this procedure, solutions of 5% cellulose cotton linters, and 10% solutions of cellulose with a lower D.P. ($\overline{DP}_n$ 275) have been

prepared. In DMSO and TMSO it is possible to obtain even greater concentrations. Cellulose solutions can be prepared over a range of temperatures. However, when the source of formaldehyde is PF added directly to the system, temperatures greater than ca. 110°C are generally required to ensure effective thermal decomposition of the PF.

It was shown earlier[1,2] that when the DMSO-PF solvent system is used to form methylol cellulose, after freeze-drying approximately one mole of formaldehyde is bound per anhydroglucose unit. Preliminary characterization of the methylol celluloses generated in the new solvent indicates that there can be substantial differences in the molar degree of substitution (MS) of the derivative when the solution is prepared at 80° as compared to 120°. We have found that the MS of the methylol cellulose can be as high as ca. 20. The high values are obtained at the lower dissolution temperatures where formaldehyde gas is bubbled into the solution and the solution is cooled immediately after dissolution is accomplished. Prolonged heating or excessive temperatures can result in the loss of bound formaldehyde and ultimately in the regeneration of unsubstituted cellulose. At lower temperatures where extended polyoxymethylene side chains are formed, gel formation occurs more readily, thus limiting the maximum cellulose concentration obtainable. A large MS due to low dissolution temperatures probably accounts for the limited concentrations of cellulose observed by Seymour and Johnson in the DMSO-PF system[4].

The presence of the methylol substituents can be confirmed and the MS determined for some of these systems by n.m.r. analysis of the triacetate. Acetylation of the methylol substituents prevents their loss during isolation of the polymer by precipitation in water. Complete acetylation of the methylol hydroxyl groups and unsubstituted glucose hydroxyl groups, as indicated by the lack of OH stretch in the i.r. spectra, is easily accomplished in the pyridine, DMF, DMA, and NMP systems using acetic anhydride and pyridine. In the sulfoxide systems however,

reaction with acetic anhydride results in undesirable side reactions such as oxidation of the cellulose[10,11]. The isolated methylol cellulose peracetates can be dissolved in deuterochloroform and the ratio of the acetate protons to the methylol protons can be determined from the p.m.r. integrals. P.m.r. spectra of two representative samples of methylol cellulose triacetate (MS 2.9 and 6.1) from the DMA-formaldehyde system are shown in Fig. 1. A p.m.r. spectrum of cellulose triacetate is also presented for comparison. The methylol protons are easily observed. Protons of methylene groups attached to O-acetyl substituents resonate at δ 5.33 p.p.m., while the other methylene protons of the polyoxymethylene chains resonate at 4.88 p.p.m. Protons of the acetyl methyl groups resonate at 2.08 p.p.m. The cellulosic ring protons are observed as a broad band occurring between ca. 3.2-5.6 p.p.m. From the intensities of the methylene resonances for the methylol cellulose of MS 2.9, it is apparent that even at this level of substitution the formaldehyde is present to some extent as polyoxymethylene side chains rather than being evenly distributed between the three hydroxyl groups of the anhydroglucose units.

In conclusion, our results have shown that methylol celluloses can be prepared and dissolved in a number of dipolar aprotic solvents. At lower dissolution temperatures, the MS of the methylol cellulose may be quite high. In solvents other than sulfoxides, methylol cellulose peracetate can be prepared with acetic anhydride and analyzed by p.m.r. to determine MS of bound formaldehyde. More detailed characterization of the new solvent systems will be reported at a later date.

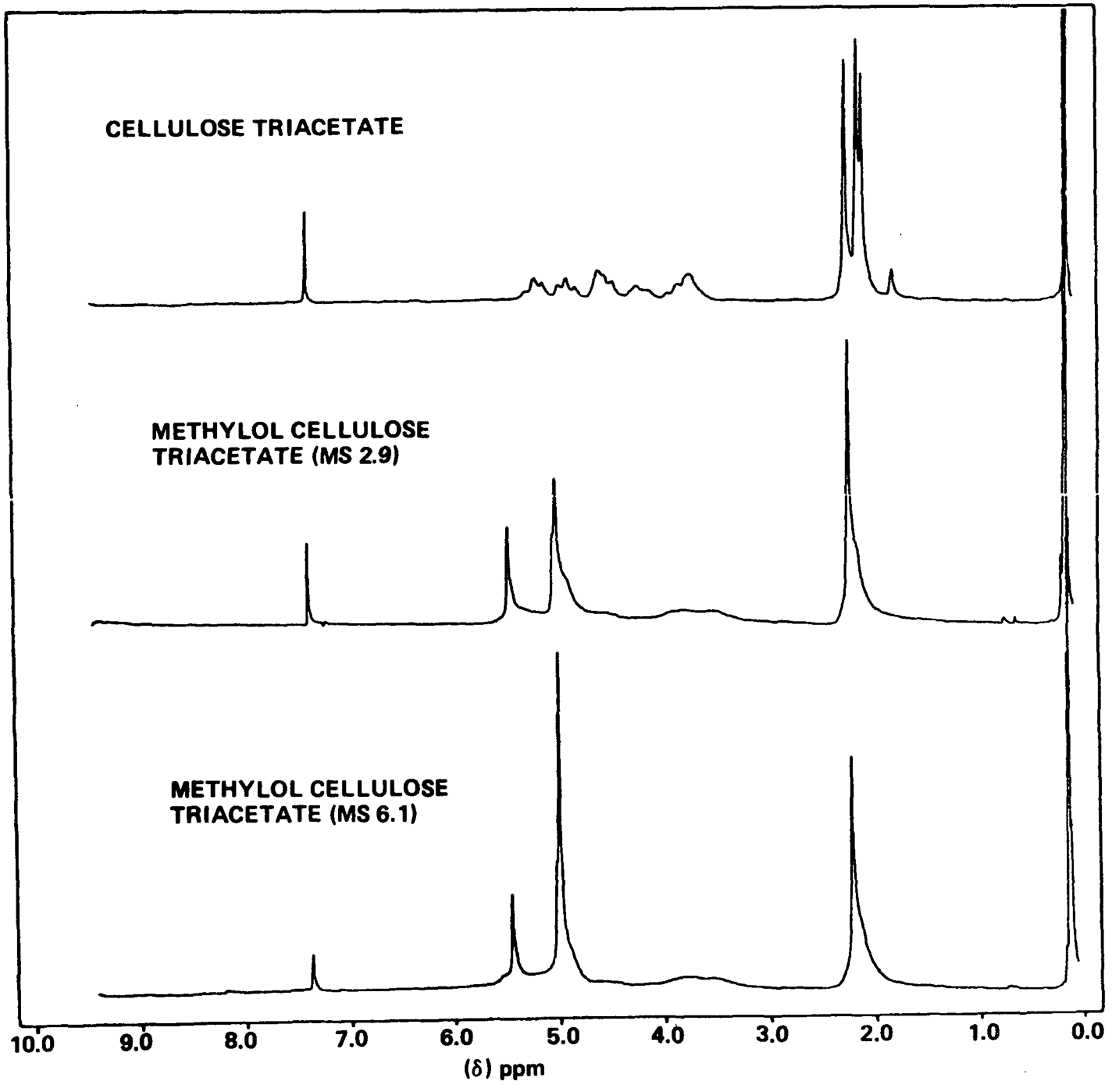

Figure 1. P.m.r. spectra of peracetates of cellulose and methylol celluloses

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