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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)
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Recently, a new solvent-system for cellulose, utilizing dimethyl sulfoxide (Me_2SO) and paraformaldehyde, was discovered at The Institute of Paper Chemistry[1,2] It has been demonstrated that the mechanism whereby cellulose dissolves in this system is dependent in part, on the formation of a hemiacetal derivative "methylol cellulose"[1,2] Thermal decomposition of paraformaldehyde generates formaldehyde, a portion of which reacts with hydroxyl groups of cellulose, especially[1 3] those at C-6 Despite previous indications that Me_2SO is the only solvent for methylol cellulose[4–6], further investigation of the mechanism of formation of methylol cellulose has shown that methylol cellulose may also be prepared and dissolved in polar aprotic solvents other than Me_2SO

We now report that cellulose may be dissolved by the action of formaldehyde in pyridine *N,N*-dimethylformamide (DMF) *N,N*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidinone (NMP), and thiolane 1-oxide (tetramethylene sulfoxide, TMSO) These solvents have the common characteristics of being polar, aprotic, and good hydrogen-bond acceptors The aprotic nature of the solvents is essential, as formaldehyde undergoes addition reactions with most protic solvents[7] The polar nature of the solvents is important in the dissolution process

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 foregoing solvents are good hydrogen-bond acceptors and are able to interact effectively with hydroxyl groups of the cellulose and thereby disrupt intermolecular hydrogen-bonding In addition, these solvent molecules are relatively small and can penetrate the cellulose structure more readily than bulky molecules

Interaction of the solvent with 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 interac-

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

tions would be expected to enhance retention of formaldehyde in solution, and would maintain it in a highly reactive state. A 1:1 formaldehyde–pyridine complex has previously been isolated[8]. Similar interactions have also been postulated as being important in other cellulose solvent-systems[9].

Solutions of methylol cellulose in the new solvents have been prepared by two slightly different experimental techniques. Such solutions may be prepared in all of the solvents by bubbling formaldehyde gas into a stirred slurry of cellulose in the organic solvent. The slurry is kept at the desired temperature, generally 80–90°, in an oil bath, and formaldehyde is generated by thermal decomposition of paraformaldehyde in an external flask. Over this temperature range, solutions are generally limited to a maximum concentration of 1–2% of cellulose. Alternatively, in DMA, NMP, and TMSO, solutions of methylol cellulose may also be prepared as previously described for Me_2SO[1,2]. Paraformaldehyde, which has a suitably low decomposition-temperature, is added directly to the stirred slurry of cellulose, which is heated to 120–125°. By this procedure, solutions of 5% cellulose cotton linters, and 10% solutions of cellulose having a lower d.p. ($\overline{dp}_n$ 275) have been prepared. In Me_2SO and TMSO, it is possible to obtain even greater concentrations. Cellulose solutions may be prepared over a range of temperatures. However, when the source of formaldehyde is paraformaldehyde added directly to the system, temperatures greater than ~110° are generally required to ensure effective thermal decomposition of paraformaldehyde.

It was shown earlier[1,2] that, when the Me_2SO–paraformaldehyde solvent-system is used to form methylol cellulose, ~1 mol of formaldehyde is bound per mol of glucose residues, after freeze-drying. Preliminary characterization of the methylol celluloses generated in the new solvents indicates that there may be substantial differences in the molecular substitution (m.s.) of the derivative when the solution is prepared at 80° as compared to 120°. We have found that the m.s. of the methylol cellulose can be as high as ~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. Prolonged heating or excessive temperatures can result in the loss of bound formaldehyde and ultimately in the regeneration of unsubstituted cellulose. At lower temperatures, when extended polyoxymethylene side-chains are formed, gel formation occurs more readily, thus limiting the maximum concentration of cellulose obtainable. A large m.s., because of low dissolution temperatures, probably accounts for the limited concentrations of cellulose observed by Seymour and Johnson in the Me_2SO–paraformaldehyde system[4].

The presence of the methylol substituents can be confirmed and the m.s. determined for some of these systems by n.m.r.-spectral 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 hydroxyl groups of D-glucose, as indicated by the lack of OH stretch in the i.r. spectra, is readily accomplished in the pyridine, DMF, DMA, and NMP systems by using acetic anhydride–pyridine. In the sulfoxide systems, however, treatment with acetic anhydride results in such undesirable side-reactions as oxidation of the cellulose[10,11]. The methylol cellulose triacetates isolated can be dissolved in chloroform-*d* and the ratio of the acetate protons to the methylol protons determined from the ^{1}H-n.m.r. integrals. ^{1}H-N.m.r. spectra of two representative samples of methylol cellulose triacetate (m.s. 2.9 and 6.1) from the DMA–formaldehyde system are shown in Fig. 1. The ^{1}H-n.m.r. spectrum of cellulose triacetate is also presented for comparison. The signals of methylol protons are readily observed. Protons of methylene groups attached to *O*-acetyl substituents resonate at δ 5.33 p.p.m., whereas 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 cellulose ring protons are observed as a broad band occurring between ~3.2–5.6 p.p.m. From the intensities of the methylene resonances for the methylol cellulose of m.s. 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 D-glucose residues.

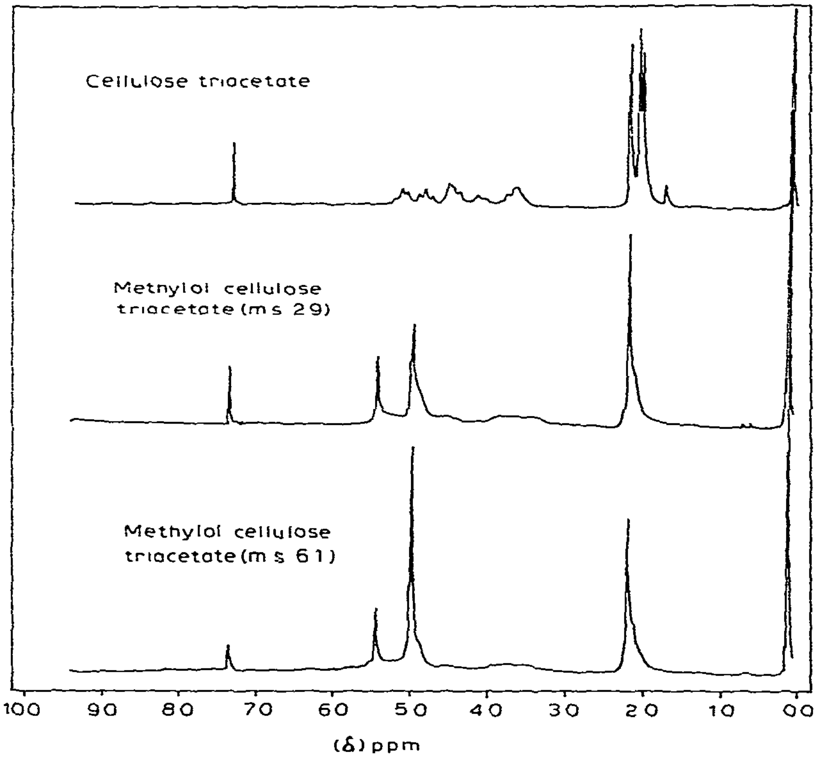

Fig. 1. ^{1}H-N.m.r. spectra of peracetates of cellulose and methylol cellulose

REFERENCES

1 M D. Nicholson, Doctoral Dissertation, The Institute of Paper Chemistry, Appleton, Wis, January 1976
2 M D Nicholson, D C Johnson, and F C Haigh, *Applied Polymer Symp*, 28 (1976) 931–943
3 M D Nicholson and D C Johnson, *Cellulose Chem. Technol*, 11 (1977) 349–359
4 R. B Seymour and E L Johnson, *J Appl Polymer Sci*, 20 (1976) 3425–3429
5 J. T Guthrie and S V Hardcastle, *Polymer*, 18 (1977) 203–204
6 H L Hergert, R B Hammer, and A F Turbak, *Tappi*, 61 (1978) 63–67
7 J. F Walker, *Formaldehyde*, R E Krieger Publishing Co, New York, 1975
8 E Formanek, *Ber*, 38 (1905) 944–945
9 B Philipp, H. Schleicher, and W Wagenknecht, *Cellulose Chem. Technol*, 9 (1975) 265–282
10 J D Albright and L Goldman, *J Am Chem Soc*, 87 (1965) 4214–4216
11 S M Ifzal and D A Wilson *J Chem. Soc C* (1969) 2168–2173