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COMMUNICATIONS FROM RESEARCH GROUPS: THE ACETYLATION OF CELLULOSE IN THE DIMETHYL-ACETAMIDE–PARAFORMALDEHYDE SYSTEM

R. LEONI & A. BALDINI

Centro Sperimentale 'Marinotti', SNIA Fibre, Cesano Maderno, Italy

Nicholson *et al.* (1976) first reported that the dimethylsulphoxide (DMSO)–paraformaldehyde solvent system was very interesting compared to other cellulose solvents for its simplicity, non-corrosiveness and its ability to readily dissolve any kind of cellulose to obtain clear solutions. The major disadvantage from the industrial point of view of using DMSO as a cosolvent is that it is expensive, not very widely used as process solvent, is not easily available and not suitable for dry spinning.

Several researchers have noted the extreme specificity of the combination of reagents. Whereas Seymour & Johnson (1976) reported that neither DMF, DMAC, acetone or HMPA could be substituted for the DMSO, we have succeeded in substituting DMSO with cheaper solvents which are widely used in industrial processes, easily available and suitable for dry spinning, i.e. DMF and DMAC (Leoni *et al.*, 1978, 1979), yielding solutions with higher cellulose concentration than in DMSO (see Fig. 1).

One of the most interesting possibilities the new organic cellulose solvents offer is that of performing derivatisation reactions on cellulose in a homogeneous phase, and a particularly interesting derivative for the producers of man-made fibres is cellulose acetate.

Seymour & Johnson (1978) described the acetylation of cellulose in the DMSO/paraformaldehyde system using acetic anhydride as reagent and pyridine as a catalyst. Using this technique, yellow solutions are produced, which become progressively darker as the acetylation process continues. The precipitation products obtained from these solutions are also coloured from yellow to brown and are not easily isolated in the pure state. The same authors and Shiraishi *et al.* (1978) have characterised these products by infrared, ^{1}H NMR, ^{13}C NMR, ultraviolet spectra as methylolcellulose acetates, CELL-$[O(CH_2O)_xCOCH_3]_y(OH)_z$, where $y + z = 3$/anhydroglucose.

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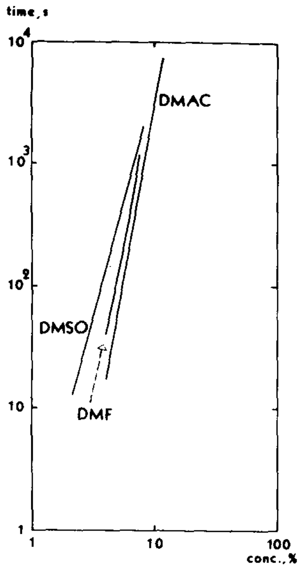

Fig. 1. Viscosity of cellulose/CH_2O/organic solvent solutions, as a function of cellulose concentration.

Seymour & Johnson (1978) also underline the importance of formation of dimethylacetoxysulphonium acetate, $[(CH_3)_2SO{-}CO{-}CH_3]^+CH_3COO^-$, in the acetylation of cellulose and in its oxidation, which is accompanied by the formation of colour. These compounds are believed to be formed by the reaction of acetic anhydride with DMSO and act as reaction intermediates. Needless to say this method of acetylation of methylolcellulose is of neither analytical (undesirable side-reactions) nor industrial (use of toxic and expensive reagents such as pyridine) interest.

Therefore we studied this reaction so as to obtain in a quantitative yield an acetylated product having a high degree of purity, potentially suitable for direct industrial use, starting from our DMF or DMAC solutions.

In this study it was soon found out that such a result cannot be obtained by simply changing the solvent and using the acetylation method described by Seymour & Johnson, because also in DMF or DMAC the acetylation of methylolcellulose with acetic anhydride and pyridine leads to coloured solutions which yield precipitation products coloured from yellow to orange quite similar to those obtained from solutions in DMSO. These results clearly indicate that this acetylation method is not suitable for acetylation of methylolcellulose. The dimethylacetoxysulphonium acetate seems also not to be relevant to the reaction and formation of byproducts.

We succeeded in solving the problem of acetylation of methylolcellulose using acetic anhydride in the presence of an acetate or oxide of an alkali metal, e.g.

potassium acetate, as a catalyst and DMF or DMAC as a solvent of methylolcellulose (Leoni *et al.*, 1980).

The acetylation product obtained in this way can be precipitated in quantitative yield from the pale yellow solution by addition of a 1:1 mixture of water and methanol.

Methylolcellulose acetate prepared by this method appears as a white powder, soluble in several common organic solvents such as dioxane, chloroform, acetone, tetrahydrofurane, ethyl acetate, etc.

It is to be noted that when the authors tried to acetylate with acetic anhydride and potassium acetate a methylolcellulose in DMSO, we obtained brown products more or less degraded, quite similar to those obtained using acetic anhydride and pyridine. The critical factor is, therefore, not the solvent taken *per se* or the catalyst taken *per se*, but the combination of the two.

The products obtained by our method have also been characterised by IR, UV, ^1H NMR, TGA, elementary analysis, analysis of acetate groups (hydrolysis), analysis of oxymethylene groups $-CH_2O-$ via decomposition by H_3PO_4 and distillation of formaldehyde.

Acetylated methylol and/or polyoxymethylene chains are present in these products, possibly together with acetylated and free cellulosic hydroxils, the extent of acetylation depending on the acetylation time, the temperature and the amount and kind of catalyst (Leoni *et al.*, 1980). The oxymethylene/cellulose ratio in the acetylated products seems strictly related to the formaldehyde/cellulose ratio in the starting solutions (Fig. 2).

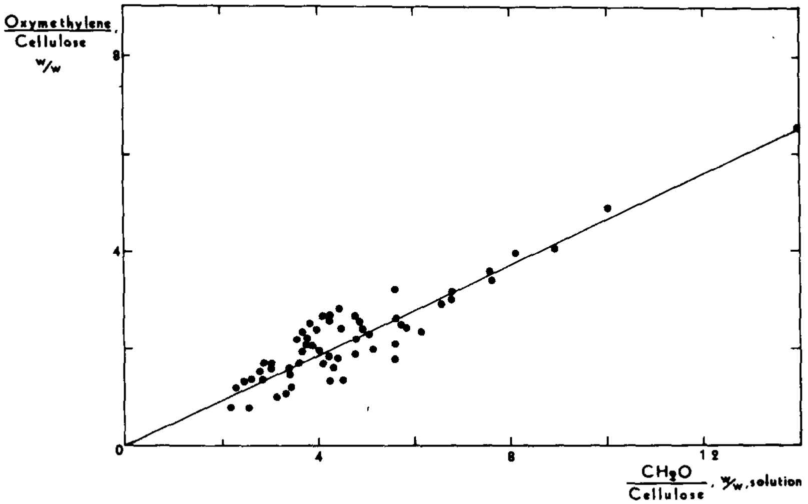

Fig. 2. Oxymethylene/cellulose ratio in the acetylated products versus formaldehyde/cellulose ratio in the solutions.

The IR and UV spectra show that these products are completely similar to those previously described by Seymour & Johnson (1978), but the difference in purity is also underlined by the UV spectrum, lacking the absorptions at 214 and 327 nm that Seymour & Johnson found in their product.

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