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The Effect of Solution Variables on the Solution of Cellulose in Dimethyl Sulfoxide

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Synopsis

Through the study of the effects of concentration, temperature, and molar ration (of paraformaldehyde to cellulose) on solution viscosity and per cent transmittance (at 530 nm), it has been demonstrated that cellulose solutions in dimethyl sulfoxide (DMSO) are readily produced. By heating 1, 2, and 50 to 100 parts by weight of cellulose, paraformaldehyde, and DMSO, respectively, extremely viscose cellulose solutions and gels were prepared. Solutions with concentrations as high as 10% were prepared. However, the optimum conditions to effect complete cellulose solution in DMSO at 75°C were found to be 0.5% cellulose and 0.8 and 1.0% paraformaldehyde. This corresponds to a paraformaldehyde-to-cellulose molar ratio of about 10:1.

INTRODUCTION

Cellulose is soluble in sulfuric acid, aqueous solutions of zinc chloride, sodium hydroxide, tetraalkylammonium hydroxide, and cupric ammonium hydroxide (Schweitzer's reagent). These solubilizing agents have been used with cellulose to produce parchment paper, vulcanized fiber, mercerized cotton, and rayon. More recently, it has been reported that cellulose is also soluble in dimethyl sulfoxide (DMSO) in the presence of paraformaldehyde. This investigation was undertaken in an attempt to determine the effect of variables on this solution process.

EXPERIMENTAL

Cellulose (Whatman filter paper, reagent grade), paraformaldehyde, and reagent-grade DMSO were used without further purification. The cellulose was dissolved by simply heating it in various mixtures of DMSO and paraformaldehyde. The proton magnetic resonance (PMR) spectra were obtained on a Varian T60 instrument using deuterated DMSO as a solvent at room temperature.

DISCUSSION

Effect of Solvents on Solubilization of Cellulose

As shown in Table I, mixtures of paraformaldehyde and cellulose (in a 10:1 molar ratio based on glucose and formaldehyde) did not dissolve in other polar

TABLE I
Solubility of Cellulose–Paraformaldehyde Mixture in Selected Solvents at 75°C[a]

Solvent	Hildebrand solubility parameters δ	Solubility[b]
Pyridine	10.7	–
N-Methyl-2-pyrrolidone	11.3	–
Acetonitrile	11.9	–
Benzyl alcohol	12.1	–
DMF	12.1	–
HMPA	12.	–
Dimethylacetamide (DMAc)	12.2	–
Nitromethane	12.7	–
Sulfolane (tetrahydrothiophene sulfane)	12.	–
Maleic anhydride	13.6	–
DMSO	12.0	+

[a] Each mixture consisted of 0.5 g cellulose, 1.0 g paraformaldehyde, and 98.5 g solvent.

[b] + Indicates Solubility; – Indicates Insolubility.

aprotic solvents such as N,N-dimethylformamide (DMF) and hexamethylphosphoramide (HMPA) nor in polar protic solvents at 75°C. It should also be noted that the cellulose and formaldehyde mixture was not soluble in anhydrous DMSO. Thus, the presence of methanediol in the solution may be assumed.[1,2]

Paraformaldehyde–cellulose (10:1 molar ratio) mixtures in DMSO produced homogeneous solutions or gels. These were all found to be miscible in all proportions with DMF, DMAc, HMPA, and pyridine. However, cellulose was precipitated from these homogeneous solutions and gels when dioxane, alcohol, water, or solvents with similar solubility parameters were added. Brittle films and weak fibers were obtained by solvent evaporation, precipitation in water or ethanol, or wet spinning in water or alcohol.

DMSO Complexes with Alcohols

DMSO forms strong bonds with alcohols,[2,8,9] and PMR techniques have demonstrated the presence of DMSO complexes with dextran and oligoglucose.[2–6] The presence of such complexes in deuterated DMSO make peak assignments

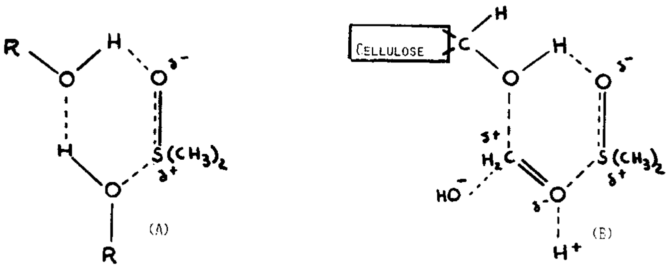

Fig. 1. Proposed DMSO:Paraformaldehyde complexes of alcohols (A) and cellulose (B).

TABLE II
Effect of Concentration on the Viscosity of Cellulose Solutions in DMSO at 25°C

Cellulose, %	0.1	0.5	1.0	1.25	1.66	2.50	5.0	10.00
log [Brookfield viscosity], cps	—	2.6	3.4	3.8	4.0	>6.0	gel	gel

possible along with the definition of coupling constants in the PMR spectra of alcohols.[7,8]

A six-membered complex of DMSO and alcohols, shown in Figure 1A, has been postulated,[9] and it may be that a comparable complex with cellulose could exist. The existence of such transient species would interfere with the intra- and intermolecular hydrogen bonding of cellulose.

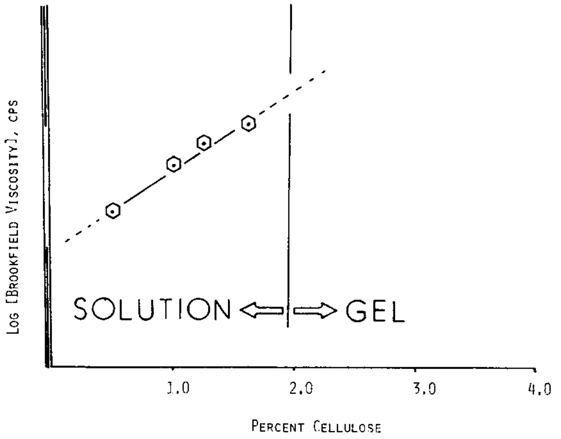

Fig. 2. Relation of logarithm of viscosity and concentration of cellulose in DMSO at 25°C.

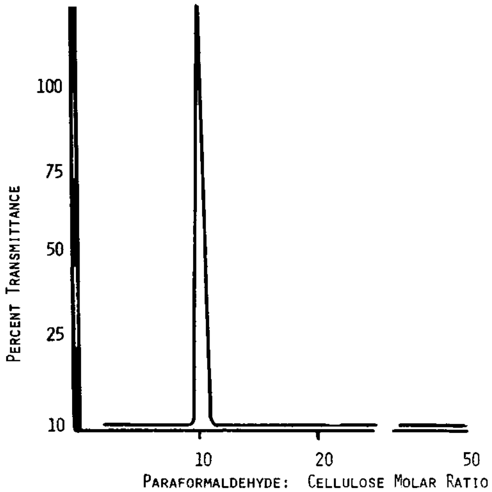

Fig. 3. Per cent transmittance of cellulose solutions at 530 nm plotted as a function of paraformaldehyde:cellulose molar ratios for 0.5% cellulose mixtures.

TABLE III
Effect of Solution Temperature on the Solubility of Cellulose in DMSO

Solution temperature, °C	27	35	55	65	75	100	135	150
Per cent transmittance T, %	[a] —	[b] —	[b] 60	100	100	95	<5[c]	0[c]

[a] No visible effect on cellulose.
[b] Cellulose suspension.
[c] Dark-brown solution.

The presence of transient hemiformal or methylol derivatives of alcohols has been demonstrated by the isolation of the corresponding trimethylsilyl ethers.[10] It has been assumed that the formation of transient six-membered rings as shown in Figure 1B precede the formation of the methylol derivative of cellulose. This postulation is reinforced by the formation of bicyclic diacetals such as di-O-methyleneerythritol and di-O-methylenegalactitol.[11,12]

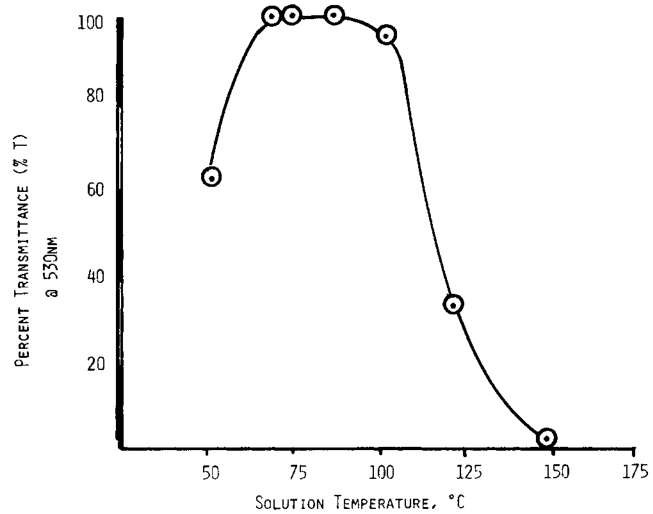

Fig. 4. Effect of temperature on the solubility of the cellulose in DMSO: 0.5% cellulose with 10:1 molar ratio.

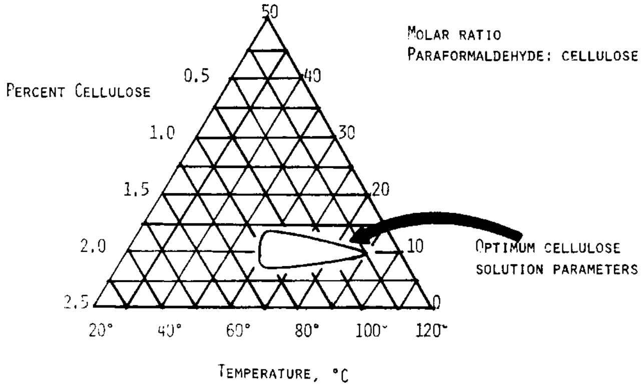

Fig. 5. Optimum solution conditions for cellulose in DMSO in the presence of paraformaldehyde.

Viscosity–Concentration Relationships

As shown in Table II and Figure 2, solutions with concentrations of cellulose as high as 2.5% could be obtained, and there was a linear relationship between the logarithm of the viscosity of these solutions and the concentration of cellulose present. Solutions more concentrated than 0.5% cellulose were opaque because of the presence of insoluble paraformaldehyde fractions.

Paraformaldehyde:Cellulose Ratios

The molar ratio of paraformaldehyde to cellulose was varied from 50:1 to 1:1, but, as shown in Figure 3, good transmission of monochromatic light at 530 nm was observed at a 10:1 ratio. At lower paraformaldehyde-to-cellulose ratios, undissolved cellulose was present; and at higher ratios, considerable amounts of insoluble paraformaldehyde were present. Cellulose is completely insoluble in DMSO; the solubility of paraformaldehyde in DMSO is less than 1.0%.

Effect of Temperature on Solubility

As shown in Table III and Figure 4, transparent solutions of 0.5% solution of cellulose and paraformaldehyde (1:10 molar ratio) in DMSO were obtained when the mixtures were heated for at least 8 hr at temperatures above 65°C. Degradation and darkening of the solutions were noted at temperatures above 100°C.

Conclusions

As shown in Figure 5, the optimum conditions for dissolving cellulose in DMSO are 0.25% to 1.0% cellulose solution with paraformaldehyde:cellulose molar ratio of 10:1 at 65° to 80°C.

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