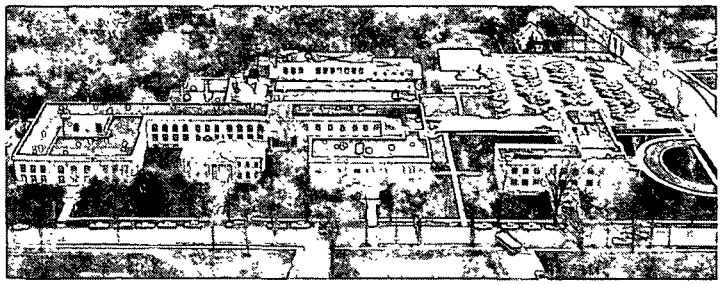

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FORMATION OF METHYLOL CELLULOSE AND ITS DISSOLUTION IN POLAR APROTIC SOLVENTS

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FORMATION OF METHYLOL CELLULOSE AND ITS DISSOLUTION IN POLAR APROTIC SOLVENTS[1]

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Methylol cellulose, which was previously demonstrated to be formed during dissolution of cellulose by formaldehyde and dimethyl sulfoxide, has also been produced in five other polar, aprotic solvents. Characterization of the methylol cellulose samples isolated from the six solvents was aided by acetylation followed by NMR analyses of the peracetates to determine their molar degrees of substitution. The results indicated that a high molar substitution (MS 15-24) was required initially to achieve dissolution at 85°; therefore, a large excess of formaldehyde was necessary. Once solution was achieved, the molar substitution level could be lowered thermally without cellulose precipitation until the MS reached 0.5-3.0, depending on the solvent used.

Methylolcellulose, die, wie kürzlich gezeigt wurde, durch Auflösen von Cellulose unter Einwirkung von Formaldehyd in Dimethylsulfoxid entsteht, wurde in fünf anderen polaren, aprotischen Lösungsmitteln dargestellt. Die Charakterisierung der aus sechs Lösungsmitteln erhaltenen Methylolcelluloseproben erfolgte durch Ermittlund des Ausmaßes molarer Substitution mittels NMR-Analyse der vollständig acetylierten Proben. Die Ergebnisse zeigten, daß anfänglich eine hohe molare Substitution (m.S. 15 — 24) erforderlich war, um bei 85° eine Lösung zu erhalten. Deshalb war auch ein großer Überschuß an Formaldehyd nötig. Sobald Auflösung erfolgt war, konnte durch termische Behandlung das Ausmaß molarer Substitution je nach Lösungsmittel bis auf 0.5 — 3.0 erniedrigt werden, ohne daß Cellulose ausgefallen wäre.

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INTRODUCTION

It has been demonstrated that the mechanism by which cellulose dissolves in the dimethyl sulfoxide (DMSO) — paraformaldehyde (PF) solvent system involves the formation of a hemiacetal-methylol cellulose — as shown in Fig. 1.[1,2] Although addition of formaldehyde to OH-6 is probably preferred, the distribution of methylol substituents undoubtedly includes the other two hydroxyl groups with the relative amounts dependent on the reaction conditions.[3] Although earlier studies suggested that DMSO was the only solvent in which methylol cellulose could be dissolved,[4-6] further investigation of cellulose dissolution revealed that methylol cellulose could be prepared and dissolved in dipolar, aprotic solvents other than DMSO.[7]

[Figure 1 here]

In the present work, solutions of methylol cellulose were prepared in each of six dipolar, aprotic solvents: DMSO, tetramethylene sulfoxide (TMSO), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), N-methyl-2-pyrollidinone (NMP), and pyridine. The methylol celluloses were characterized by conversion to their triacetate derivatives, and the MS of the methylol substituents were determined from the ^{1}H NMR spectra of the peracetates.[3] With this procedure, changes in the MS of the methylol cellulose both as a function of solvent and the time after dissolution (at 85°) could be determined.

EXPERIMENTAL

General

The organic solvents used for the dissolution of cellulose were purified by fractional distillation prior to use. The cellulose source was chromatographic

grade Whatman CF-1 cellulose powder. Paraformaldehyde was obtained from Tridom Chemical Company, Hauppauge, N.Y.

NMR spectra were determined on a JEOL FX 100 (100 MHz) Fourier transform spectrometer. Infrared spectra were determined on a Perkin-Elmer 621 grating spectophotomer.

Cellulose Solutions

Solutions of cellulose were prepared by heating a slurry of cellulose (1.0 g) in the organic solvent (100 mL) to 85° in a thermostatically controlled oil bath. Formaldehyde gas, generated by the thermal decomposition of paraformaldehyde (ca. 10 g) in an external flask, was then bubbled through the hot slurry until a clear solution was obtained (15-45 min). This procedure was found to be effective for preparing cellulose solutions limited to 1-2% (w/v).

An alternate procedure that can be used for preparing cellulose solutions in DMSO, TMSO, DMA, and NMP employs paraformaldehyde which is added directly to the cellulose slurry and then thermally decomposed. This procedure was previously described for preparing DMSO solutions of methylol cellulose.[1,2] Solutions containing 5% cotton linters or over 10% Whatman CF-1 have been prepared with this alternate procedure. It has not been effective for preparing solutions of methylol cellulose in either pyridine or DMF.

Acetylation of Methylol Cellulose

Freshly prepared cellulose solutions were maintained at 85° and aliquots (10 mL) were taken at prescribed time intervals. Cooled samples containing about 0.1 g of dissolved cellulose in either DMF, DMA, NMP or pyridine were acetylated using acetic anhydride (10 mL) and pyridine (15 mL). Acetylations proceeded for 18 hr at room temperature. The fully acetylated methylol cellulose was isolated by

precipitation in ice water (300 mL), followed by filtration, washing with water, and drying in *vacuo* (45°). Complete acetylation was verified by the absence of hydroxyl absorption in the infrared spectrum.

The aliquots from the DMSO and TMSO solutions were acetylated by a modified procedure to avoid side reactions such as oxidation and formation of methyl thiomethyl ethers which may result from action of acetic anhydride on sulfoxides.[8,9] A nonsolvent, ethyl ether (150 mL), was added to the 10-mL aliquot. The supernatant was decanted and the precipitate was washed with additional ethyl ether (150 mL). Pyridine (25 mL) and acetic anhydride (10 mL) were then added, and the acetylation proceeded as described above.

Determination of the Molar Degree of Substitution (MS)

The methylol cellulose triacetate (15-30 mg) was dissolved in deuterochloroform (0.4 mL) and the ^{1}H-NMR spectrum was recorded. A typical proton spectrum of methylol cellulose triacetate (MS *ca.* 9.5) is shown in Fig. 2. Acetyl protons are responsible for the signal at 2.08 ppm while the cellulosic ring protons give the broad signal in the 3.2-5.2 ppm range. The methylene signals of the oxymethylene chain are found at 5.33 and 4.88 ppm with the former due to the $O\underline{CH_2}OCOCH_3$ moiety and the latter due to the other $O\text{-}\underline{CH_2}\text{-}O$ units in the oxymethylene repeating units. The integral of the spectrum allowed calculation of the MS of the methylol-cellulose sample. That portion of the integral due to the O-acetyl substituents was set equal to nine protons. The seven ring protons of the anhydroglucose unit were then subtracted from the remaining integral which left the number of protons per anhydroglucose unit contributed by the methylol substituents. The MS is equal to one-half the value of the methylol protons per anhydroglucose unit.

[Figure 2 here]

As a check on whether the isolation procedure for the methylol cellulose triacetate gave material containing low molecular weight polyoxymethylene acetate as a contaminant, several samples were further purified by means of gel permeation chromatography on Porasil. The MS values determined by NMR before and after fractionation of samples prepared initially in various solvents were: pyridine, MS 13.1 before and 13.2 after; dimethyl formamide, MS 18.4 and 18.4; dimethyl acetamide, MS 15.8 and 15.6.

RESULTS AND DISCUSSION

Earlier work[10] on solutions of methylol cellulose in DMSO indicated that formation of the methylol cellulose and its dissolution occurred without degradation of the cellulose chain length. The question of possible degradation of cellulose in some of the new solvent systems was investigated using gel permeation chromatography of the cellulose tricarbanilate derivative.[11] The results of this investigation for the pyridine, DMF, and DMA systems are included in Table 1. Although a slight decrease in the initial degrees of polymerization was noted, it appeared that this was mainly influenced by the conditions employed for regeneration (addition to water at 75°) rather than the formation and dissolution of methylol cellulose. Thus, DMA, DMF and pyridine are also nondegrading solvents for methylol cellulose. Analyses of this type were not performed for the NMP and TMSO systems.

[Table 1 here]

Acetylation of the dissolved methylol cellulose with acetic anhydride and pyridine resulted in the formation of a modified cellulose triacetate which was found to contain methylol substituents. Acetylation of the methylol substituents prevented their loss during isolation by precipitation in water. NMR analysis of the acetylated methylol cellulose provided a convenient experimental procedure for the analysis of the MS of the methylol cellulose.

Infrared analysis provided experimental evidence that the derivative was, in fact, completely acetylated. As shown in Fig. 3, the lack of absorbance in the OH stretching region (3000-4000 cm^{-1}) indicates that there are essentially no free hydroxyl groups. Comparison of the spectrum of methylol cellulose triacetate with that of cellulose triacetate indicates the presence of methylol substituents. The extra absorbance at ca. 950 and 1100 cm^{-1} corresponds to stong bands observed at 940 and 1090 cm^{-1} for paraformaldehyde polymers and their derivatives[12,13] as well as aromatic compounds which contain an $-O-CH_2-O-$ group.[14]

[Figure 3 here]

The ^{1}H-NMR spectra of representative samples of methylol cellulose triacetate (MS 2.9 and 6.1) from the DMA-formaldehyde system are shown in Fig. 4. A ^{1}H-NMR spectrum of cellulose triacetate is also presented for comparison. Three signals are observed for the acetyl methyl substituents in the spectrum of cellulose triacetate. The peaks are observed at 2.09, 1.99, and 1.94 ppm and have been assigned to O-acetyl substituents at OH-6, OH-2, and OH-3, respectively.[15] For the methylol cellulose acetate samples shown in Fig. 4, only one resonance (2.08 ppm) is observed for the acetyl methyl groups. Previous substitution of the hydroxyl groups of the anhydroglucose units by methylol substituents allows all of the O-acetyl groups to be located in magnetically similar environments. This difference in the NMR spectra of cellulose triacetate and an acetylated methylol cellulose was also noted by Shiraishi, et al.[3] However, at low degrees of methylol substitution, when a significant proportion of the O-acetyl substituents are attached directly to the cellulose backbone, the expected additional absorbances at 1.99 and 1.94 ppm are observed. The signal at 5.33 ppm is due to the protons of methylene groups attached to O-acetyl substituents while the signal at 4.88 ppm is assigned to the other methylene protons of the polyoxymethylene chains. For methylol celluloses with high MS values and consequently methylol substituents at each of the

anhydroglucose hydroxyls, the integral for the resonance at 5.33 ppm was 2/3 of the integral for the acetyl methyl protons at 2.08 ppm. This is equivalent to one methylol unit per O-acetyl substituent and further verifies the above assignments for methylene resonances.

[Figure 4 here]

Under the conditions used to obtain methylol cellulose solutions in these several media, it was obvious that a substantial molar excess of formaldehyde to anhydroglucose units was required. The MS of the methylol celluloses at the point of dissolution (at 85°) was determined by NMR analyses of the acetylated methylol celluloses. These data are given in Table 2. Solutions which were maintained at 85° for up to 20 hr were shown to gradually lose methylol content (decrease in M.S.). Eventually, the MS decreased to a level that resulted in precipitation. Estimates of the MS values at precipitation are also included in Table 2. These values correspond to the minimum MS required to maintain solution (at 85°). The decrease in MS with time is shown for the six solvent systems in Fig. 5 and 6.

[Table 2 and Figures 5-6]

The highest MS required to achieve solution was observed for DMF (23.6) whereas the lowest MS was required for pyridine (15.1). The MS required for dissolution and the MS at the precipitation point were reproducible for each of the solvents. The rate of loss of MS, however, was variable. Further study is required to determine how experimental factors affect the loss of the methylol substituents. The DMSO system was characterized by an extended period at which solution was maintained at a very low (<1.0) MS level. In this solvent system, at 85°, precipitation occurred at an approximate MS of 0.5.

The pyridine system was unique in that it required the lowest MS to achieve a 1% solution of methylol cellulose, but it reached the precipitation point at the highest MS level (3.0) of the six solvents studied.

These apparent influences of MS on solubility were confirmed with methylol cellulose samples of various MS levels isolated from solution by precipitation into ether. The samples which had an MS of ca. 3 were soluble in each of the six solvents. A sample of MS between 1.5 and 2.0 was insoluble in both pyridine and DMF. A methylol cellulose isolated by freeze-drying had an MS ca. 1.0 and was soluble only in DMSO and TMSO. Thus, the values of MS required to obtain redissolution were consistent with the MS precipitation point data (Table 2).

Mechanism of Dissolution

In order for cellulose to be dissolved, the solvent must penetrate and swell the cellulose structure, including ultimately the ordered crystalline regions. Intermolecular hydrogen bonds must be disrupted and the hydroxyl groups of the cellulose must be stabilized in some manner to prevent reformation of hydrogen bonds. The swelling that occurs in the solvent systems is necessary to achieve reasonably uniform reaction of formaldehyde to form the methylol cellulose with high initial M.S. Indeed, a property that these solvents share in common is that they are excellent swelling agents for cellulose.[16,17] On the other hand, many excellent cellulose-swelling liquids do not provide stable methylol cellulose solutions. Thus, swelling ability is a necessary but not sufficient condition for obtaining methylol cellulose solutions in a given liquid.

Another important factor in the dissolution mechanism which has been clarified in the present work is the initial formation of long pendant chains of oxymethylene substituents. These pendant chains may assist dissolution in two ways: (a) as bulky substituents they can impede recombination of separated molecular chains,

and (b) they may act as an "associated reagent" which provides formaldehyde from the ends of oxymethylene chains to unreacted regions of the cellulose; in this way, dissolution is aided by redistribution of initially bound formaldehyde.

Any detailed consideration of dissolution mechanism must include an explanation for the inability of the methylol cellulose to form a crosslinked polymer. This reaction is effectively blocked because of the interaction or stabilization of the methylol units by the solvents. Another common feature of these solvents is that they are excellent hydrogen bond acceptors. The relative basicity (as proton acceptors) of various solvents has been measured from the shift in the frequency of the O-H bond of p-fluorophenol (PFP).[18] Using this frequency shift as a measure of the relative basicity of our six solvents, we have noted that there is a correlation between the proton-accepting ability of the solvent and the initial MS of the methylol cellulose. The data in Table 3 shows that as the basicity of the solvent decreases, the MS required to achieve dissolution increases. It may also be noted that tetramethylene sulfone, another aprotic and highly polar solvent, was found <u>not</u> to form methylol cellulose solutions. It is also distinguished from the six good solvents in that it has a much lower proton accepting ability (186 cm^{-1} frequency shift of PFP[18]).

[Table 3 here]

An alternative approach to ranking the basicity of organic solvents is that referred to by Gutmann[19] as solvent donicity. This criterion measures the interaction between a nucleophilic solvent (Lewis base) and the acceptor antimony pentachloride. The ranking (Table 3) is in the same order as that found for the frequency shift for PFP with pyridine having the highest and DMF the lowest donor numbers. Again, the nonsolvent tetramethylene sulfone has a much lower donor number (14.8) than the successful solvents.

The stabilization of the methylol groups by associated solvent has been further demonstrated in the case of DMSO by experiments involving prolonged freeze-drying. The Raman spectrum of freeze-dried methylol cellulose shows a persistent quantity of DMSO which is not diminished by further freeze-drying. The sulfoxide-stretching frequency in the sample was shifted 22 cm^{-1} downward by the association to methylol cellulose.[20] This indicates that the principal interaction is due to association at the oxygen atom of the sulfoxide bond.[21]

Differences are evident in the stabilizing ability of the various solvents as the MS of methylol cellulose decreases (Fig. 5 and 6). Substantial stabilization of methylol groups is evident at low MS values for both DMSO and TMSO. This greater stabilization in the sulfoxide systems may be due to the sulfoxide moiety behaving both as an electron donor and acceptor. Philipp and coworkers[22,23] have attempted to explain the action of nonaqueous cellulose solvent systems in terms of electron donor-acceptor interactions. By analogy with their suggestion for the dissolving action of methyl amine and DMSO, an association shown in Fig. 7 may be important to the high stabilization of methylol cellulose by the sulfoxides. Here the oxygen atom of the sulfoxide acts as an electron donor while the sulfur atom "accepts" electrons from a hemiacetal oxygen conferring additional stabilization to the complex. This view that the electron acceptor ability of sulfur may be the reason for the additional stabilization observed in the sulfoxide solvents is further supported by Gutmann's work.[19] An acceptor number (AN) is defined based on the interaction between solvent (electron acceptor) and triethyl phosphine oxide (electron donor). The AN for DMSO is substantially greater than values found for NMP, DMA, DMF or pyridine.

[Figure 7 here]

It thus appears that in addition to swelling ability, both the electron donor (proton acceptor) and electron acceptor properties are important in determining whether or not an organic liquid will be a good solvent for methylol cellulose.

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TABLE 1

Effect of Dissolution and Regeneration on Cellulose Degree of Polymerization

Sample	$\overline{DP}_n$ [a]	$\overline{DP}_w$ [a]
Original cellulose	280	510
Cellulose treated by regeneration process[b]	230	430
Regenerated celluloses:		
Pyridine	250	460
DMF	240	460
DMA	220	450

[a] Determined on tricarbanilate derivatives.[11]

[b] Undissolved material treated by regeneration conditions: water at 75°

TABLE 2

Initial and Final MS Values for
Dissolved Methylol Cellulose

Solvent	MS at T=0	Estimate of MS at Precipitation Point
DMF	23.6 ± 1.2	2.0
NMP	21.9 ± 1.1	1.5
DMA	20.9 ± 0.3	1.5
DMSO	18.8 ± 1.2	0.5
TMSO	16.2[a]	0.5
Pyridine	15.1 ± 1.1	3.0

[a]One experiment for TMSO; other values are averages of three experiments.

TABLE 3

Correlation Between Initial MS of Methylol Cellulose and Proton-Accepting Ability of the Solvent

Solvent	MS at T=0	Frequency Shift in cm^{-1} (PFP[a])[18]	Donor Number[19]
Pyridine	15.1	485	33.1
TMSO	16.2	380	--
DMSO	18.8	367	29.8
DMA	20.9	356	27.8
NMP	21.9	339	27.3
DMF	23.6	305	26.6

[a] p-fluorophenol.

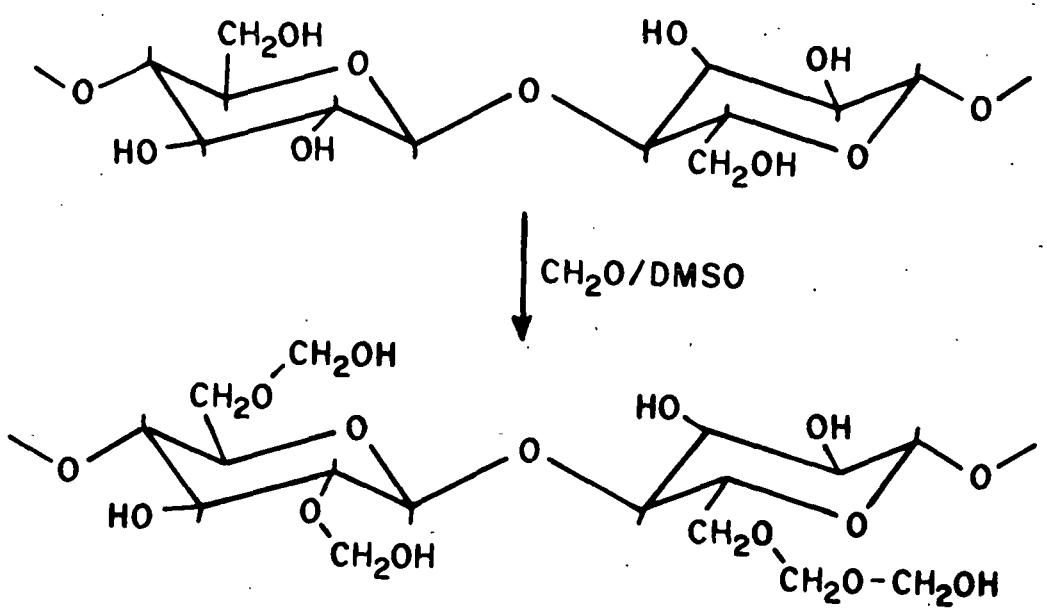

Figure 1. The Dissolution Mechanism for Cellulose in the DMSO/PF Solvent System. Formation of Methylol Cellulose

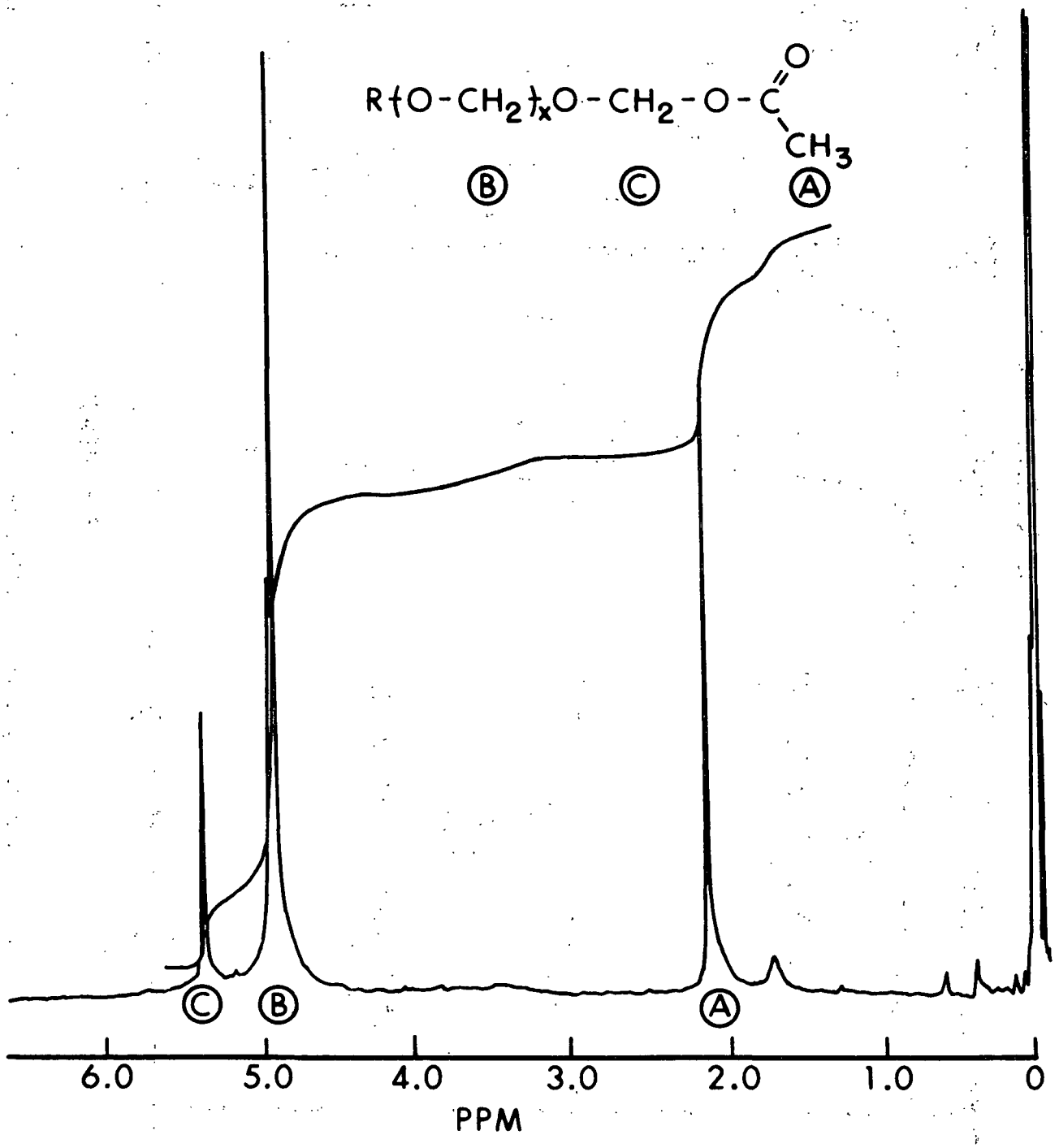

Figure 2. ^{1}H-NMR Spectrum ($CDCl_3$) of Methylol Cellulose Triacetate (MS ca. 9.5)

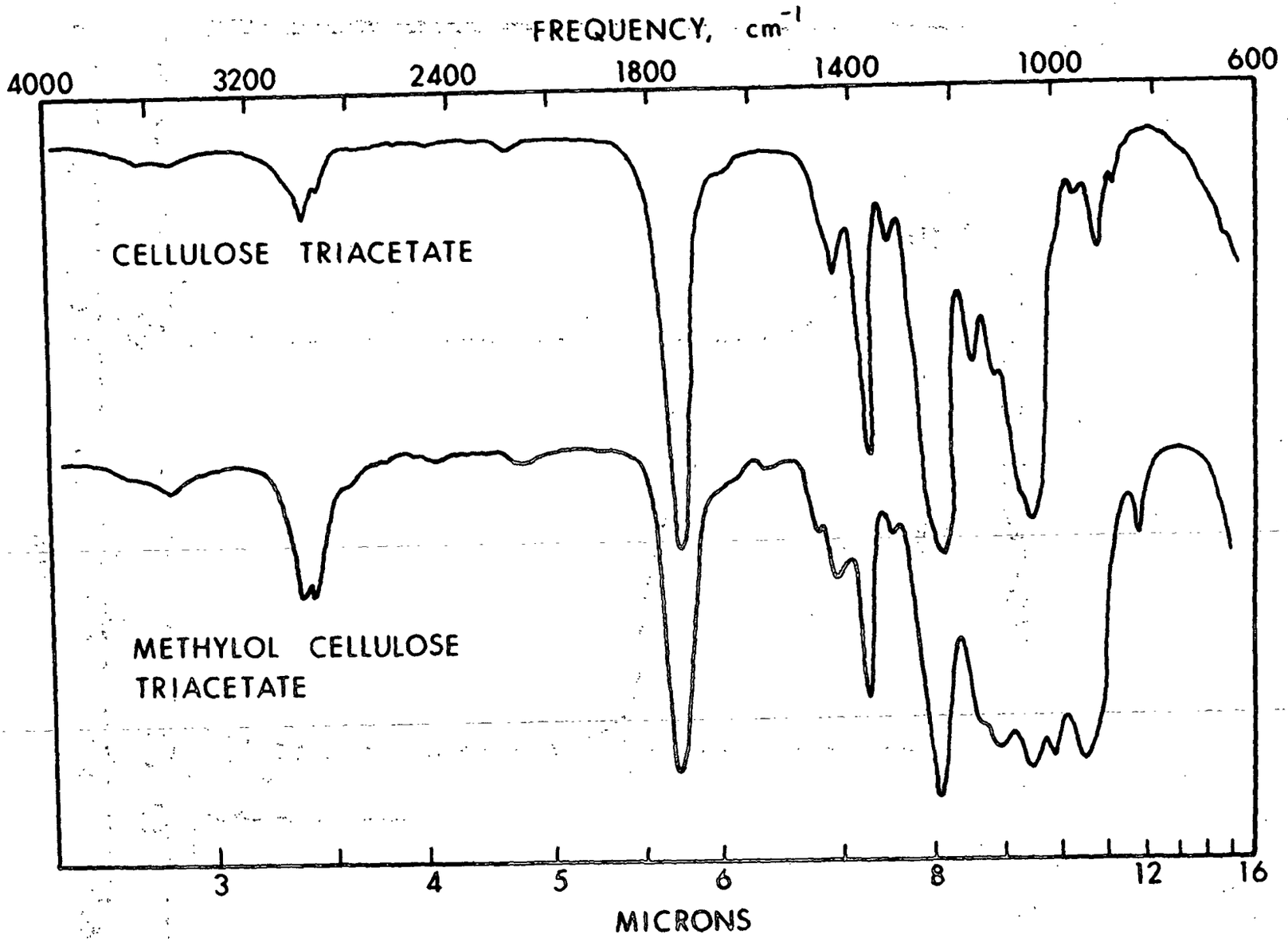

Figure 3. Infrared Spectra of Cellulose Triacetate and Methylol Cellulose Triacetate

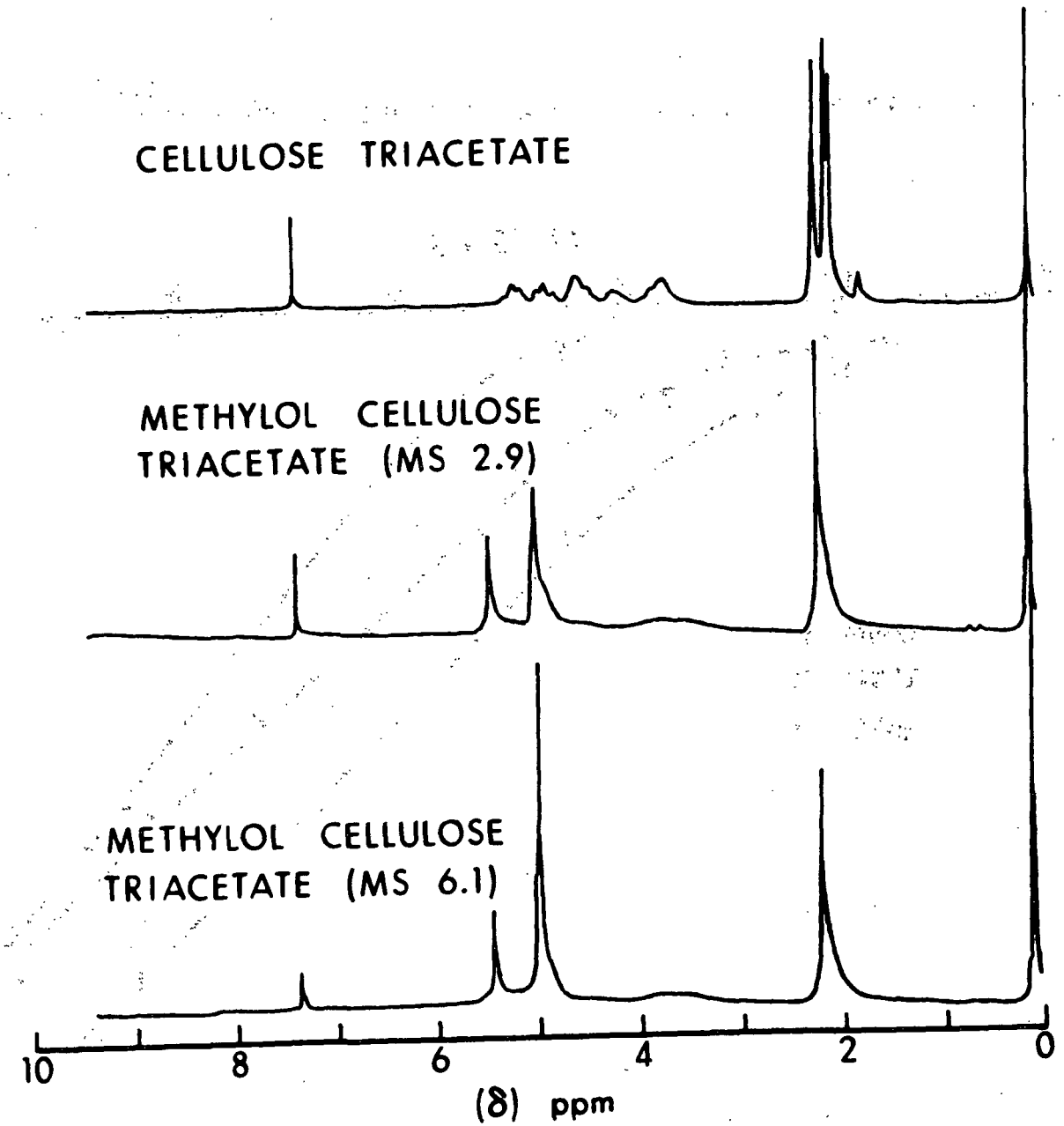

Figure 4. ^{1}H-NMR Spectra of Cellulose Triacetate and Methylol Cellulose Triacetate ($CDCl_3$)

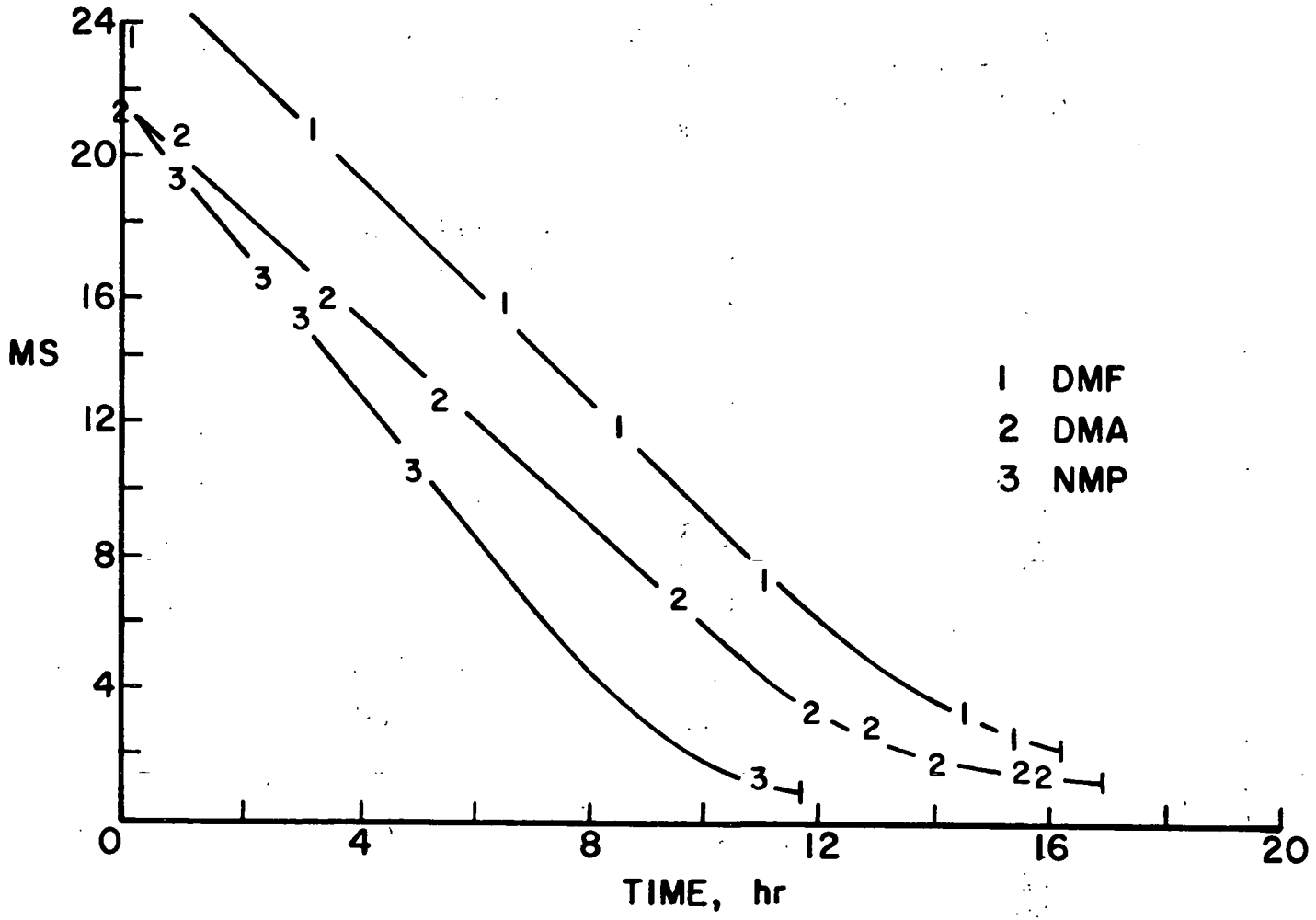

Figure 5. Changes in the MS of Methylol Cellulose with Time at Constant Temperature (85°)

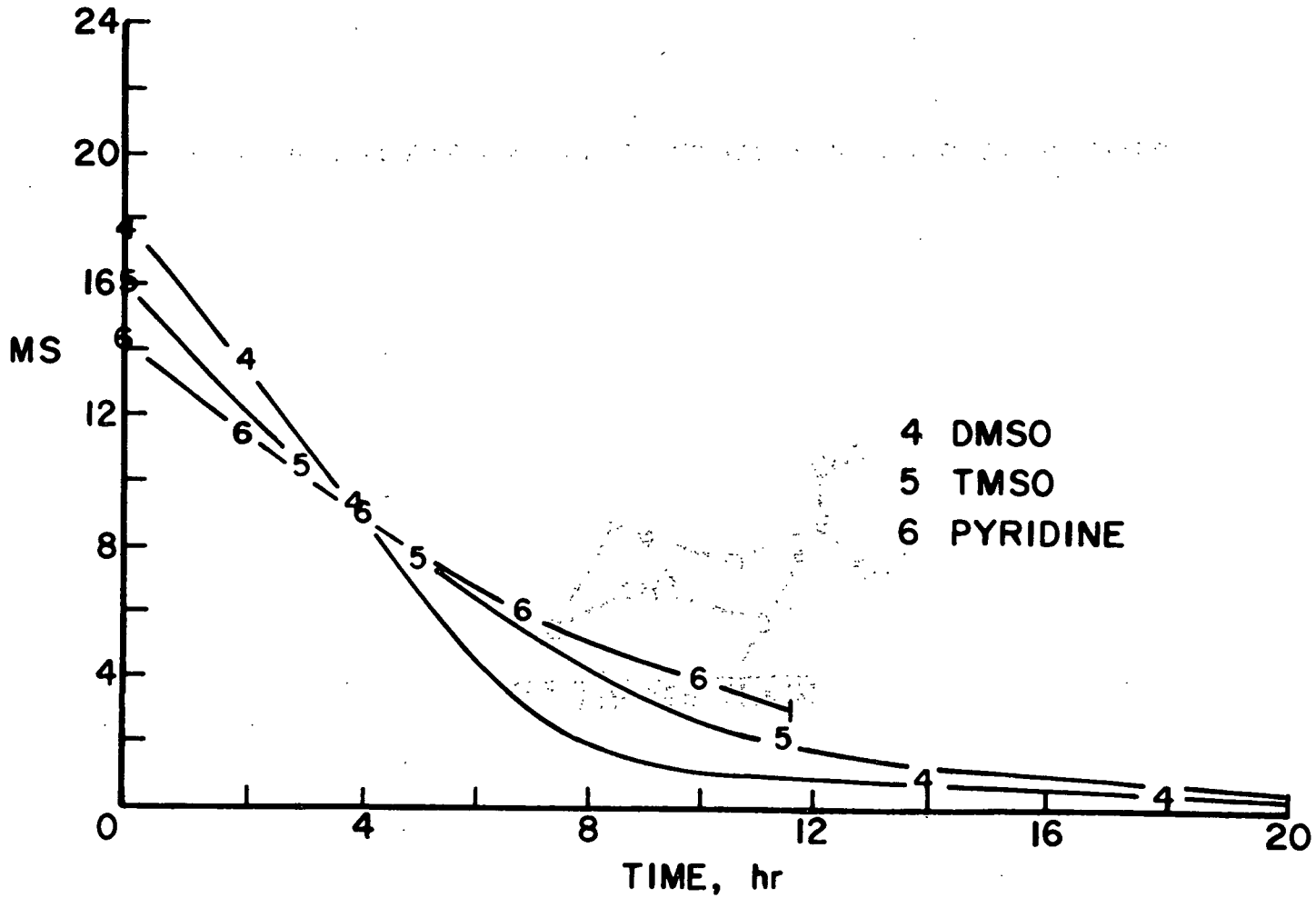

Figure 6. Changes in the MS of Methylol Cellulose with Time at Constant Temperature (85°)

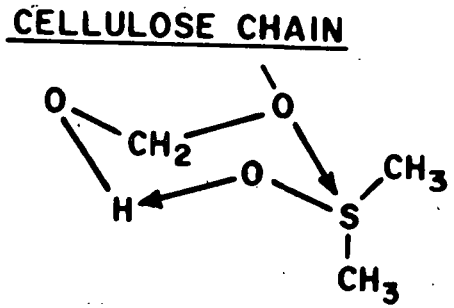

Figure 7. Potential Role of DMSO in Stabilization of Methylol Cellulose