

Investigation of the Cellulose/LiCl/ Dimethylacetamide and Cellulose/LiCl/*N*-Methyl-2- Pyrrolidinone Solutions by ^{13}C NMR Spectroscopy*

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Synopsis

The cellulose/lithium chloride/dimethylacetamide (DMAc) and cellulose/lithium chloride/*N*-methyl-2-pyrrolidinone (NMP) solutions were investigated by ^{13}C NMR spectroscopy. Well-resolved spectra were obtained for both solutions and indicated that cellulose was present in these systems in the form of underivatized cellulose. The change in ^{13}C chemical shifts of DMAc and NMP in the presence of LiCl and LiBr was compared with that of several salt/aprotic solvents, and the results point to the existence of a cellulose–LiCl–DMAc (or NMP) complex in which the lithium cation is strongly bound to the amide carbonyl oxygen and the chloride anion involved in the dissociation of the cellulose hydrogen bonds. Spin–lattice relaxation times (T_1) of the ^{13}C carbons of the solvent molecules, DMAc and NMP, show a large decrease in T_1 for all solvent carbons upon addition of LiCl. Further decrease in T_1 is observed when cellulose is introduced to the LiCl/NMP but not to the LiCl/DMAc systems. These observations are attributed to slower molecular motions of DMAc and NMP in the presence of LiCl, and, in the case of NMP, in the presence of cellulose.

INTRODUCTION

Over the last decade, there has been increased interest in developing organic solvent systems for cellulose. Such interest is not only academic but also has significant commercial potentials, one of which is the development of a new process for the manufacture of rayon. So far, rayon is almost exclusively produced by the conventional viscose process. However, due to increasing economic and environmental pressures regarding this process, alternative processes for dissolving cellulose have been sought. Recent reviews of cellulose solvent systems summarizing the various known methods for dissolving cellulose have been published.^{1,2}

Recently, two new solvent systems for cellulose were discovered in our laboratory, namely LiCl in dimethylacetamide (DMAc) and LiCl in *N*-methyl-2-pyrrolidinone (NMP).³ It was found that cellulose solutions of high concentrations, up to 16% cellulose, can be prepared by the dissolution of activated cellulose pulp in these solvent systems. It was also observed that reconstituted, undegraded cellulose is recovered upon coagulation of these solutions in various nonsolvents. Furthermore, investigations of a large number of salt/aprotic solvents revealed that LiCl/DMAc and LiCl/NMP are unique solvent systems for cellulose.

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The mechanism of dissolution of cellulose in these solvent systems is not well understood, and the present investigation is an attempt to elucidate the nature of the cellulose in solution and to study the role of the salt/aprotic solvent in the dissolution process by ^{13}C NMR spectroscopy.

EXPERIMENTAL

Materials

A prehydrolyzed kraft bleached pulp (ITT Rayonier Cordenier-J-LV grade) with a DP of 500 was Abbé-cut into a finely powdered form and used in the preparation of the cellulose solutions.

The aprotic solvents, dimethylformamide (DMF), dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylpropionamide (DMPA), and tetramethylurea (TMU) were supplied by Aldrich. Anhydrous lithium chloride was obtained from Lithium Corporation of America, Gastonia, N.C.

^{13}C NMR Analysis

The ^{13}C NMR spectra of the cellulose/LiCl/DMAc and cellulose/LiCl/NMP solutions (6.0/8.5/85.5) as well as the salt/aprotic solvent solutions were recorded on a JEOL FX-90Q (90 MHz) pulsed FT-NMR spectrometer, operated at 22.5 MHz and spectral width of 5,000 Hz, with 8K real data points in the transformed spectra. The observed spectra for the cellulose solutions in LiCl/DMAc and LiCl/NMP systems were obtained after 27,569 and 25,000 accumulations, respectively, each after an excitation pulse corresponding to a "flip angle" of 60° . The temperature of the probe was 65°C and 110°C , respectively. Chemical shifts were determined relative to tetramethylsilane (TMS).

Spin-lattice relaxation times (T_1) of the ^{13}C carbons were obtained on the same spectrometer using the automated multiple-pulse inversion-recovery sequence ($180^\circ-t-90^\circ$) with at least five t values and an estimated error of $\pm 10\%$. Viscosity measurements were determined at 23°C using a Brookfield viscometer.

Solution Preparations

The salt/aprotic solvent solutions were prepared by using the appropriate amounts of anhydrous salt and solvents to form solutions with concentrations of 0.2 mole fraction.

The cellulose/LiCl/DMAc and cellulose/LiCl/NMP solutions were prepared as described in Ref. 3.

RESULTS AND DISCUSSION

The LiCl/DMAc and LiCl/NMP solvent systems were found to be excellent solvents for cellulose pulp with a wide range of degrees of polymerization. Even cotton linters formed good solutions in LiCl/DMAc. Several issues regarding the mechanism of cellulose dissolution required consideration, such as the chemical composition of the cellulose in solution, the uniqueness of these salt/

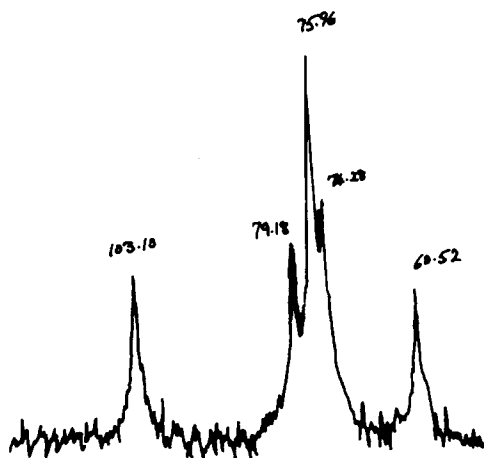


Fig. 1. ^{13}C NMR spectrum of cellulose in LiCl/DMAc solution.

polar aprotic liquids as solvent systems for cellulose, and an understanding of the molecular dynamics of cellulose in these two solvent systems.

In order to ascertain the chemical composition of cellulose in solution, the ^{13}C NMR spectra of 6/8.5/85.5 cellulose/LiCl/DMAc (Fig. 1) and cellulose/LiCl/NMP (Fig. 2) solutions were obtained.

The ^{13}C NMR spectrum of cellulose in LiCl/DMAc solution (Fig. 1) displayed six distinct signals corresponding to the six carbon atoms of the anhydroglucose repeating unit of the cellulose polymer chain. The anomeric C-1 carbon, expected to be the most deshielded carbon atom, appeared at 103.10 ppm, whereas the less deshielded C-4 displayed a signal at 79.10 ppm. The only primary carbon in the anhydroglucose moiety, C-6, expected to be the most shielded carbon appeared at 60.52 ppm. The remaining three signals at 74.28, 75.09, and 75.96 ppm were not as well resolved and were attributed to C-2, C-3, and C-5, although not necessarily in that order.

Similarly, the ^{13}C NMR spectrum of cellulose in LiCl/NMP solution (Fig. 2) showed signals at 103.16 ppm (C-1), 79.21 ppm (C-4), 76.23 ppm (C-5, C-3), 74.38 ppm (C-2), and 60.73 ppm (C-6).

These assignments are in general agreement with the ^{13}C chemical shifts of cellulose in various solvent systems as reported by Gagnaire, Mancier, and Vincendon⁴ and illustrated in the bar chart in Figure 3. There are, however, some differences, such as the chemical shifts of C-2 and C-3. The signals due

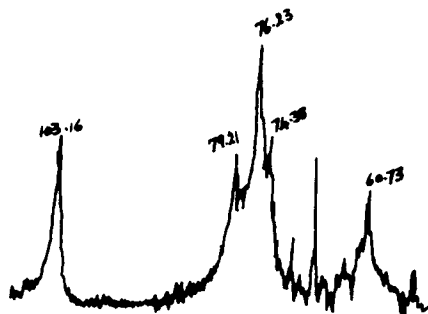


Fig. 2. ^{13}C NMR spectrum of cellulose in LiCl/NMP solution.

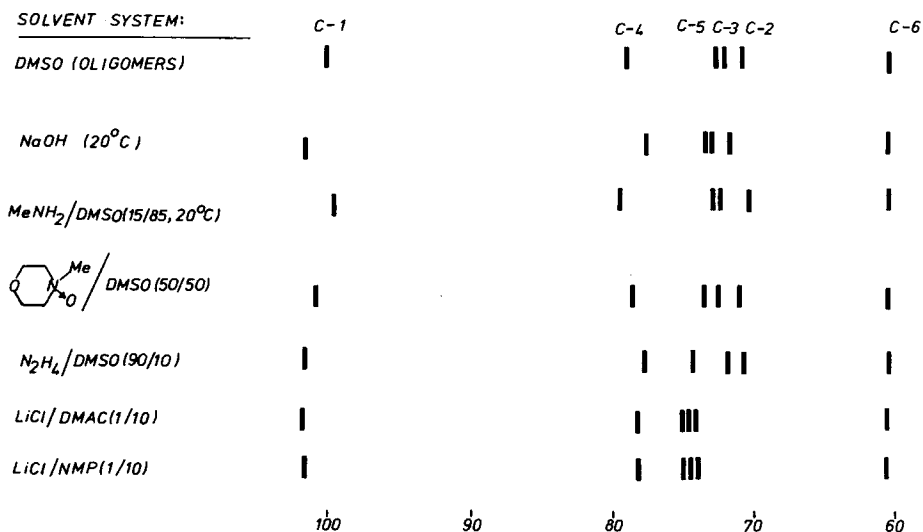


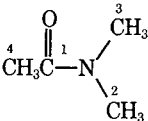
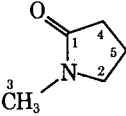
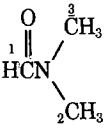
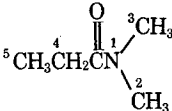
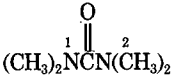
Fig. 3. ¹³C chemical shifts of cellulose in various solvents (ppm). (Chemical shifts of cellulose in previously known solvent systems were obtained from Ref. 4.)

to C-2 and C-3 of cellulose in LiCl/DMAc and LiCl/NMP appear slightly more downfield compared to those in the other solvent systems. This is attributed to the presence of an electron-rich environment surrounding C-2. This situation can arise from hydrogen bonding between a chloride anion and the C-2 hydroxyl hydrogen atom. A similar explanation can be applied to the C-3 situation.

The spectra of cellulose in LiCl/DMAc or LiCl/NMP displayed no additional signals due to the presence of a cellulose derivative. The fact that the six signals due to the cellulose carbons appeared at the expected chemical shifts of undervatized cellulose demonstrated that the LiCl/DMAc and LiCl/NMP systems were true solvents for cellulose, and that they did not form chemical bonds with the cellulose molecule. In this respect, these solvent systems were different from the paraformaldehyde/DMSO or the N₂O₄/DMF solvent systems, in which an unstable cellulose derivative was formed, but were similar to the *N*-methylmorpholine-*N*-oxide/DMSO, CH₃NH₂/DMSO, and hydrazine solvent systems, where only physical dissolution took place.⁴

The uniqueness of LiCl in DMAc or NMP as solvent systems for cellulose pulp is intriguing. A variety of other salts dissolved in different polar aprotic organic solvents were screened under various conditions, but none was found to dissolve cellulose. In order to discern common characteristics between the LiCl/DMAc and LiCl/NMP solvent systems on the one hand, and LiCl dissolved in other *N,N*-disubstituted amide solvents on the other hand, the effect of added salt on the ¹³C NMR chemical shifts of the solvent carbon atoms was investigated. The role of the anion in the dissolution of cellulose in lithium salts dissolved in amide solvents was also investigated by the study of the magnitude of the change in the ¹³C chemical shift of amide carbons in the presence of LiBr. Table I displays ¹³C chemical shift data of LiCl and LiBr solutions in select *N,N*-disubstituted amide solvents. The choice of these potential cellulose solvent systems was based on the similarity of chemical and electronic structures of the aprotic solvents to DMAc and NMP. The results indicate downfield (deshielding) shifts for all carbon atoms of the amides upon addition of salts, with the carbonyl

TABLE I
Effect of Added Lithium Salt on ^{13}C NMR Chemical Shifts of Selected *N,N*-Disubstituted Amides (30°C)^a

Amide	Neat	LiCl	LiBr
			
C-1	168.93	170.61 (-1.68)	172.02 (-3.09)
C-2	36.73	37.60 (-0.87)	38.79 (-2.06)
C-3	33.65	34.40 (-0.75)	35.38 (-1.73)
C-4	20.53	21.02 (-0.49)	22.16 (-1.63)
			
C-1	173.32	174.78 (-1.46)	176.14 (-2.82)
C-2	48.44	48.87 (-0.43)	50.01 (-1.57)
C-3	29.96	30.23 (-0.27)	31.32 (-1.36)
C-4	28.39	28.88 (-0.49)	30.07 (-1.68)
C-5	17.28	17.18 (-0.10)	18.04 (-0.76)
			
C-1	162.76	163.90 (-1.14)	nd ^b
C-2	36.03	36.63 (-0.60)	nd ^b
C-3	30.94	31.32 (-0.38)	nd ^b
			
C-1	172.83	173.97 (-1.14)	174.52 (-1.69)
C-2	36.84	37.44 (-0.60)	37.98 (-1.14)
C-3	34.95	35.27 (-0.32)	35.65 (-0.70)
C-4	26.44	26.60 (-0.16)	26.82 (-0.38)
C-5	9.54	9.59 (-0.05)	9.59 (-0.05)
			
C-1	165.08	165.30 (-0.22)	165.41 (-0.33)
C-2	38.47	38.63 (-0.16)	39.06 (-0.59)

^a Concentration of all solutions, 0.2 mol fraction.

^b Not determined due to low solubility.

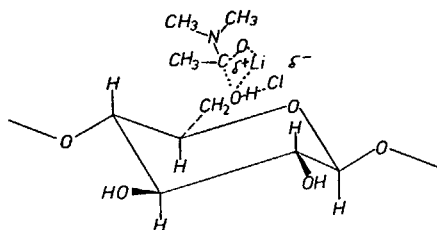
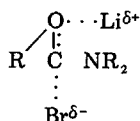


Fig. 4. Transition state for cellulose/LiCl/DMAc solution.

carbons displaying the largest change. These observations are in agreement with the view that metal cations interact directly with the carbonyl oxygen of the amide, which causes a general decrease in electron density of the entire amide molecule particularly at the carbonyl carbons and to lesser degrees at each of the other carbon atoms. Similar results were reported by Rao and co-workers⁵ in which the magnitude of the ^{13}C chemical shifts of amide carbons were shown to depend on the ionic potential of alkali and alkali earth cations.⁶ The data in Table I also show that larger downfield shifts of the ^{13}C chemical shifts of the carbonyl carbons of DMAc (-1.68 ppm) and NMP (-1.46 ppm) occurred in comparison to those of DMF (-1.14 ppm), DMPA (-1.14 ppm), and TMU (-0.22 ppm). The same trend in the change of the ^{13}C chemical shifts of the amide solvents upon addition of LiBr was observed; however, the magnitude of the changes was considerably higher than in the case of LiCl. The observed trend was DMAc (-3.09 ppm) \approx NMP (-2.82 ppm) $>$ DMPA (-1.69 ppm) \gg TMU (-0.33 ppm).

The above results point to the conclusion that the polarization of the carbonyl carbon of the amide solvent, upon the addition of LiCl or LiBr, is greatest in DMAc and NMP compared to that of the other amides. It is also apparent that the anion plays a significant role in the interaction between salt and amide. The greater deshielding effect of the bromide anion over the chloride anion is in agreement with the fact that bromide is a stronger nucleophile than chloride and therefore could enhance the polarizability of the carbonyl group by nucleophilic attack to form the complex



This situation tightly binds the bromide anion to the amide solvent more than in the case of the chloride anion. Consequently, the latter remains relatively free and strongly basic, and therefore capable of overcoming the strong cellulose hydrogen bonds by proton abstraction from the cellulose molecules causing the solubilization of the cellulose to occur. Figure 4 represents a possible transition state for a cellulose/LiCl/DMAc solution system. This model of interaction between cellulose, LiCl, and DMAc (or NMP) is consistent with the one proposed by Hanley, Helminiak, and Benner in their conductivity and viscosity studies of poly(5,5'-bibenzimidazole-2,2'-diyl-1,3-phenylene) in LiCl/DMAc solutions.⁷

^{13}C spin-lattice relaxation time (T_1) measurements can also aid in the un-

understanding of the nature of interaction between various components in a solution of cellulose in LiCl/DMAc or LiCl/NMP.⁸⁻¹⁰ Spin-lattice relaxation involves energy exchange between the nuclear spin system and the environment (lattice) which acts as a heat sink for the energy absorbed by the nucleus upon irradiation. Of the four generally accepted spin-lattice relaxation mechanisms, the dipole-dipole (DD) mechanism is the most dominant in most molecules of interest. The first-order rate constant of the dipole-dipole relaxation for a $^{13}\text{C}-\text{H}_n$ carbon is given by

$$1/T_1^{\text{DD}} = n_{\text{H}}(\hbar^2) \gamma_{\text{H}}^2 \cdot \gamma_{\text{C}}^2 (r_{\text{CH}})^{-6} \tau_c$$

where n_{H} is the number of protons directly attached to the particular ^{13}C , \hbar is Planck's constant divided by 2π , γ_{H} and γ_{C} are the magnetogyric ratios for the ^1H and ^{13}C nuclei, r is the C—H internuclear distance, and τ_c is the molecular rotational correlation time, or the average time required for a molecule to rotate through an angle of one radian.

Table II presents ^{13}C T_1 data for the carbon atoms of DMAc and NMP in the presence of LiCl and also LiCl/cellulose. In the first place, the T_1 values of the carbonyl carbons are long relative to the methyl group carbons of DMAc and NMP in all environments. This is to be expected for carbons bearing no protons. Secondly, upon saturation of DMAc or NMP with anhydrous LiCl, the ^{13}C T_1 values of the DMAc carbons experience a significant decrease ranging from 64% (C-1), 71% (C-4), 76% (C-2), to 77% (C-3), and those of the NMP carbons show decreases in the range of 80% (C-1), 80% (C-4), 88% (C-5), 90% (C-2), and 90% (C-3). These results are comparable to those of Stilbs, Forsén, and Hartman,¹¹ in which decreases in T_1 on the order of 70–80% were observed upon protonation of DMAc in CDCl_3 solution. The decreases in T_1 are directly attributed to slower molecular motions of DMAc and NMP upon addition of LiCl.

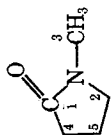
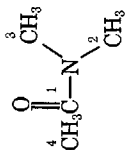
Upon addition of cellulose to the saturated LiCl/DMAc solvent system to form a 6/8.5/85.5 solution, ^{13}C T_1 values of all the DMAc carbons remain unchanged. In the case of the more concentrated cellulose/LiCl/DMAc solution (11.2/9.3/79.5), the T_1 's of DMAc change in both magnitude and direction as compared to the T_1 values of DMAc in 6% cellulose solutions (Table II): C-1 (+16%), C-2 (–5%), C-3 (+37%), and C-4 (–49%).

The effect of addition of cellulose to a saturated LiCl/NMP solution on the ^{13}C T_1 values of the NMP carbons is different from that in the case of cellulose/LiCl/DMAc solutions. In NMP the ^{13}C T_1 values of all solvent carbons decrease as follows: C-1 (–42%), C-2 (–51%), C-3 (–38%), C-4 (–44%), C-5 (–52%). No data was obtained from an 11% cellulose/LiCl/NMP solution due to difficulties in solution preparation.

The difference in the trends of ^{13}C T_1 values of DMAc and NMP in both cellulose/LiCl/aprotic solvent solutions can be attributed to differences in electronic and structural properties of the two aprotic polar solvents which in turn result in different conformations of the cellulose/LiCl/aprotic solvent complex. It was concluded that in the LiCl/DMAc solution system, the LiCl is strongly bound to the DMAc molecules, more so than in the case of NMP, as evidenced by the larger change in ^{13}C chemical shifts (Table I). It can therefore be reasoned that, upon the introduction of cellulose to each solvent system, the system which is less strongly associated, namely the LiCl/NMP, will exhibit the greater change in molecular motions in order to accommodate the cellulose molecules. This

TABLE II
 ^{13}C Spin-Lattice Relaxation Times (s) of DMAc and NMP under Various Conditions (30°C)

^{13}C Sample	DMAc					NMP					Viscosity (Cp)
	C ₁	C ₂	C ₃	C ₄	C ₅	C ₁	C ₂	C ₃	C ₄	C ₅	
Pure solvent	39.2	16.09	16.84	12.91	0.9	37.4	4.90	4.95	10.14	5.52	1.65
Sat LiCl/solvent	14.02	3.79	3.91	3.83	35	7.32	0.51	0.50	2.08	0.67	48
Cellulose/LiCl/solvent (6/8.5/85.5)	14.9	3.8	3.8	4.1	6×10^4	4.27	0.25	0.31	1.16	0.32	$\sim 1 \times 10^6$
Cellulose/LiCl/solvent (11.2/9.3/79.5)	17.3	3.57	5.17	2.11	$\sim 7 \times 10^5$	—	—	—	—	—	—



molecular reorientation results in further motional restrictions for NMP which causes the decrease in the ^{13}C T_1 values.

The virtual invariance of the ^{13}C T_1 values of DMAc toward the presence of 6% or 11% cellulose in LiCl/DMAc solution can be rationalized by the presence of a stable and strong interaction between LiCl and DMAc which restricts the molecular motions of DMAc, and which does not change upon the addition of cellulose.

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