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Theory and applications of DMAC/LICL in the analysis of polysaccharides

André M. Striegel[a]

[a]*Plant Polymer Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, United States Department of Agriculture*[1]*, Peoria, IL 61604, USA*

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DMAc/LiCl has become a favored solvent in the analysis of polysaccharides. Although much is understood about its interaction with carbohydrate molecules, a great deal remains to be known in order for a comprehensive mechanism of dissolution to be discerned. These limitations, however, have not precluded the extended use of DMAc/LiCl in the study of chitin, cellulose, etc. This article reviews the theory of DMAc/LiCl as a solvent and new developments in this area, as well as the variety of applications which have been found for it. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Polysaccharides are essential to virtually all biological systems (Varki, 1993) and are also extremely important in the medical and pharmaceutical fields, as well as in the food, pulp and paper, and textile industries (Whistler & BeMiller, 1993). Optimization of their end-use functions has been found to be directly dependent on knowledge of their structures and molecular weight distributions, and of the extent to which these affect polymer properties.

Finding an appropriate solvent for these polymers has been a source of considerable problems, as the majority of the techniques used to study them require their being in solution. A large number of polysaccharides are water soluble and thus may be analyzed using aqueous solvents. This property is by no means universal, however. Polysaccharides such as cellulose, chitin, etc. are extremely difficult to dissolve. For cellulose, solutions of metal complexes, which tend to degrade the molecule via oxidation, are unstable and many are colored. A different approach that has been used extensively with cellulose involves converting the molecule into a derivative soluble in an organic solvent for subsequent characterization. The methods used to obtain solutions of cellulose derivatives can also cause hydrolytic and/or oxidative cleavage. In addition to the steps necessary to prepare a derivative with strict attention to avoid degradation, dissolution is possible only for molecules with a very narrow degree of substitution. Compounds such as sodium hydroxide or other alkali solvents, which are capable of removing non-cellulosic material, also tend to effect changes in the molecule: the remaining cellulose is either degraded, its crystallinity has been altered and/or it is not absolutely pure (Dawsey & McCormick, 1990). The characterization of a cellulose polymer that is truly representative of a fiber matrix has been a challenge. An even greater challenge has been finding a method not only to characterize cellulose but also other polymers and polysaccharides that may coexist in cotton fibers or in plants at different stages of development, or in biological samples.

One of the most useful solvent systems to emerge over the last two decades is N,N-dimethyl acetamide with lithium chloride (DMAc/LiCl). Originally developed in 1976 to dissolve chitin (Austin, 1977), a linear long-chain polysaccharide composed of a β-(1→4)-linked N-acetyl-D-glucosaminyl backbone, its use was quickly extended to cellulose (McCormick, 1981; Turbak *et al.*, 1982), a linear β-(1→4) glucan. The latter is found in its purest form (~96%) in mature cotton fiber and its characterization is of extreme interest to the textile and pulp and paper industries, among others. DMAc/LiCl has become the solvent of

[1]Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

choice for high-molecular weight cellulose analysis, as well as for the determination of solution characteristics of a number of other polysaccharides. After more than 15 years of use, however, the dissolution mechanism of cellulose in DMAc/LiCl has still not been clearly postulated.

THEORY

Progress in this problem has been made by many groups with the aid of a number of analytical techniques, principally ^{13}C nuclear magnetic resonance (^{13}C NMR). In 1980, Rao and co-workers showed that ^{13}C resonances of carbonyl and methyl groups in amides are shifted downfield on interaction with alkali salts (Rao *et al.*, 1980). They related the magnitude of the shifts to the ionic potential of the cations and found the carbonyl carbon resonance to be affected to a much greater extent compared to the methyl carbon resonances. In 1982, El-Kafrawy examined the cellulose/DMAc/LiCl system using the same technique (El-Kafrawy, 1982). He observed and identified six distinct signals corresponding to the six carbon atoms of the β-glucosyl repeat unit of cellulose. The lack of additional signals in the NMR spectrum, and the fact that this spectrum compared well with the solid-state spectrum of cellulose, was taken as evidence that DMAc/LiCl is a true solvent for the polysaccharide, one that does not form chemical bonds with the cellulose molecule. Confirmation of this was provided by the virtual invariance in ^{13}C spin-lattice relaxation times (T_1s) of all the DMAc carbons on addition of cellulose to DMAc/LiCl solutions. In experiments involving only DMAc and lithium salts, a greater downfield shift in the signal of the carbonyl carbon was noted with the addition of LiBr over LiCl. This was attributed to the greater nucleophilicity of Br^- over Cl^-. The larger anion, being more polarizable, is more tightly bound to the solvent. Thus the chloride anion, which has been postulated to interact with the hydroxyl hydrogens of cellulose to produce bonding similar to their bonding to oxygen atoms, i.e. similar to hydrogen bonding, would interact more readily than the bromide anion, which is more tightly bound to the solvent.

Simultaneous work on cellulose dissolution in DMAc/LiCl demonstrated the exclusivity and uniqueness of the solvent (Turbak *et al.*, 1982; Dawsey & McCormick, 1990). With the exception of N-methyl-2-pyrrolidinone (NMP), the cyclic analog of DMAc, a number of other organic solvents, even polar aprotic ones, were not conducive to the dissolution, or caused degradation, of the cellulose molecule. These included dimethyl sulfoxide (DMSO), formamide, ethanolamine, etc. Also ineffective were salts other than LiCl, be they other lithium halides, such as bromide and iodide, or nitrate and sulfate salts, or other alkali and alkali-earth chlorides, such as sodium, potassium, barium, calcium, magnesium and zinc chlorides. Wagenknecht *et al.* (1992) showed that dissolution of cellulose in DMF/N_2O_4 or DMSO/N_2O_4 actually led to the formation of a cellulose trinitrite. It should be noted that reports have appeared in the literature on the suitability of DMAc/LiBr as a solvent for cellulose or one in which bromination of cellulose may be conducted (Furuhata *et al.*, 1992b).

The polar aprotic nature of DMAc allows ionic compounds to dissolve in it readily and their cations to be extensively solvated. Because of its inability to form hydrogen bonds, DMAc does not solvate anions to any appreciable extent. The anions will therefore be unencumbered by a layer of solvent molecules and, consequently, poorly stabilized by solvation. Such 'naked' anions will be highly active as nucleophilic bases (Solomons, 1984). Additionally, studies of the ^{13}C NMR chemical shifts of carbonyl carbons of N,N-disubstituted amides showed that on addition of LiCl to the neat solvents the magnitude of the downfield shifts followed the trend DMAc$\approx$NMP > dimethyl formamide (DMF)$\gg$tetramethyl urea (TMU). DMAc and NMP, the only two successful solvents for cellulose in this series, also displayed the greater polarizability, as indicated by their chemical shifts (Dawsey, 1989).

Panar and Beste's work on amide solvents showed the formation of a new absorbance in the infra-red (IR) spectrum of DMAc on addition of LiCl (Panar & Beste, 1977). From these experiments and others with polyamides, and the NMR experiments mentioned above, the concept of a $[DMAc + Li]^+$ macrocation, in the form of an ion–dipole complex, emerged. The lithium cation was postulated to be located adjacent to the carbonyl oxygen of DMAc. This concept proved to be consistent with decreases in the ^{13}C T_1s of the DMAc carbons on addition of LiCl (El-Kafrawy, 1982) and with reports of increases in the viscosity of DMAc when LiCl was added to the solvent (Dawsey & McCormick, 1990). More recently, ionic interactions have been observed between the lithium cation and the carbonyl oxygens of DMAc and cellulose acetate butyrates using ^{13}C NMR (Davé *et al.*, 1994).

RECENT DEVELOPMENTS

In recent years our group has undertaken a series of fundamental studies of the DMAc/LiCl solvent system. These were carried out using electrospray ionization mass spectrometry (ESI-MS), computer modeling and size exclusion chromatography (SEC). Other work has also been carried out by Glasser and co-workers (Davé *et al.*, 1994) with cellulose acetate butyrate using ^{13}C NMR, dynamic viscosity and mechanosorptive creep measurements.

In the first set of experiments by our group both the organic and inorganic portions of the solvent were varied (Striegel *et al.*, 1997b). Results were obtained using a combination of ESI-MS and computer modeling. First, we studied solutions of DMAc in which different alkali chlorides were individually dissolved: LiCl, NaCl, KCl, and CsCl. The $[DMAc+Cat]^+$ ion (Cat = alkali cation) was observed with all the salts. The peak intensities of the singly solvated cations could be related to the size of the cations (Table 1). It is evident from the data in Table 1 that as the ionic radii of the alkali cations increase, thus providing for a smaller charge-to-radius ratio and weaker ion–dipole interactions between cation and solvent, the intensities of the $[DMAc+Cat]^+$ peaks decrease, in response to poorer solvation of the alkali cations by the DMAc. From these experiments, the cations' solvation by DMAc may be ranked as $Li > Na > K \approx Cs$. Analogous results were obtained when using DMF as the solvent.

To investigate the role of the organic portion of the solvent, equimolar amounts of N,N-dimethyl propionamide (DMP), DMAc and DMF were combined, and LiCl was dissolved into this mixed solvent system. The largest lithium–solvent adduct peak observed using ESI-MS was attributed to $[DMP+Li]^+$. Table 2 shows that the intensity of the $[DMP+Li]^+$ adduct ion predominates in the mass spectrum. Moreover, the solvation of lithium by DMP and DMAc was so great that no trace of DMF solvation is observed (solvation by DMF may be observed when DMP is not present in the solution). From these experiments, and others with NaCl and with *n*-alcohols, it was concluded that the solvents follow the order DMP > DMAc≫DMF with respect to their propensity to form alkali–solvent adduct ions in the gas phase.

The order displayed by the amides is also the order of decreasing electron density at the carbonyl oxygen, which is where the lithium cation is most likely to reside. This appears to be a manifestation of the inductive effect (I effect) of substituents with increasing electronegativities. To test if the I effect was present, the range of the electrostatic potentials, and the electrostatic charge on the carbonyl oxygen derived from the electrostatic potential, were calculated using computer modeling for DMF, DMAc, DMP, N,N-dimethyl butanamide and N,N-dimethyl pentanamide. The minimum of the range of the electrostatic potential, centered on the carbonyl oxygen, becomes increasingly negative as the alkyl group becomes larger, −47 kcal/mol for DMF vs. −50 kcal/mol for dimethyl pentanamide. Simultaneously, the charge on the carbonyl oxygen also becomes more negative, −0.38 e for DMF vs. −0.43 e for the pentanamide (e = electron units). Figure 1, which represents the electrostatic potential surfaces of DMF (above) and dimethyl butanamide (below), shows that the minimum of the potential surface (in red) of both amides is centered on the carbonyl oxygen (purple atom), which also bears the bulk of the negative charge. The oxygen atom, being most negative, tends to bind the lithium cation, while the amides with larger alkyl groups tend to stabilize the cation most effectively, thereby giving rise to more intense signals in the ESI mass spectrum. Thus, both the location and the magnitude of the charge support the influence of an inductive effect on the part of the alkyl substituents. It should be noted that the modest changes in the electrostatic potentials appear to be insufficient in fully accounting for the observed mass spectrometric data. Current experiments by our group are examining contributions from both

Table 1. $[DMAc+Cat]^+$ peak intensities and cation radii

Li	Li	Na	K	Cs
$I_{[DMAc+Cat]^+}$	2500	1050	250	310
d (Å)	3.40	2.76	2.32	2.28
r (Å)	0.68	0.97	1.33	1.67

I = Mass spectrometrically determined peak intensity (arbitrary units).
Cat = Li, Na, K, Cs.
d = Hydrated radius of ion (Cotton & Wilkinson, 1988).
r = Ionic radius (Lide, 1990).

Table 2. Peak intensities in ESI mass spectrum of DMF/DMAc/DMP/LiCl

m/z	Peak ID	Peak intensity[a]
108	$[DMP+Li]^+$	1900
209	$[2DMP+Li]^+$	1330
195	$[DMP+DMAc+Li]^+$	1300
94	$[DMAc+Li]^+$	1200
181	$[2DMAc+Li]^+$	600
167	$[DMAc+DMF+Li]^+$	320

[a]In arbitrary units.

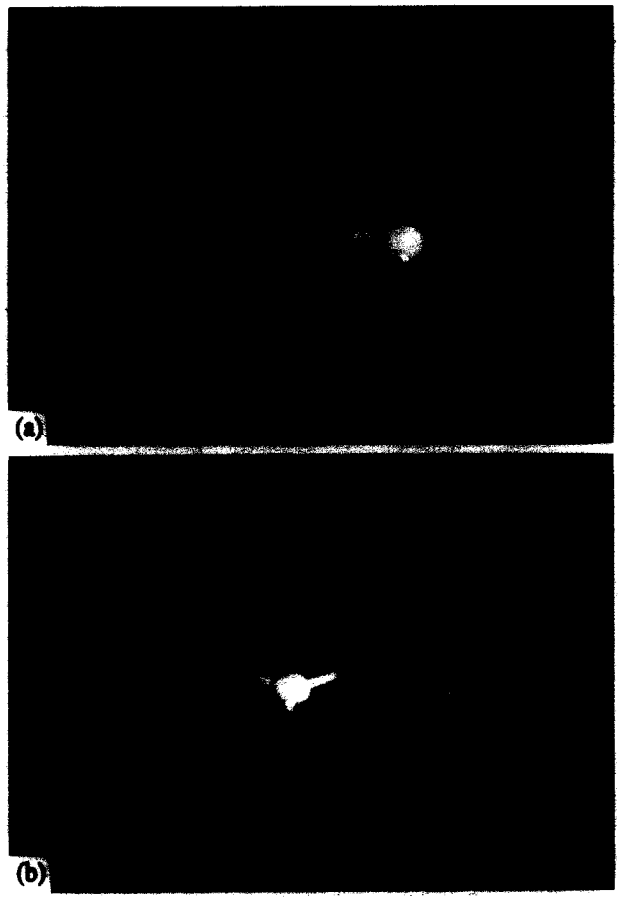

Fig. 1. Computer modeling of electrostatic potential surfaces of DMF (above) and dimethyl butanamide (below). Color code: white = carbon; green = nitrogen; purple = oxygen; hydrogens have been omitted for clarity.

the polarizability of the solvent and the induced dipole generated by Li^+, and from the effect of the size of the molecules in the dissipation of thermal energy via internal degrees of freedom and modes of vibration.

For these studies we used a Vestec 201 electrospray ionization mass spectrometer (Vestec Corp., formerly of Houston, TX) (Allen & Vestal, 1992). Computer modeling was carried out using SPARTAN (Wavefunction, Inc., Irvine, CA). For the modeling, semi-empirical geometry optimization was done with Austin method 1 (AM1), followed by *ab initio* calculation of the charges and electrostatic potentials, assuming single-point energy and using an expansion of Slater-type orbitals in terms of three Gaussian functions (STO3G) as the basis set.

In the next set of experiments, a series of oligosaccharides, maltose homologs consisting of maltose through maltoheptaose, were dissolved in DMAc/LiCl and analyzed using ESI-MS and computer modeling (Striegel *et al.*, 1997a). The ESI mass spectra showed the presence of numerous attachments of LiCl molecules onto the lithium adduct ion. These attachments are of the form $[G_x + Li + nLiCl]^+$ (Fig. 2) and $[2G_x + Li + nLiCl]^+$, where G_x represents the

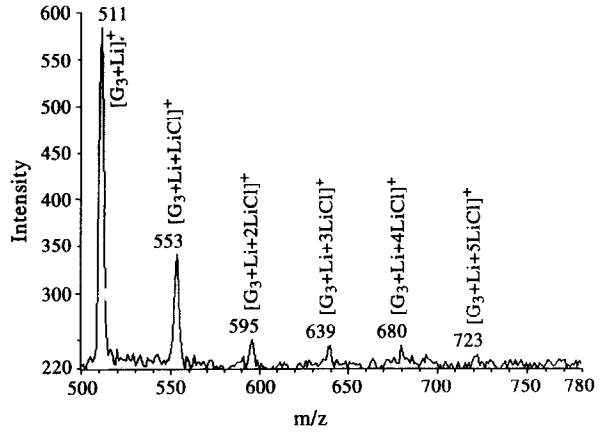

Fig. 2. ESI mass spectrum of 0.3 mM maltotriose (G_3) in DMAc/0.01% LiCl.

oligosaccharide molecule G comprised of x α-glucose oligomers and $2G_x$ is the non-covalently bound sugar dimer, with the largest value of n observed being eight. The number of attachments increased with increasing value of x, corresponding to a higher degree of polymerization of the oligosaccharides. These neutral attachments were observed only with LiCl, and to a lesser extent with LiBr, but not with LiF, NaCl, KCl or CsCl. Due to the exceptional stability of LiF (high lattice energy), the lithium adduct ion was not observed in solutions containing oligosaccharides mixed with this salt. A mechanism to explain the relative ease with which the neutral attachments form has been proposed (Striegel *et al.*, 1997a). Also observed, in high abundances, were peaks corresponding to lithium adducts of one or more solvent molecules, of the form $[DMAc + Li]^+$ and $[2DMAc + Li]^+$. Higher degrees of lithium solvation could also be observed under appropriate instrumental conditions. $[Li(LiCl)_n]^+$ salt clusters were not observed in solutions of DMAc with or without the oligosaccharides.

The coordination of lithium to maltose observed with ESI-MS was also studied using computer modeling. The relative stabilities of different modes of coordination were derived from their heats of formation (ΔH_f). Modeling of other disaccharides such as lactose, laminarbiose and gentiobiose has yielded conformations in which lithium forms a tetravalent bridge between the two monosaccharide rings (Hofmeister *et al.*, 1991). For maltose, we did not find a specific conformation of overwhelming relative stability. We did find that trivalent coordination produced arrangements approximately 20 kcal/mol more favorable than tetravalent coordination. Moreover, this trivalent coordination need not be ring-bridging. The discrepancy in results is probably due to the specific glycosidic linkage and anomeric configuration of maltose (α-1→4, vs. β-1→4 for lactose, β-1→3 for laminarbiose and β-1→6 for gentiobiose) and to the steric arrangement of its ring

and hydroxyl oxygens, all of which differ from the other disaccharides mentioned. It is thus not surprising that a single thermodynamically preferred mode of coordination does not exist for all disaccharides. Additionally, trivalent coordination of maltose by lithium is in accord with four being the most common coordination number for lithium, if DMAc is to occupy the fourth coordination site. Further experiments in this regard are currently underway in our laboratory. However, initial results seem to indicate that optimizing the level of solvation in the maltose–Li^+–$(DMAc)_n$ complex affords the disaccharide more stability than preferential (e.g. trivalent) Li^+ coordination.

ΔH_f calculations were carried out on SPARTAN, semi-empirical geometry optimization being performed using modified neglect of differential overlap (MNDO). ESI-MS studies were carried out using the Vestec 201 system.

For the size exclusion chromatography studies, various polysaccharides were dissolved in DMAc/LiCl and analyzed using SEC (Table 3) (Striegel & Timpa, 1995; Striegel & Timpa, 1996a). LiCl concentration was 0.5%. The concept of universal calibration was applied and the results demonstrated that DMAc/LiCl is a thermodynamically 'good' solvent for all of the compounds studied. This was based, in part, on results obtained for the exponent a of the Mark–Houwink equation (equation (1)):

$$[\eta] = KM^a \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight and K and a are the Mark–Houwink coefficient and exponent, respectively. The intrinsic viscosity is obtained by using dual detection, concentration (e.g. differential refractive index) and differential viscometry. In a theta (θ) solvent a will be 0.5. In a good solvent the chain density of the polymer will decrease. Due to the buttressing effect of the solvent on the chains, which affords them higher rigidity, the coils will expand and occupy a larger hydrodynamic volume. The intrinsic viscosity and radius of gyration will thus be larger in a good solvent, and a will be closer to 0.6 or 0.8, or even 1 or 2 for polymers with bulky chains (Flory, 1953; Vollmert, 1973). With the exception of polysaccharides with a higher degree of branching (for which a will have a diminished value), such as corn and potato amylopectin, arabinogalactan and high-molecular weight dextrans, we obtained values for a of 0.6–1.8 for the compounds studied (Table 3). These results indicate that DMAc/LiCl is a good solvent for a large variety of polysaccharides. In addition, the fact that the solvent and chromatographic mobile phases are identical simplifies experimental variables, which enabled us to study and compare molecular weight distributions, branching parameters and solution properties of the various sugars.

In these experiments we utilized a system consisting of a differential viscosity detector (Viscotek, Houston, TX) and a differential refractive index detector (Waters, Milford, MA). A multi-angle laser light scattering (MALLS) detector (Wyatt, Santa Barbara, CA) was later added to the system (Striegel & Timpa, 1996b). Separation occurred over three 10 μm Mixed-B columns (Burdick and Jackson/Polymer Labs, Amherst, MA).

Table 3. Calculated M_w and a for polysaccharides in DMAc/LiCl

Polysaccharide	M_w[a]	M_w[b]	a[b]
Amylopectin (potato)	N/A[c]	1.6×10^6	0.4
Amylopectin (corn)	N/A	2.1×10^7	0.2
Amylose (potato)	N/A	4.9×10^5	0.9
Amylose (corn)	N/A	6.2×10^5	0.7
Arabinogalactan	8.0×10^4	8.4×10^4	−0.1
Cellulose 4	1.8×10^5[d]	1.8×10^5	1.0
Cellulose 5	3.2×10^5[d]	3.3×10^5	0.7
Dextran T10	1.0×10^4	1.9×10^4	1.1
Dextran T40	4.4×10^4	4.7×10^4	1.8
Dextran T70	7.0×10^4	7.6×10^4	1.4
Dextran low fraction	$6.0–9.0\times10^4$	8.4×10^4	1.1
Dextran high fraction	$2.0–3.0\times10^5$	2.5×10^5	0.5
Dextran T500	5.0×10^5	5.5×10^5	0.4
Dextran T2000	2.0×10^6	1.9×10^6	0.4
Dextran industrial grade	$5.0–40.0\times10^6$	5.1×10^6	0.4
Pullulan 1	1.0×10^5	1.1×10^5	1.1
Pullulan 3	3.0×10^5	3.1×10^5	0.8
Chitin, decalcified	N/A	5.4×10^6	0.6

[a]Values supplied by manufacturer.
[b]Determined by SEC (Striegel & Timpa, 1995).
[c]N/A = not available.
[d]Values from McCormick *et al.*, 1985.

Glasser and co-workers studied the effects of LiCl on acetate/butyrate esters (Davé *et al.*, 1994). Cellulose acetate butyrate (CAB) fibers were prepared by spinning from liquid crystalline solutions containing LiCl. They observed ionic interactions between the carbonyl oxygens of DMAc and CAB and the lithium cation by ^{13}C NMR and also postulated the formation of electrostatic bonds between Li^+ and the CAB backbone to explain the reduction in mechanosorptive creep behavior of the fibers in the presence of residual LiCl. Isotropization of the anisotropic phase was attributed responsible for the rise in viscosity of anisotropic solutions containing LiCl. The mechanosorptive creep exhibited by CAB fibers was attributed to the presence of hydrogen bonds.

APPLICATIONS

The use of DMAc/LiCl as a solvent system to characterize or in which to conduct reactions of polysaccharides has grown rapidly over the years. This article attempts to cover applications from 1990 until the present. It is by no means an exhaustive list but is instead meant to convey the variety of work being done using this solvent system.

Extensive work has been done by Timpa and co-workers on cellulose from mature cotton fiber and of cell-wall polymers in cotton ovules and during development of the cell wall (Timpa, 1991; Timpa & Triplett, 1993; Triplett & Timpa, 1995). They used DMAc/LiCl as the solvent and mobile phase in SEC to obtain and contrast molecular weight distributions (MWD), cumulative weight fractions, intrinsic viscosities and branching frequencies of cellulose at different stages of fiber development. DMAc/LiCl has also been used to dissolve and analyze cotton fiber in work done to relate fiber strength to cellulose MWD, crystallinity and chain length using SEC, ^{13}C NMR and high volume instrumentation (HVI) measurements of bundle fiber strength (Timpa & Ramey, 1994; Benedict *et al.*, 1994).

Lloyd *et al.* (1991) utilized SEC to determine the molecular weights of wood and cotton cellulose in DMAc/LiCl, and Kvernheim & Lystad (1989) used the solvent to perform SEC and methylation analysis of wood and cotton celluloses and cellulose powder. Silva & Laver (1997) determined that optimization of dissolution conditions of wood pulp cellulose in DMAc/LiCl is highly dependent of molecular weight, crystallinity and lignin content. These authors used SEC with refractive index detection to analyze the MWD of wood pulp celluloses and to determine the effect of acid hydrolysis on MWD patterns. Other work on wood cellulose has involved using viscosity measurements to investigate the accessibility of DMAc/LiCl to steam-exploded cellulose from yellow poplar wood chips (Samaranayake *et al.*, 1994). The results were compared to and proved consistent with observations on enzyme accessibility, rumen digestibility and porosity.

Sapag-Hagar *et al.* (1994) investigated the dissolution of mechanical pulp in DMAc/LiCl. Mechanical pulp consisting of lignin, ligno-cellulose, cellulose and hemicellulose was dissolved both at high temperature (150°C) and room temperature. The number of temperature cycles and the time necessary to obtain the highest percentage (63.5%) of dissolved pulp were optimized. The authors noted that the high temperature method permitted both higher concentrations of pulp in solution and lower viscosities of the solutions, and commented on the possibilities for future esterification of the mechanical pulp in the synthesis of methylcellulose.

As mentioned at the beginning of this article, the solvent system was originally developed to facilitate the study of chitin and applications to this effect continue. Sakamoto *et al.* (1994) chlorinated chitin with N-chlorosuccinimide and triphenylphosphine in DMAc/LiCl. ^{13}C NMR and GC-MS analyses showed regioselective chlorine substitution at C-6. Polymer chain scission was found to be dependent on the temperature and concentration of reagents. Hasegawa *et al.* (1993) used DMAc/LiCl when comparing the SEC elution patterns of crab-shell chitin to those of different types of celluloses. They concluded from these patterns that the molecular mass of the commercial chitins was higher than that of the cellulose studied and that the MWD of the chitins is bimodal. Focher *et al.* (1992) studied structural differences of polymorphs of α-chitin from shrimp and β-chitin from squid precipitated in DMAc/LiCl. From CP-MAS ^{13}C NMR they derived a higher degree of structural homogeneity in the α-chitin. These results agreed with those obtained using FT-IR and FT-Raman spectroscopy. They deduced that the precipitation treatments created more disorder in the α-chitin chain than in the more metastable structure of its β counterpart.

Politz and co-workers used DMAc/LiCl in quantifying the extrusion-induced fragmentation of corn and wheat starches by SEC (Politz *et al.*, 1994a, b). Fragmentation was found to be related to the molecular weight of the starch fractions (amylose and amylopectin), being most pronounced in amylopectins with molecular weights in the 10^7–10^8 Da range. Fragmentation was also related to extrusion conditions, low die temperature and low moisture content leading to extensive fragmentation.

As mentioned earlier, work by our group used DMAc/LiCl to dissolve and analyze a number of representative polysaccharides (Table 3) (Striegel & Timpa, 1995; Striegel & Timpa, 1996a). We used SEC with dual detection to obtain and compare MWDs, intrinsic viscosities, radii of gyration, branching numbers and branching frequencies of polysaccharides

over a range of molecular weights. Incorporation of a light scattering detector into the experimental set-up also permitted observation of solution aggregates of pullulans (Striegel & Timpa, 1996b).

Derivatization reactions of cellulose may also be conducted in DMAc/LiCl. Furuhata *et al.* (1992a) have performed regioselective chlorination of the molecule with N-chlorosuccinimide-triphenylphosphine. They also achieved homogeneous bromination of cellulose using DMAc/LiBr as a solvent (Furuhata *et al.*, 1992b). Samaranayake & Glasser (1993) acylated cellulose in DMAc/LiCl with acid anhydrides and carboxylic acids using N,N-dicyclohexylcarbodiimide and 4-pyrrolidinopyridine. They prepared cellulose propionates to stearates with a degree of substitution between <0.1 and 2.5. The preparation of cellulose acetate butyrate esters is discussed in the preceding section (Davé *et al.*, 1994).

De Oliveira & Glasser (1996) also prepared cellulosic hydrogels in bead form. Solutions of cellulose in DMAc/LiCl were added to azeotropic methanol or isopropanol, which are non-solvents. They related bead properties to concentration, viscosity and molecular weight of the cellulose solutions, and determined bead size, pore dimensions, mechanical strength, flow characteristics and solids content of the beads.

Finally, Hirai *et al.* (1994) used DMAc/LiCl to determine the effects of drawing and heat treatment on the tensile properties of aromatic polyamides. In studying poly [1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneimino(chloroterephthaloyl)imino-1,4-phenylene] (abbreviated PBO-CIT) and poly (1,3,4-oxadiazole-2,5-diyl-1,4-phenyleneiminoterephthaloylimino-1,4-phenylene) (abbreviated PBO-T), they found DMAc/LiCl and NMP/LiCl to be the only common solvents in which to study the properties of both polyamides. Unsuitable, mostly due to insolubility of PBO-T but also to the need for heating solutions of PBO-CIT to achieve dissolution, were DMF/LiCl, HMPA/LiCl, DMF, DMAc, NMP and HMPA. Results from their experiments showed the high-temperature durability of the drawn and heat-treated materials. No explanation was given for the solubility behavior of the amides.

CONCLUSIONS

Although the picture of how DMAc/LiCl effects dissolution of cellulose and other important polysaccharides is not fully developed, many of the major characters and some of the shadows have been filled in. What remains to be revealed is a generally accepted mechanism accounting for the presence of the solvent–lithium macrocation, while adequately describing the role of the chloride anion in disrupting the extensive hydrogen bond network existing in cellulose, chitin, etc. In other words, what is the specific interplay between alkali cation, halide anion, organic solvent and polysaccharide?

While advances continue to be made in the above area, the focus has shifted toward the realm of 'real-world' functions. Use of DMAc/LiCl has proliferated as its versatility is more fully realized, with applications as solvent, mobile phase and derivatizing medium increasing. One can hope that with a keen and discerning eye fundamental aspects of the nature of this solvent system will be detailed from the growing applications output.

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