JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

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Comment on "Instantaneous Dissolution of Cellulose in Organic Electrolyte Solutions"†

André Pinkert*

Biomolecular Interaction Centre & Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

In a recently published manuscript, Rinaldi studied the dissolution of cellulose in solvent mixtures composed of an ionic liquid (IL) and an organic solvent (S).[1] Striking results were reported, and a number of organic solvents were studied to finally conclude that the outstanding dissolution abilities of some IL + solvent mixtures are due to a synergism that results in good H-bonding acceptor characteristics—while simultaneously limiting the H-bond acidities—of the resulting solvent systems.[1] One particular observation in this study, however, is surprising and could not be explained: although being structural analogues with similar polarity, 1,3-dimethyl-2-imidazolidinone (DMI) was significantly more effective for dissolving cellulose in IL + solvent mixtures than *N*,*N*,*N*′,*N*′-tetramethylurea (TMU). The intention of this comment is to offer an explanation to this observation, with the aim to stimulate further discussion on this debated topic. To facilitate understanding for the nonspecialized reader, the following sections will briefly summarize the relevant knowledge on this topic prior to discussing the actual matter of this comment.

The first attempts to fully dissolve cellulose date back 150 years ago, but even today we do not understand the mechanism of cellulose dissolution.[2] This is especially true for the dissolution of cellulose in ILs, which are particularly interesting solvent systems for the biopolymer because of their potential to avoid many of the drawbacks associated with traditional cellulose solvents.[3−8] ILs are nonderivatizing solvents for cellulose, which means that cellulose is not chemically modified on dissolution. Dissolving cellulose requires cleaving the intermolecular hydrogen bond (H-bond) network in the polymer. It is widely accepted that small and strongly polarized ion species—such as Li^+, Na^+, Zn^{2+}, Cl^-, and F^-—are beneficial for disrupting the cellulosic H-bonds in traditional nonderivatizing solvent systems, but curiously IL fluorides do not perform well in this respect.[9,10] Several experimental and computational studies investigated the dissolution of cellulose, but none of them proposed a detailed mechanism.[11−19] Until recently there has been debate as to whether both IL ions are involved in the dissolution of cellulose or whether the IL anion dominates this process.[16,17,20−22]

A number of handicapping factors need to be considered if one aims to directly compare the dissolution power of two ILs: (i) the mechanism of cellulose dissolution (derivatizing vs nonderivatizing), (ii) the varying viscosities of ILs, (iii) the considerable effect of IL impurities (mainly water) on its dissolution ability, and (iv) the nature of the cellulose sample (crystallinity and degree of polymerization).[10] To add to the difficulties, many dissolution experiments were performed at different stirring conditions (temperature, time, atmosphere), and frequently the IL water content was not determined.[10] Moreover, only a little information is available on ILs that are not able to dissolve cellulose; however, this knowledge is crucial if one is interested in the structural features of ILs that allow dissolution.[10]

Consequently, our group prepared a comprehensive literature review,[10] which presents an important source of information for the cellulose research community and from which a number of conclusions could be drawn. First of all, it became evident that both IL ions are important for an IL to efficiently dissolve cellulose: the 1-butyl-3-methylimidazolium $[BMIM]^+$ cation is able to dissolve cellulose if paired with a Cl^- anion, but not if the counterion is bis(trifluoromethanesulfonyl)amide $[Tf_2N]^-$. On the other hand, Cl^- containing ILs are very poor solvents for cellulose if the IL cation is pyrrolidinium or piperidinium, instead of $[BMIM]^+$.[23] Second, it was then possible—supported by additional dissolution studies[24]—to identify IL ions that are only present in cellulose-dissolving ILs, allowing us to define the structural features of IL ions that assist cellulose dissolution.[23]

Based on the assumption that all nonderivatizing solvents follow the same pattern to dissolve cellulose, we postulated the first detailed mechanism for the dissolution of the biopolymer.[23,25−27] The key concept of this theory is that potent cellulose solvents are able to arrange their components—ions or highly polarized molecules—in an energetically favored geometry, which consequently enables the solvent to offer H-bonds of competitive stability compared to those present in native cellulose. Supporting evidence for the necessity of ordered solvent geometries to successfully dissolve cellulose is found in the literature: aqueous solutions of both $NaOH\cdot 5H_2O$ and NaOH + thiourea are able to rapidly dissolve cellulose, but only at temperatures of −5 °C.[28,29] The inability of these solvent systems to dissolve the polymer at increased temperatures strongly suggests that an ordered solvent state of some kind is required to achieve dissolution.

Although appropriate experiments to validate the postulated dissolution mechanism are still to be designed, the proposed theory can explain the unaccounted findings by Rinaldi.[1] The unresolved observations of these studies lead to one question: what is the reason for DMI being a considerably better cosolvent for cellulose—requiring only a 0.18 mole fraction of IL (χ_{IL}) to be present to achieve dissolution—than compared to TMU (requiring $\chi_{IL} = 0.59$), despite being structural analogues with similar polarities? According to our reflections on the solubility of cellulose, polarized solvent molecules assist

Received: October 16, 2011
Accepted: February 28, 2012
Published: March 7, 2012

in dissolving cellulose by facilitating the IL ions to position themselves in ordered geometries that are beneficial for competing with the cellulosic OH−groups to form stable H-bonds.[23] As a consequence, one needs to identify the structural disparities of the polarized molecules to answer this question, as shown in Figure 1. The difference between the two analogues is that the rotation of the N−C bond is restricted in DMI, resulting in static nitrogen π-orbitals that are ready to hybridize to sp^2 orbitals. In contrast, TMU does not have these geometrical restrictions, and free N−C bond rotation decreases the probability of both nitrogen atoms being sp^2-hybridized at the same time. Due to the differing electronic characteristics of DMI and TMU, the nonhybridized lone pair electrons of TMU are much more likely to interfere with the correct positioning of the IL anion than compared to the conjugated sp^2-hybridized electrons of DMI (Figure 2). In other words, it is the electronic structure of the polarized organic solvent molecule that determines whether it assists or hinders the correct positioning of the IL ions to successfully compete with the strong intermolecular H-bond network of cellulose.

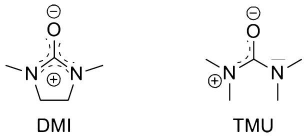

Figure 1. Polarized structures of the chemical analogues 1,3-dimethyl-2-imidazolidinone (DMI) and *N,N,N′,N′*-tetramethylurea (TMU). In contrast to TMU, restricted N−C bond rotation in DMI results in static nitrogen π-orbitals that are ready to hybridize. As a consequence, the electronic characteristics of both molecules differ from each other.

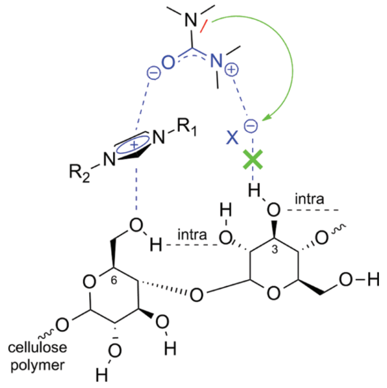

Figure 2. Polarized organic solvent molecules, which can either assist or prevent the IL to position its ions in the correct geometry that is required to compete with the strong intermolecular H-bonds of cellulose. The lone pair electrons of TMU are believed to be responsible for interfering with the positioning of the IL anion.

The same concept can be applied to all the other organic solvents that were studied by Rinaldi.[1] Least efficient for dissolving cellulose were IL + solvent mixtures with organic solvents that display poor dipolar characteristics, such as tertiary alcohols or acetylacetone. The tested sulfones and amides performed much better in this respect, but only if all their lone pair electron orbitals were sp^2-hybridized, so that no p-orbital electrons were present to interfere with the positioning of the IL anion during the dissolution process (Figure 2). Geometrical restrictions hindering the formation of sp^2-hybridized orbitals which are necessary for solvent polarization can explain the observed differences in dissolution efficiencies, particularly when comparing TMU to its aziridine derivative *N,N′*-dimethylpropylene urea (DMPU). The 60° bond angle of the aziridine substituent hinders its ring nitrogen to hybridize to sp^2, qualifying the p-orbital lone pair electrons of the ring nitrogen as a potential candidate to interfere with the positioning of the IL anion during the cellulose dissolution process, as discussed earlier (Figure 3). Sterical restrictions imposed by the aziridine substituent, however, result in restricted N−C bond rotation, forcing the relevant lone pair electrons to face away from the dipoles of the polarized molecule. As a result, DMPU's performance for dissolving cellulose in an IL + solvent mixture ranks between DMI and TMU.

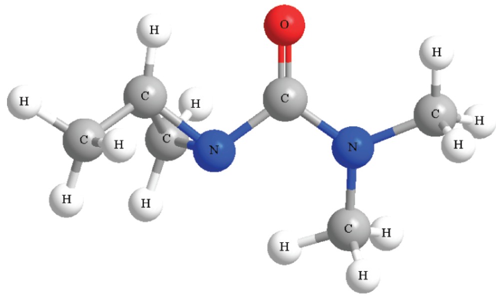

Figure 3. Ball and stick model of *N,N′*-dimethylpropylene urea (DMPU). Although the 60 bond angle of the aziridine substituent hinders its ring nitrogen to hybridize to sp^2, the resulting p-orbital lone pair electrons face away from the oxygen atom due to sterical restrictions.

We do acknowledge that our proposed mechanism for the dissolution of cellulose still lacks experimental proof; however, it is encouraging that it serves to explain unexpected experimental observations. Eventually, it is not essential whether the mechanism presented here will be supported or rejected by further experimental results; however, it is important to communicate new ideas to advance science. After almost a decade of research on the interaction of cellulose with ILs, we still get surprised by the results of straightforward experiments, which should remind us how little we actually know about this topic.

AUTHOR INFORMATION

Corresponding Author

*Fax: + 643 364 2543. Tel.: + 64 3 364 2543. E-mail: andre.pinkert@canterbury.ac.nz.

Funding

The author thanks Prof. Conan J. Fee for postdoctoral funding through the Biomolecular Interaction Centre of the University of Canterbury.

ACKNOWLEDGMENTS

The author wishes to thank Prof. Kenneth N. Marsh and Dr. Dagmar F. Goeke for critically reviewing the manuscript.

DEDICATION

†This paper is dedicated to Prof. Kenneth N. Marsh, who has been an inspiration to me and many others.

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