Reply to "Comment on 'Instantaneous Dissolution of Cellulose in Organic Electrolyte Solutions'"

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S *Supporting Information*

Pinkert put forward a number of propositions about the competitive interactions among cellulose, the ionic liquid, 1-ethyl-3-butylimidazolium acetate [EMIM][AcO], and the cosolvent, 1,3-dimethyl-2-imidazolidinone (DMI) or 1,1,3,3-tetramethylurea (TMU). Based on arguments relying too heavily on qualitative analysis of the electronic structures of the cosolvents, a model was proposed to explain why TMU requires a larger mole fraction of [EMIM][AcO] (χ_{IL} = 0.59) being present in the electrolyte solution, than DMI (χ_{IL} = 0.18), for the instantaneous dissolution of cellulose at 100 °C.[1] In the model, TMU was proposed to interfere with the correct positioning of the ionic liquid anion, due to its electronic characteristics, hampering the dissolution.

To verify whether DMI and TMU do markedly differ one from another with regard to their electronic structures, we performed calculations on DMI and TMU using the B3LYP density functional and the 6-311++G(d,p) basis set. To provide information on the localized orbitals, natural bond orbital (NBO) analysis was also carried out.

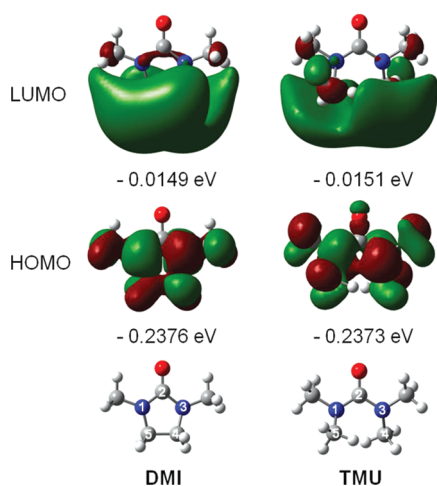Figure 1 shows the optimized geometries and the frontier molecular orbitals of DMI and TMU. The major structural

Figure 1. Minimized geometries and frontier molecular orbitals (FMOs) of the cosolvents. The values indicate FMO energies.

feature distinguishing DMI from TMU is the dihedral angle N(1)−C(2)−N(3)−C(4). The dihedral angle of DMI is 9.868°, whereas that of TMU is 41.465°. Despite of this, no difference between DMI and TMU was found in the energies of frontier molecular orbitals. HOMO in both molecules is delocalized throughout *N*-sites and alkyl substituents, whereas

the LUMO is delocalized over the "axial" methyl or ethylene group.

In TMU, a minor difference is perceived in the linear combination of atomic orbitals for HOMO. While the *O*-atomic orbitals 2*s* and 2*p* make no contribution to the HOMO of DMI, the *O*-atomic orbital p_z contributes 3.8 % of its electron density toward the HOMO of TMU.

According to the NBO analysis, there is either no striking difference between DMI and TMU with regard to the NPA charges of the atoms belonging to the urea skeletons (Figure 2). The molecules differ, however, in the delocalization $n_N \rightarrow \sigma_{C-O}{}^*$. This secondary interaction of natural orbitals led to (50.7 and 41.8) kcal·mol^{-1} of stabilization energy to DMI and to TMU, respectively. To compensate the stabilization loss, two interactions $n_N \rightarrow \sigma_{C(5)-H}{}^*$, which are nonexistent in DMI, were established in TMU. Together, they released 10.3 kcal·mol^{-1}. Moreover, the two interactions $n_N \rightarrow \sigma_{C(5)-H}{}^*$ increased the NPA charges at both C(4) and C(5) of TMU, which are twice as large as those found for DMI. In overall, the current quantitative evidence blatantly contradict those from the qualitative analysis of the electronic structures.

The density functional theory (DFT) calculations on TMU and DMI reveal that the *dipole moment is the major electronic feature distinguishing one molecule from other* (Figure 2). While the dipole moment of DMI is 4.11 D, that of TMU is only 3.48 D. These values compare to those experimentally determined (DMI: 4.07 D; TMU 3.50 D).[2]

Revisiting our data,[1] we plotted the mole fraction of [EMIM][AcO] (χ_{IL}), required for dissolving cellulose in the electrolyte solutions, against the calculated dipole moments (μ) of the cosolvents (Figure 3). In this analysis, only the amide solvents were taken into consideration to ensure that specific patterns of H-bond interactions, linking cellulose, IL, and cosolvent, are consistent, to some extent, among the different solvent systems.

Figure 3 shows an excellent linear correlation when excluding *N,N'*-dimethyl-*N,N'*-trimethyleneurea (DMPU) from the analysis. As it is well-known, solvents with a high dipole moment interact more intensively with ions than those with a low dipole moment.[2] The correlation from Figure 3 strongly supports that the efficient solvation of the ions by solvents with a high dipole moment is a key factor accounting for different χ_{IL} required for the dissolution of cellulose in the amide cosolvents. Actually, the high moment dipole of DMI appears to assist better, than
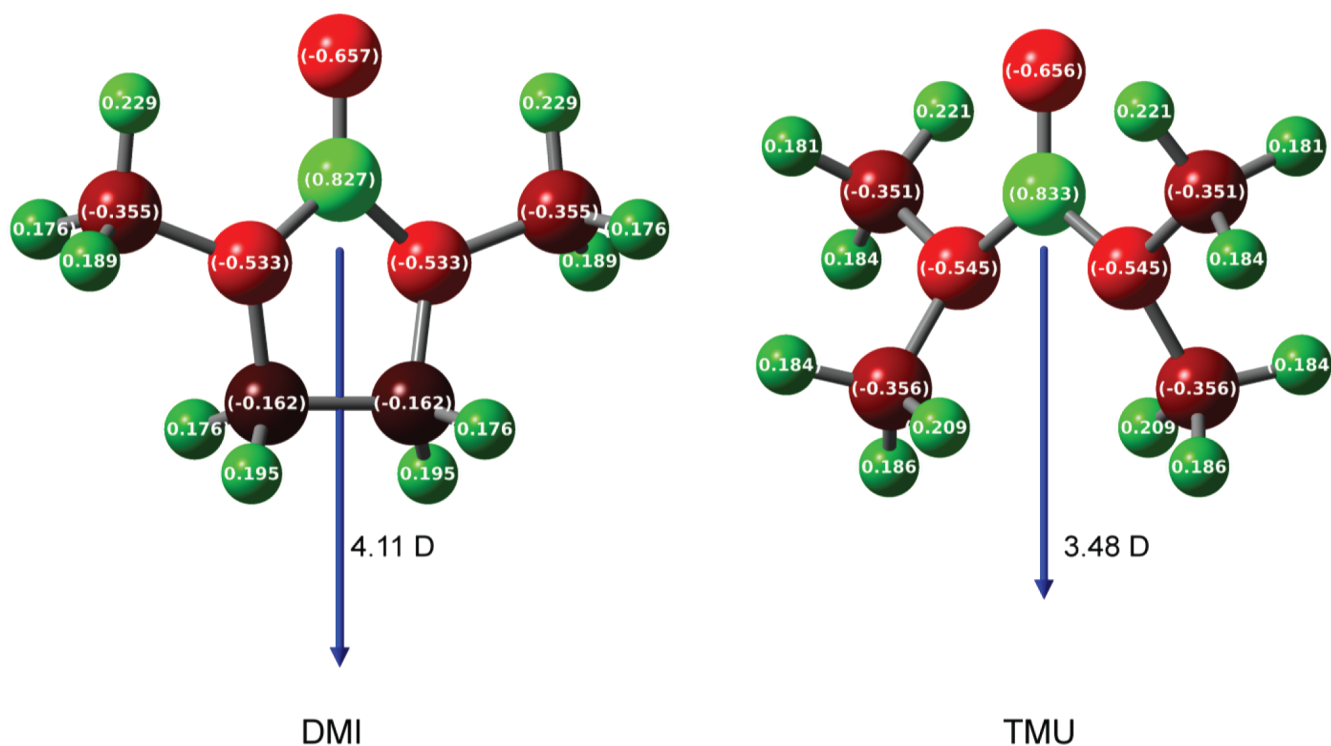
Figure 2. Natural population analysis (NPA) charges found for DMI and TMU. Note that the vectors display the dipole moment for DMI and TMU calculated from the minimized geometries using the B3LYP density functional and the 6-311++G(d,p) basis set.
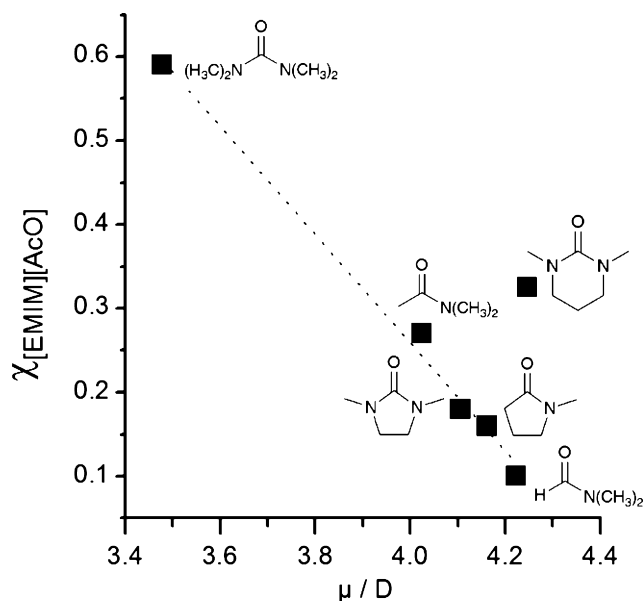

Figure 3. Mole fraction of [EMIM][AcO] (χ_{IL}) required for dissolving cellulose in the amide cosolvents versus calculated dipole moments of the respective amide solvents.

Figure 4. Mole fraction of [EMIM][AcO] (χ_{IL}) required for dissolving cellulose in the amide cosolvents versus molar volume (V_m) of the respective cosolvents.

that of DMU, the loosening of the ion pair (IL). As a result, the loose ion pair has its specific interactions with cellulose facilitated, to such a great extent, that the instantaneous dissolution of cellulose can take place even at χ_{IL} as low as 0.10, as reported for [EMIM][AcO]/N,N-dimethylformamide solution.[1]

Figure 4 reveals that bulky solvents require large χ_{IL} for the dissolution of cellulose. This is other convincing evidence indicating that the efficient solvation of the IL ions by the
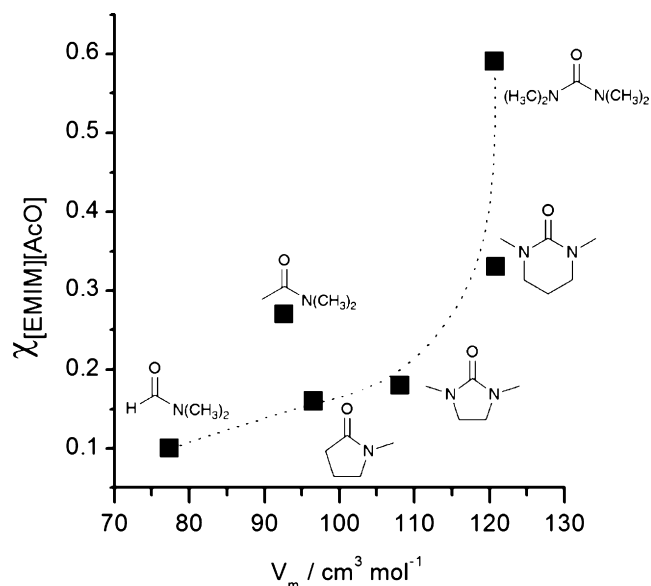
cosolvent is essential for the dissolution process. DMPU is a proof of this evidence. Although DMPU shows a dipole moment as high as that of N,N-dimethylformamide (4.2 D), a large χ_{IL} is still required for the dissolution of cellulose in DMPU, as its large volume supposedly raises steric difficulties for the efficient solvation of the ions. As a result, DMPU appears as an outlier in the correlation shown in Figure 3.

One question that needs to be asked, however, is whether an IL-based electrolyte solution in formamide would require the lowest χ_{IL} for dissolving cellulose. Formamide is the smallest

amide in the series ($V_m = 39.8$ cm^3·mol^{-1}) and also shows a large dipole moment (4.04 D). Both features suggest that only a very small χ_{IL} would be required for dissolving the biopolymer in the electrolyte solution. Nonetheless, the dissolution is only achieved at $\chi_{IL} = 0.42$. This reveals that the pattern of specific interactions among cellulose, IL, and cosolvent is also a very important factor. As formamide is an excellent H-bond donor ($\alpha = 0.71$),[3] this cosolvent apparently establishes other specific patterns of H-bond interactions than that present in non-H-bond donor amide solvents, shown in Figure 4. This confirms our former conclusions.[1] Indeed, an H-bond donor solvent also competes with cellulose for the H-bond basicity of the IL-anion. Hence, while using an H-bond donor cosolvent, a large χ_{IL} must be present in the electrolyte solution to level the H-bond acceptor ability of solvent system, at a value high enough to make possible the dissolution of cellulose.

In summary, this discussion added an important point to the debate of the role of the cosolvent: the effect of dipole moment of the cosolvent on loosening the ion pair (IL). Good solvation of the IL ions appears to facilitate their interaction with cellulose. Incidentally, this leads also to the outstanding ability of the IL−electrolyte solutions to dissolve cellulose. Despite of these advances, additional theoretical and experimental evidence need still to come to light to draw a clear picture of the specific interactions among cellulose, IL, and cosolvent on a molecular level.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Output files of the theoretical calculations on DMI and DPU (zip file). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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