In this study, we evaluated the molar conductivity and dynamic viscosity of 1-ethyl-3-methylimidazolium acetate based solvent systems containing dissolved cellulose (cotton or microcrystalline cellulose), cellulobiose, or glucose. Matrix variables included solute concentration, as well as concentration of acetonitrile or water (typical molecular species present in IL-based biopolymer solutions). Ion conductivity, dynamic viscosity, and density were measured for each solution, and the data was correlated graphically on Walden plots. When this approach is used, the systems containing dissolved cellulose appear superionic. This apparent superionicity results from large (up to 140-fold) increases in solution viscosity due to dissolved biopolymer, and correspondingly small (ca. 0.7-fold) decreases in solution conductivity. Differences in solution hydroxyl content as well as cellulose content and degree of polymerization are proposed as the physical explanation behind the apparent superionic behavior.

Ionic liquids (ILs) represent a unique class of solvents that offer unprecedented versatility and tunability.1,2 The low melting points of ILs (commonly below 100 °C) let them provide strongly ionic solvating media for chemical synthesis, whereas common inorganic salts’ drastically higher melting temperatures preclude their use in most chemical media for chemical synthesis, whereas common inorganic salts’ drastically higher melting temperatures preclude their use in most chemical syntheses due to thermal decomposition of most organic reactants. One fascinating capability of certain ILs is that they can dissolve recalcitrant biopolymers such as cellulose, starch, silk, wool, chitin and chitosan.3-13 Most often these biopolymers are dissolved with ILs composed of 1-3-dialkylimidazolium cations with halide, acetate, or dialkylphosphate anions.

Biopolymer dissolution using ionic liquids is valuable because it provides a highly flexible method to fluid process abundant, renewable, biodegradable materials like cellulose.14 In practice, ILs are typically mixed with molecular co-solvents (i.e., acetonitrile (AN), dimethylformamide (DMF), or dimethylsulfoxide (DMSO)) to decrease solution viscosity and improve the dissolution process. After fluid processing, the biopolymers are precipitated by adding ‘anti-solvents’ (i.e., water) to facilitate dissolution.26 Lovell, et al. used pulsed-field gradient spin-echo (PFGSE) 1H NMR to show how cellulose slows the diffusivity of EMIAc and Ac.27 Additionally, Lovell’s data related these measured effects to the concentration of cellulose in solution, suggesting that biopolymers may critically impact ion transport in IL solutions. Finally, Ries, et al. used PFGSE NMR to show similar effects when the solutes cellulose, cellulobiose, or glucose were dissolved in EMIAc.30

The aforementioned studies have primarily used IR or NMR to evaluate specific interactions between ions from neat IL and dissolved carbohydrate moieties. However, to the best of our knowledge, there are no published studies that thoroughly investigate the effect of cellulose on ion conductivity of EMIAc-based solvent systems, despite the fact that it is a direct measurement of ion transport. Therefore, in the present study, we evaluate the ion (and molar) conductivity and viscosity behavior of representative EMIAc-based solvent systems. We study solutions containing 0 to 3.0 wt.-% of cellulose, cellulobiose, and/or glucose solutes in each of the following solvents: (1) neat EMIAc, (2) EMIAc and acetonitrile (1:1 mole ratio) and (3) EMIAc with water (1:1 mole ratio). These solution matrices model what are encountered during cellulose composites manufacturing, where acetonitrile is a common co-solvent, water is a common anti-solvent (or contaminant), and the four carbohydrate solutes are forms of cellulose (cotton, MCC) or model compounds for this biopolymer (cellulobiose and glucose). Changes in conductivity, and hence ion mobility, in these model systems should support our hypothesis that EMIAc ions interact strongly with anhydroglucopyranose moieties present in each solute.

**Experimental**

Materials.—In this section, experimental materials and methods are outlined, with a more detailed description provided in the Supplementary Materials (SM). EMIAc > 95% was purchased from IoLiTec and used as received. Two lots were used, and they were determined to have 0.33 and 0.24 wt.-% water (Karl-Fischer coulometry), respectively, and 1.02 and 0.75 wt.- % acetic acid (NaOH titration), respectively. Acetonitrile, anhydrous, 99.8% (AN) was used as received from Sigma. Water was obtained from a Barnstead E-pure filtration system and used as received. Two lots were used, and they were determined to have 0.33 and 0.24 wt.-% water (Karl-Fischer coulometry), respectively, and 1.02 and 0.75 wt.-% acetic acid (NaOH titration), respectively. Acetonitrile, anhydrous, 99.8% (AN) was used as received from Sigma. Water was obtained from a Barnstead E-pure filtration system and had a conductivity of > 18 MΩ. The microcrystalline cellulose (MCC) had a stated degree of polymerization (DP) of 221; the USP cotton purchased from Parke-Davis had no DP listed, but researchers claim cotton has a DP of 2000 to 300031 and possibly higher.32,33 MCC, cellulobiose, and glucose were dried in a conventional oven (100 °C for...
24 h) then transferred into a glove box for solution preparation. Cotton was dried in a conventional oven (60°C for 72 h) then dried under vacuum (60°C for 24 h) before being transferred into a glove box.

Test-solution preparation.—The test solutions varied by solvent system, solute type, and solute concentration. Three main solvent systems were evaluated: (1) EMIAc; (2) EMIAc and AN in a 1:1 mole ratio (1:1 EMIAc:AN); and (3) EMIAc and H₂O in a 1:1 mole ratio (1:1 EMIAc:H₂O), notwithstanding the measured impurities in the IL. Four solutes (cotton, MCC, cellulbiose, and glucose) were evaluated at 0.1, 0.5, 1.0, and 3.0 wt.% in the three main solvent systems. Of note, 3.0 wt.% cotton was not evaluated in this study because it was too viscous. Additional test solutions containing EMIAc:AN and EMIAc:H₂O mole ratios at 3:1, 1:3, and 1:9 were evaluated.

Test solutions based upon EMIAc or EMIAc-AN were prepared and maintained in a N₂-filled (H₂O < 1 ppm) glove box to eliminate humidity absorbing into the hygroscopic materials, and sealed to eliminate loss of solvent through the caps of the vessels. Solutions based upon EMIAc:H₂O were prepared, sealed and maintained outside the glove box.

Test solutions were prepared gravimetrically (see Table S1). Typically, overnight stirring was required for complete dissolution of the solid solutes. Heat was never applied, in order to minimize any possible loss of AN or H₂O. Each solution was tested as soon as possible after preparation.

Methods.—Measuring viscosity and density.—Viscosity and density were measured simultaneously using an SVM 3000 Stabinger viscometer (Anton Paar). (Density was measured primarily to determine molar conductivity, as described in the subsection “Determining Molar Conductivity” within the section “Calculation Methods” of the SM.) Solutions were evaluated from 20 to 80°C at 5°C intervals. Instrument calibration was checked daily before sample measurements using a Cannon S3 viscosity standard. Typically, two tests were performed in immediate succession, with the second measurement using freshly injected test solution. Detailed descriptions of the instrumental methods and measurement uncertainty calculations are provided in the SM.

Measuring ionic conductivity.—Ionic conductivity was measured by frequency-response analysis (FRA) using an MCS-10 instrument (Bio-Logic SAS). Cell constants were determined using 0.0100-M aqueous KCl before each test solution. Test solutions were ramped from ambient (~25°C) to 100°C, then decreased to ~20°C at 5°C intervals. Twenty minutes were allowed between intervals, enabling ca. 6–11 data points of stable temperature and conductance after each temperature transition from the previous step. Each stable period was ca. 6–11 data points of stable temperature and conductance after each temperature transition from the previous step. Each stable period was

Results and Discussion

Walden plots reveal ‘Superionic’ behavior.—The ‘Fractional Walden Rule’ (Equation 1) is a model for the relationship between molar conductivity (Λ) and dynamic viscosity (η) of electrolyte solutions, where α and C are constants. After rearrangement, the logarithm of molar conductivity becomes a linear function of the logarithm of inverse dynamic viscosity η⁻¹, or ‘fluidity’ (Equation 2). Many electrolytes display a near linear relationship when presented in this form as a ‘Walden plot.’

\[ \Lambda = C \eta^{-\alpha} \]  
\[ \log_{10}\Lambda = \alpha \log_{10}(\eta^{-1}) + \log_{10}C \]  

The Walden plots of Figures 1 through 3 summarize how dissolved cotton affects the molar conductivity and dynamic viscosity in EMIAc, 1:1 EMIAc:AN, and 1:1 EMIAc:H₂O, respectively. Interestingly, these Walden plots show that adding small concentrations of cellulose (0.5 or 1.0 wt.% cotton) caused these solutions to appear ‘superionic.’ A solution may appear ‘superionic’ when its data series lies above or left of the dashed line representing ideal Walden behavior (α = 1 and C = 1 S cm² mol⁻¹ Poise, often stated to describe aqueous KCl). In our solvent systems, however this ‘apparent superionicity’ was the result of the cellulose increasing the solution’s dynamic viscosity.
of cellulose. It is possible that the solvent system affects cellulose’s polymer chain shape properties (e.g., persistence length), resulting in different mass concentrations at which polymer chains overlap one another.

These data partially support an hypothesis that the MCC solutions transitioned from dilute to semi-dilute region, which can be observed upon plotting log-log plots for dynamic viscosity and MCC concentration (see Figures S6 through S8). A sharply increased slope (as concentration increases) is visible very near or within the 0.5 and 1.0 wt.-% range for each solvent system. (Cotton remains more ambiguous due to having only three data points.) While more data would be required to precisely locate these solution regime transitions, this was outside the scope of the present work; however, it is worth noting that these rough values for regime transitions to semi-dilute are similar to the ca. 2% MCC value observed for cellulose in EMIAc by Sesouesse et al.35 and Gerick et al.36

Molar and ion conductivity. —The Walden plots reveal that cellulose decreases molar conductivity to a small extent in each solvent system. Figure 7 highlights more precisely the extent to which all four carbohydrate solutes decreased molar conductivity of EMIAc at both 20 and 60°C. Each carbohydrate solute did not significantly reduce EMIAc solution molar conductivity until solute content increased to either 1.0 or 3.0 wt.-%. By 3.0 wt.-% MCC, the molar conductivity was reduced only by a factor of ca. 0.7-0.8, depending on temperature. Similar small reductions in molar conductivity were also seen with 1:1 EMIAc:AN and 1:1 EMIAc:H2O solvent systems (Figures S9 and S10).

Simple dilution of EMIAc (or further dilution of EMIAc in 1:1 EMIAc:AN or 1:1 EMIAc:H2O) by the 0.1 to 3.0 wt.-% carbohydrate additions was likely not the cause of these decreases in molar conductivity. We offer two explanations for this conclusion. First, a reduction in molar conductivity requires the decrease in ion conductivity to be larger than the corresponding decrease in EMIAc concentration. The observed reduction in molar conductivity means that the ions, as a whole, became inherently less conductive, which would be due to a change in how the ions interact with their surrounding molecules in solution. Second, molar conductivity actually increased when EMIAc was diluted with either AN or H2O by up to molar ratios of 1:9 EMIAc:neutral-solvent (Figures S11, S12, and Table S4). Ion
conductivity (which is not normalized by concentration of EMIAc) also increased when EMIAc was diluted up to 1:3 or 1:9 mole ratios with AN and H2O, respectively (Figures S13 and S14).

We propose that cellulose reduces EMIAc molar conductivity via the previously reported hydrogen bonding between EMIAc and the carbohydrates’ hydroxyl groups (C-OH).27,28 In an earlier work, Ries, et al. similarly correlated reductions in ion diffusivity with increased C-OH:EMIAc mole ratio.29 From our data, we observe that molar conductivity decreases as the C-OH:EMIAc mole ratio increases. (Our method of calculating the C-OH:EMIAc mole ratio is described in its own subsection “Determining Hydroxyl-to-EMIAc Mole Ratio” within the section “Calculation Methods” of the SM.) This correlation is seen in EMIAc (Figure 8), as well as 1:1 EMIAc:AN and 1:1 EMIAc:H2O (Figures S15 and S16, respectively). The only data that did not correlate were the 1.0 wt.-% cotton in 1:1 EMIAc:AN, where cotton was already shown to cause larger molar-conductivity decreases than the other solutes at 1.0 wt.-% in 1:1 EMIAc:AN.

In this analysis, it is necessary to distinguish hydroxyl groups based on their parent molecule, because (within the ranges of our test solutions) carbohydrates decrease conductivity while H2O increases conductivity. Consider the extreme OH:EMIAc mole ratios observed with carbohydrates versus H2O. There, the maximum C-OH:EMIAc mole ratio in all carbohydrate test solutions was only ca. 0.19 for 3.0 wt.-% glucose in 1:1 EMIAc:AN (Table S3), and it reduced molar conductivity of 1:1 EMIAc:AN by 22% at 20°C (Figure S9 and Table S2). The maximum OH:EMIAc mole ratio was drastically larger at ca. 9.2 for the 1:9.2 EMIAc:H2O test solution (assuming just one hydroxyl group per H2O molecule), and it increased molar conductivity by a factor of ~25 (Figure S11 and Table S4). Therefore our correlations between OH:EMIAc ratio and molar conductivity are specific to either water or carbohydrate-bound hydroxyl groups.

The carbohydrate solutes likely decrease molar conductivity because they (1) provide hydroxyl groups and (2) diffuse more slowly than the EMIAc ions, the AN or the H2O molecules. While H2O molecules are small and diffuse quickly, larger glucopyranose rings and joined anhydroglucopyranose rings likely obstruct the movement of hydrogen-bonded ions. Additionally, some ions might be more strongly attracted to the hydroxyl groups of carbohydrates than hydroxyl groups of H2O due to the possibility of simultaneous attraction to multiple hydroxyl groups within a single carbohydrate molecule.28 It is likely that the decreases in molar conductivity seen from 0.1 to 3.0 wt.-% carbohydrates are small due to the relatively small number of ionic liquid ions involved in hydrogen bonding to the C-OH. As already pointed out, our most concentrated solutions had C-OH:EMIAc mole ratios that reached only ca. 0.19. This (maximum-case) ratio suggests that EMIAc outnumbers the slow-moving, carbohydrate-bound hydroxyl groups by roughly 81% (or more) in the test solutions. It is likely that many EMIAc ions are not participating in hydrogen bonds with carbohydrates due to competition for a limited number of C-OHs. The remaining EMIAc ions (not hydrogen bonded to slow diffusing carbohydrates) are therefore still available for ion conduction.

In general, the four carbohydrate solutes caused similar reductions in solution molar conductivity. The only exception to this trend was the 1.0 wt.-% cotton in 1:1 EMIAc:AN at 20°C, which showed a more severe reduction in molar conductivity. (Note: high viscosities prevented evaluation of solutions containing 3.0 wt.-% cotton.) The fact that cotton, MCC, cellulose, and glucose provided similar decreases in molar conductivity suggests polymerization of glucopyranose units was not important to ion transport at concentrations up to 3.0 wt.-% in the evaluated solutions. We hypothesize that glucose, cellulose, and cellulose are all very slow diffusers compared to EMIAc, AN, and

![Figure 5](https://example.com/figure5.png)  
**Figure 5.** Dynamic viscosity (η) as a function of solute concentration in the EMIAc solvent system at (a) 60 and (b) 20°C. The data series are represented by the following data markers: ● EMIAc; ◆ cotton; ◆ MCC; ▲ cellulose; and □ glucose. The markers for glucose are mostly underneath the markers for cellulose. Most error bars are barely visible because they are smaller than the data markers.

![Figure 6](https://example.com/figure6.png)  
**Figure 6.** Relative viscosity (ηrel) as a function of solute concentration at 20°C. The data series are represented by the following data markers: △ cotton in EMIAc; ● cotton in 1:1 EMIAc:AN; ◆ cotton in 1:1 EMIAc:H2O; ▲ MCC in EMIAc; ◆ MCC in 1:1 EMIAc:AN; and ▲ MCC in 1:1 EMIAc:H2O. Error bars were eliminated because they were smaller than the data series markers and were preventing reliable identification of cotton’s hollow data markers.
H₂O; therefore, reductions in solution conductivity should be primarily determined by the C-OH:EMIAc ratio.

Ries et al. studied diffusivity of EMIAc ions in solution with MCC, cellobiose, and glucose, and showed that the logarithm of both the anion’s and cation’s diffusion coefficients correlated well to the C-OH:EMIAc mole ratio. It is uncertain why their diffusivities depended upon an exponential function of C-OH:EMIAc ratio while the molar conductivities in our study depended upon a linear function of C-OH:EMIAc ratio. This contrasting behavior is surprising given that in ideal electrolyte solutions, molar conductivity (\(\Lambda\)) and diffusivity (\(D_+\) and \(D_-\)) should relate in a linear fashion through the Nernst-Einstein relationship (Equation 3).

\[
\Lambda = \frac{N_{e^2}(D_+ + D_-)}{k_B T}
\]

Moving forward with improved understanding of cellulose-EMIAc ion transport behavior.—IL-based processing techniques are emerging and present countless opportunities to make new biocomposites. They also reveal sustainable, green technologies that can reduce our dependence on environmentally harmful synthetic polymers. For engineering in this area to advance, we must further develop our knowledge and understanding of the solution properties of IL-based biopolymer systems. This study is one step toward advancing this effort. An improved knowledge of ion transport can help the IL-facilitated engineering of composites and enable the design of new materials in technologies such as manufacturing of textiles, gel electrolytes, and biopolymer binders for battery electrodes.

This study focused upon solutions containing relatively small solute concentrations, and high mole fractions of IL. However, in some IL processing methods, such as Natural Fiber Welding or natural fiber electrospinning, critically important final steps involve IL removal/recycle. This step often involves solutions containing lower IL and higher H₂O mole fractions, and different ranges of solute concentrations. In order to further develop those areas, biocomposite manufacture, future work evaluating ion transport in those solution regimes should be considered.

Conclusions

Cotton, MCC, cellobiose, and glucose were evaluated in three EMIAc based solvent systems for their effect on molar conductivity and viscosity from 0 to 3.0 wt.-%. The 3.0 wt.-% MCC and 0.5 and 1.0 wt.-% cotton solutions appear superionic due to very large increases in viscosity (factors of 10 or more) and very small decreases in molar conductivity (10 to 30%). Whether the solute was cellulose (polymer), cellobiose (dimer), or glucose (monomer) made no significant difference in the molar conductivity decrease for a given weight.
percent of solute. Both cellobiose and glucose produced very small increases in viscosity, reaching only factors of roughly 1.5. The reduction in molar conductivity is believed to be due to interaction with carbohydrate-bound hydroxyl groups, as EMIAc is known to hydrogen bond with carbohydrate hydroxyl groups.

Acknowledgments

This work was funded by the Air Force Office of Scientific Research. Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the U.S. Navy or U.S. Air Force.

ORCID

David P. Durkin https://orcid.org/0000-0001-5979-8449

References

1. R. D. Rogers and K. R. Seddon, Science, 302, 792 (2003).
2. T. Welton, Biophys. Rev., 10, 691 (2018).
3. D. L. Minnick, R. A. Flores, M. R. DeStefano, and A. M. Scurto, J. Phys. Chem. B, 120, 7906 (2016).
4. X. Tan, X. Li, L. Chen, and F. Xie, Phys. Chem. Chem. Phys., 18, 27584 (2016).
5. R. P. Swatloski, S. K. Spear, J. D. Holbrey, and R. D. Rogers, J. Am. Chem. Soc., 124(18), 4974 (2002).
6. K. A. Le, C. Rudaz, and T. Budtova, Carbohydr. Polym., 105, 237, (2014).
7. D. G. Stevenson, A. Biswas, J. Jane, and G. E. Inglett, Carbohydr. Polym., 67, 21 (2007).
8. D. M. Phillips, L. F. Drummy, D. G. Conrady, D. M. Fox, R. R. Naik, M. O. Stone, P. C. Trulove, H. C. De Long, and R. A. Maniz, J. Am. Chem. Soc., 126(44), 14350 (2004).
9. H. Xie, S. Lib, and S. Zhang, Green Chem., 7, 606 (2005).
10. A. Idris, R. Vijayaraghavan, U. A. Rana, A. F. Pattia, and D. R. MacFarlane, Green Chem., 16, 2857 (2014).
11. S. Zheng, Y. Nie, S. Zhang, X. Zhang, and L. Wang, ACS Sustain. Chem. Eng., 3(11), 2925 (2015).
12. H. Xie, S. Zhang, and S. Li, Green Chem., 8, 630 (2006).
13. Z. Zhang, C. Li, Q. Wang, and Z. K. Zhao, Carbohydr. Polym., 78, 685 (2009).
14. U.S. Department of Energy, 2016, 2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy, Volume I: Economic Availability of Feedstocks, M. H. Langholtz, B. J. Stokes, and L. M. Eaton, (Leads). ORNL/TM-2016/160. Oak Ridge National Laboratory, Oak Ridge, TN. 448p.
15. B. Kovan, C. Michels, and F. Meister, Cellulose, 15, 59 (2008).
16. S. Xu, J. Zhang, A. He, J. Li, H. Zhang, and C. C. Han, Polymer, 49(12), 2911 (2008).
17. K. Markstedt, J. Sundberg, and P. Gatenholm, 3D Print. Addit. Manuf., 115 (2014).
18. L. M. Haverhals, W. M. Reichert, H. C. De Long, and P. C. Trulove, Macromol. Mater. Eng., 295, 425 (2010).
19. L. M. Haverhals, H. M. Sulpizio, Z. A. Fayos, M. A. Trulove, W. M. Reichert, M. P. Foley, H. C. De Long, and P. C. Trulove, Cellulose, 19(1), 13 (2012).
20. K. Jost, D. P. Durkin, L. M. Haverhals, E. K. Brown, M. Langenstein, H. C. De Long, P. C. Trulove, Y. Gogotsi, and G. Dion, Adv. Energy Mater., 5(4), 1401286 (2015).
21. N. Sun, R. P. Swatloski, M. L. Maxim, M. Rahman, A. G. Harland, A. Haque, S. K. Spear, D. T. Daly, and R. D. Rogers, J. Mater. Chem., 18(3), 283 (2008).
22. M. L. Maxim, N. Sun, H. Wang, J. R. Sterner, A. Haque, and R. D. Rogers, Nanomaterials and Energy, 1(NMM1), 225 (2012).
23. D. P. Durkin, T. Ye, E. G. Larson, L. M. Haverhals, K. J. T. Livi, H. C. De Long, P. C. Trulove, D. H. Fairbrother, and D. Shuai, ACS Sustain. Chem. Eng., 4, 551 (2016).
24. D. P. Durkin, T. Ye, J. Choi, Kenneth J. T. Livi, H. C. De Long, P. C. Trulove, D. H. Fairbrother, L. M. Haverhals, and D. Shuai, Appl. Catal. B-Environ., 221, 290 (2017).
25. M. B. Turner, S. K. Spear, J. D. Holbrey, and R. D. Rogers, Biomacromolecules, 5(4), 1379 (2004).
26. M. B. Turner, S. K. Spear, J. D. Holbrey, D. T. Daly, and R. D. Rogers, Biomacromolecules, 6, 2947 (2005).
27. T. G. A. Youngs, J. D. Holbrey, C. L. Mullan, S. E. Norman, M. C. Lagunas, C. D’Agostino, M. D. Mantle, F. P. Gladden, D. T. Bowron, and C. Hardacre, Chem. Sci., 2, 1594 (2011).
28. J. Zhang, H. Zhang, J. Wu, J. Zhang, J. He, and J. Xiang, Phys. Chem. Chem. Phys., 12, 1941 (2010).
29. C. S. Lovett, A. Walker, R. A. Damion, A. Radhi, S. F. Tanner, T. Budtova, and Michael E. Ries, Biomacromolecules, 11, 2927 (2010).
30. M. E. Ries, A. Radhi, A. S. Keating, O. Parker, and T. Budtova, Biomacromolecules, 15(4), 609 (2014).
31. O. A. Battista, Ind. Eng. Chem., 16, 351 (1944).
32. D. Klenm, B. Heublein, H. Fink, and A. Bohn, Angew. Chem., 44, 3358 (2005).
33. J. D. Timpa, J. Agric. Food Chem., 16, 351 (1991).
34. W. Xu, E. I. Cooper, and C. A. Angell, J. Am. Chem. Soc., 107, (2003).
35. R. Scicouesse, K. A. Ho, M. E. Ries, and T. Budtova, J. Phys. Chem. B, 114, 7222 (2010).
36. M. Gerick, K. Schlufert, T. Liebert, T. Heinze, and T. Budtova, Biomacromolecules, 10, 1188 (2009).