Insight into molecular level interactions between imidazolium based ionic liquids and cellulose combining NMR, SAXS and MD simulations

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Cellulose, the most abundant carbon containing polymer on earth, is structurally composed of repeat d-anhydroglucose ring units connected by β-1,4 glycosidic oxygen linkages. Cellulose has a wide-range of applications due to its biodegradability and broad chemical modification ability. However, cellulose is not soluble in water and common organic solvents due to the extensive network of inter and intra molecular hydrogen bonding. An environmentally friendly "green" solvent for cellulose was reported in 2001 when ionic liquids (ILs) demonstrated exceptional ability to dissolve cellulose. The study presented here utilizes four different carboxylate ILs with 1,3 dialkyl imidazolium (1-ethyl-3-methylimidazolium [EMIM] and 1-allyl-3-methylimidazolium [AMIM]) cations and carboxylate (formate and acetate) anions. Cellulose polymer conformation in these different ILs was investigated by small angle X-ray scattering (SAXS) and interactions between specific atoms in cellulose and IL were determined by solution-state ^{13}C Nuclear Magnetic Resonance (NMR). All four ILs completely dissociate cellulose strands from its microfibril organization and the smallest structure observed for all ILs is ~4-5 Å, consistent with the cross-sectional dimension of a single cellulose strand. Preliminary analysis of the SAXS profiles suggest that the cellulose polymer chains in AMIM ILs exhibit stiff rod like conformation, while in EMIM [acetate] a swollen chain is observed. To understand the mechanism of cellulose dissolution in ILs, ^{13}C NMR of different concentrations (2, 4, 6, 8 and 10 wt.%) of cellulose in ILs were recorded at 80 °C. The chemical resonance changes of all carbons (cation and anion) in ILs were tracked with cellulose concentration. For all the four ILs among the cation carbons, C2 carbon sandwiched between two nitrogen atoms exhibit statistically significant upfield shift, suggestive of possible interaction with cellulose. A significant downfield shift of anion carbonyl carbon was observed, indicative of a possible H-bond interaction with the hydroxyl group of cellulose. Additionally, with increasing cellulose concentration, the changes in chemical shift value of carbons fit a linear trend for acetate ILs, [EMIM]acetate and [AMIM]acetate, while a non-linear fit works well for formate set of ILs. For all the four ILs, the chemical shift values obtained indicate that the dominant interactions are between cellulose and the anion of the IL. MD simulations are currently underway to complement ^{13}C NMR results on local interactions and SAXS on molecular interactions.