Cellulose is insoluble in nearly all aqueous and organic solvents due to the rigid inter- and intra- molecular hydrogen bonding network. However, select ionic liquids (ILs) are capable of dissolving significant quantities of biomass. Anti-solvents precipitation of cellulose from ILs using water, alcohols, etc. as a pretreatment method has been shown in many studies to lead to more efficient downstream conversion to fuels and chemicals due to de-crystallization, fractionation, etc. Viable separation technologies will hinge upon removal of the antisolvent to recycle the ionic liquid. Water as an antisolvent (or contaminant from biomass) can decrease cellulose solubility in ionic liquids to zero even at only a few percent. Thus, high levels of purification are needed. In addition, current IL systems with biomass have high viscosity and require a large inventory of IL. In order to overcome some of these difficulties, we use a multi-scale approach to investigate the role of solvents in potential biomass processing schemes using ionic liquids. We will show that “cosolvents” may be the key to unlocking ionic liquid’s potential for biomass processing. Fundamental phase equilibrium thermodynamic studies are often quite difficult with ionic liquid/cellulose systems as several ILs form gels and other solid forms with cellulose. Here we will primarily use a model ionic liquid, 1-ethyl-3-methylimidazolium diethylphosphate, [EMIm][DEP] which is capable of demonstrating true solid-liquid equilibrium. The effects of various anti-solvents and co-solvents on equilibrium will be demonstrated. Spectroscopic techniques (solvatochromic, NMR, FTIR, etc.) will help elucidate molecular interactions between ionic liquid and solvent species and provide an understanding of cellulose solubility or precipitation. For pretreatment of biomass using ionic liquids and liquid antisolvents, preliminary analyses from this thermodynamic data indicate that the quantitative recycling of the IL from a liquid antisolvent (water, alcohol, etc.) is highly energy intensive and could impede large scale viability. However, we will show our compressed CO2-based method could lead to substantial energy savings. Alternatively, these mixed IL solvent systems may provide an interesting platform for further downstream conversion of cellulose to fuels and chemicals.