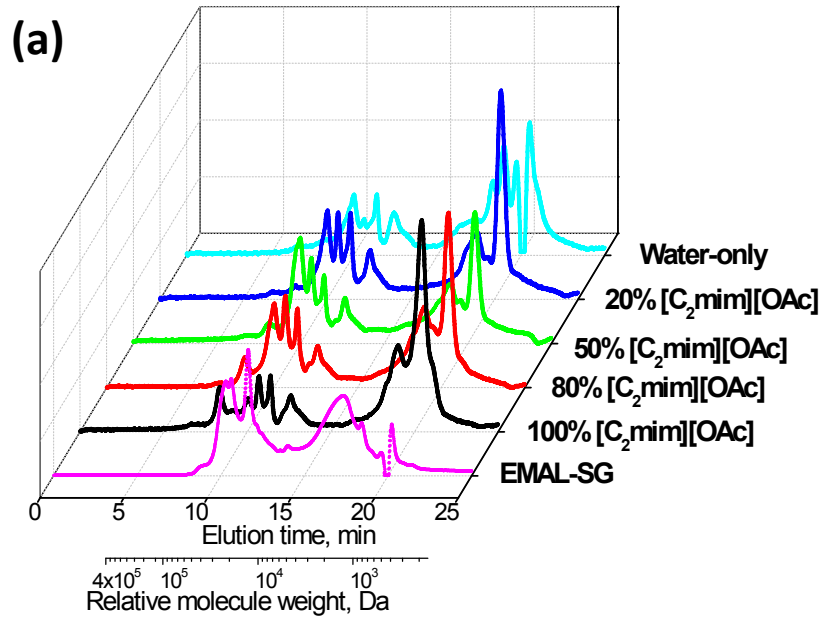
Electronic Supplementary Information (ESI)

Fig. S1 Area-normalized SEC chromatograms of lignin **a)** solublized in aqueous [C_2mim][OAc] and **b)** retained in pretreated solids by [C_2mim][OAc]-water mixtures at 160 °C for 3h. See **Table 3** for relative area of excluded and retained regions.

Fig. S2 Diagram of the model simulation results showing the effect of [C_2mim][OAc]-water mixtures on disrupting a representative cellulose I_β substructure consisting 9 chains with each chain having a polymerization of 6 glucose units at 160 °C.

Fig. S3 Schematics of [C_2mim][OAc]-Water dissolution process – (a) cellulose structure showing inter/intramolecular interactions; (b) [C_2mim][OAc] solvates cellulose; (c & d) water in [C_2mim][OAc] and assisting the dissolution process (below 50 % ratio of water in [C_2mim][OAc] act as co-solvent) (d) above 50 % ratio of water in [C_2mim][OAc] solvates ions and reduces cellulose dissolution; (f) water solvates cellulose.

Figure S4 Extrapolation of Kamlet-Taft values of [C_2mim][OAc]-water mixture (the Y-intercept indicates the extrapolated K-T parameters at 1000/T(K)=2.31 or 160 °C).



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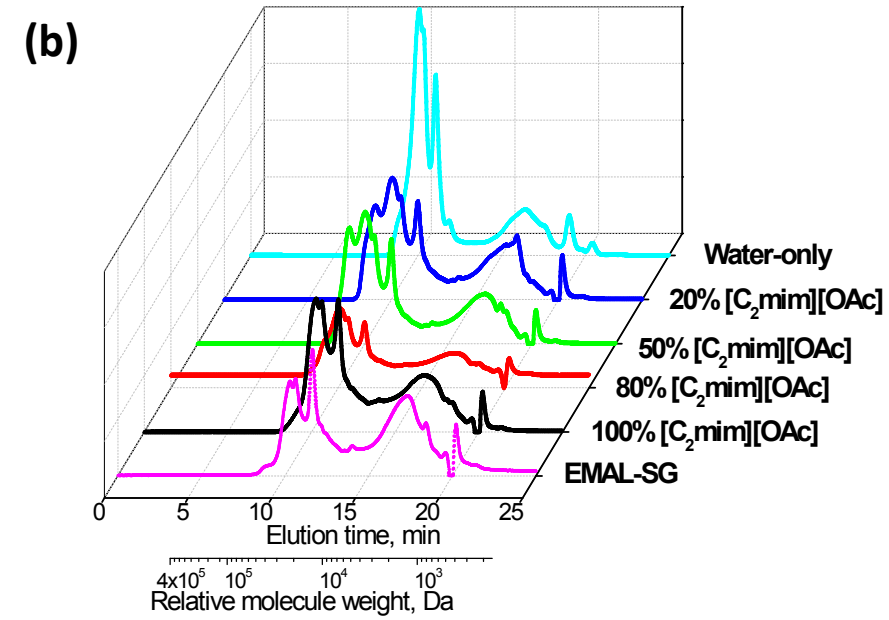

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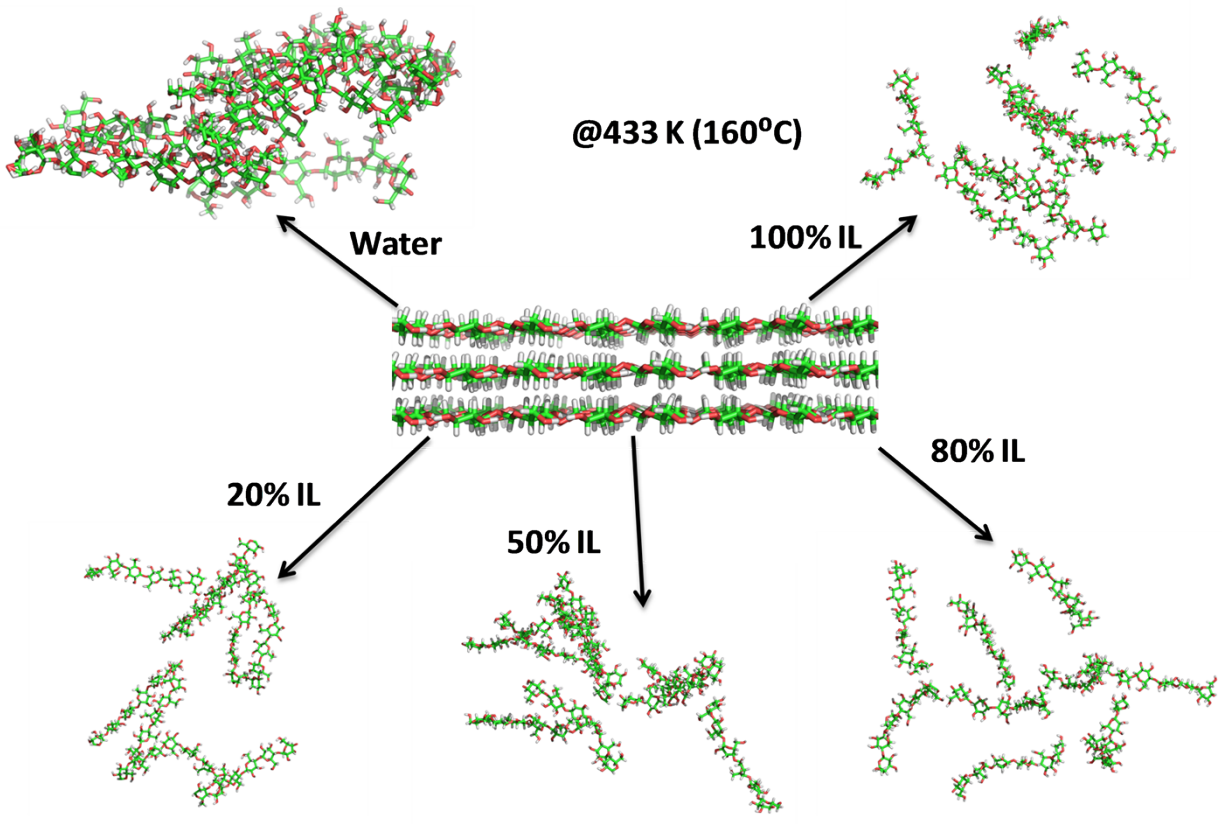
20 **Figure S1** Area-normalized size exclusion chromatography (SEC) of lignin **a)** solublized in
21 aqueous [C_2mim][OAc] and **b)** retained in pretreated solids by [C_2mim][OAc]-water
22 mixtures at 160 °C for 3h using EMAL of untreated switchgrass as a control. See **Table 3**
23 for relative area of excluded and retained regions.



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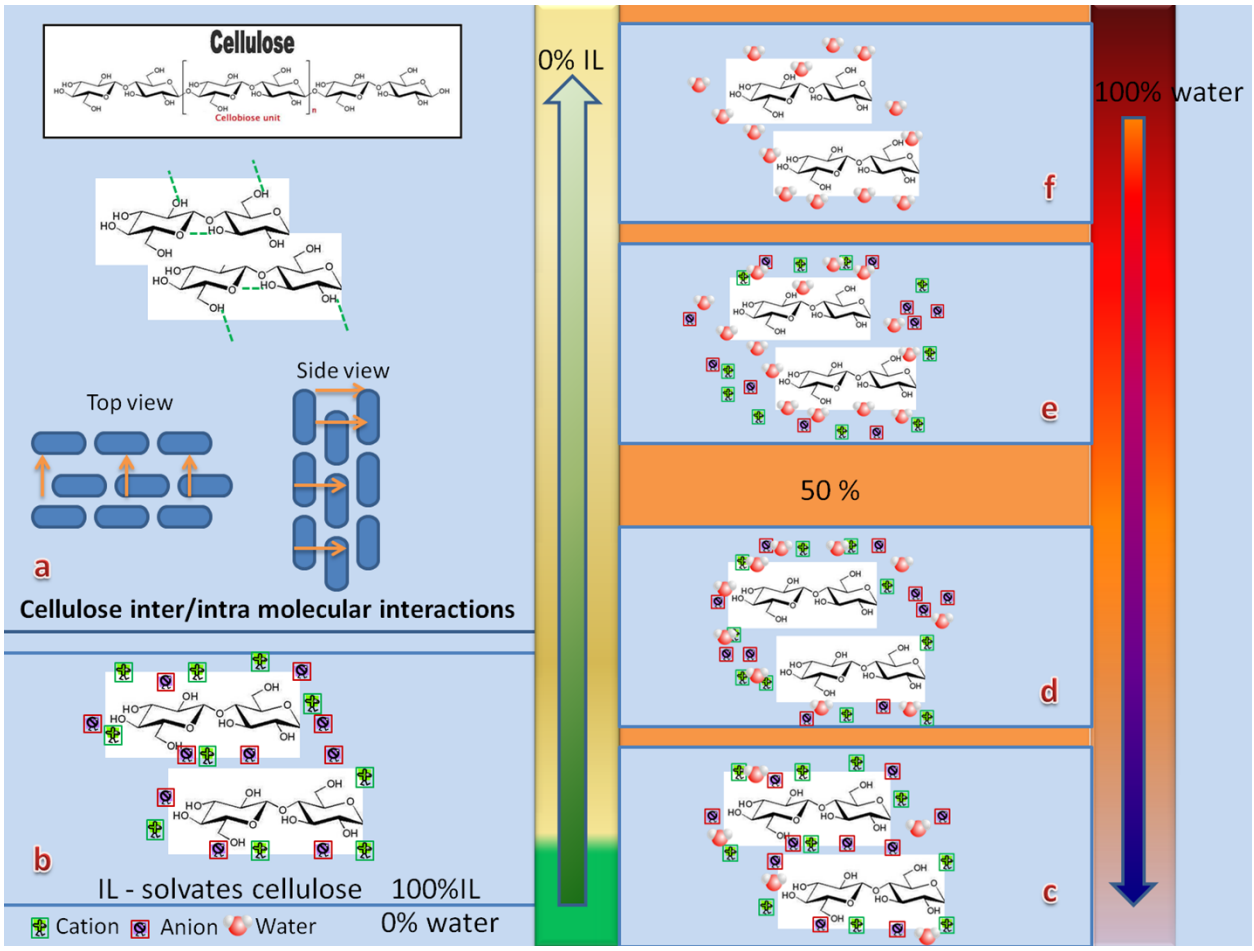

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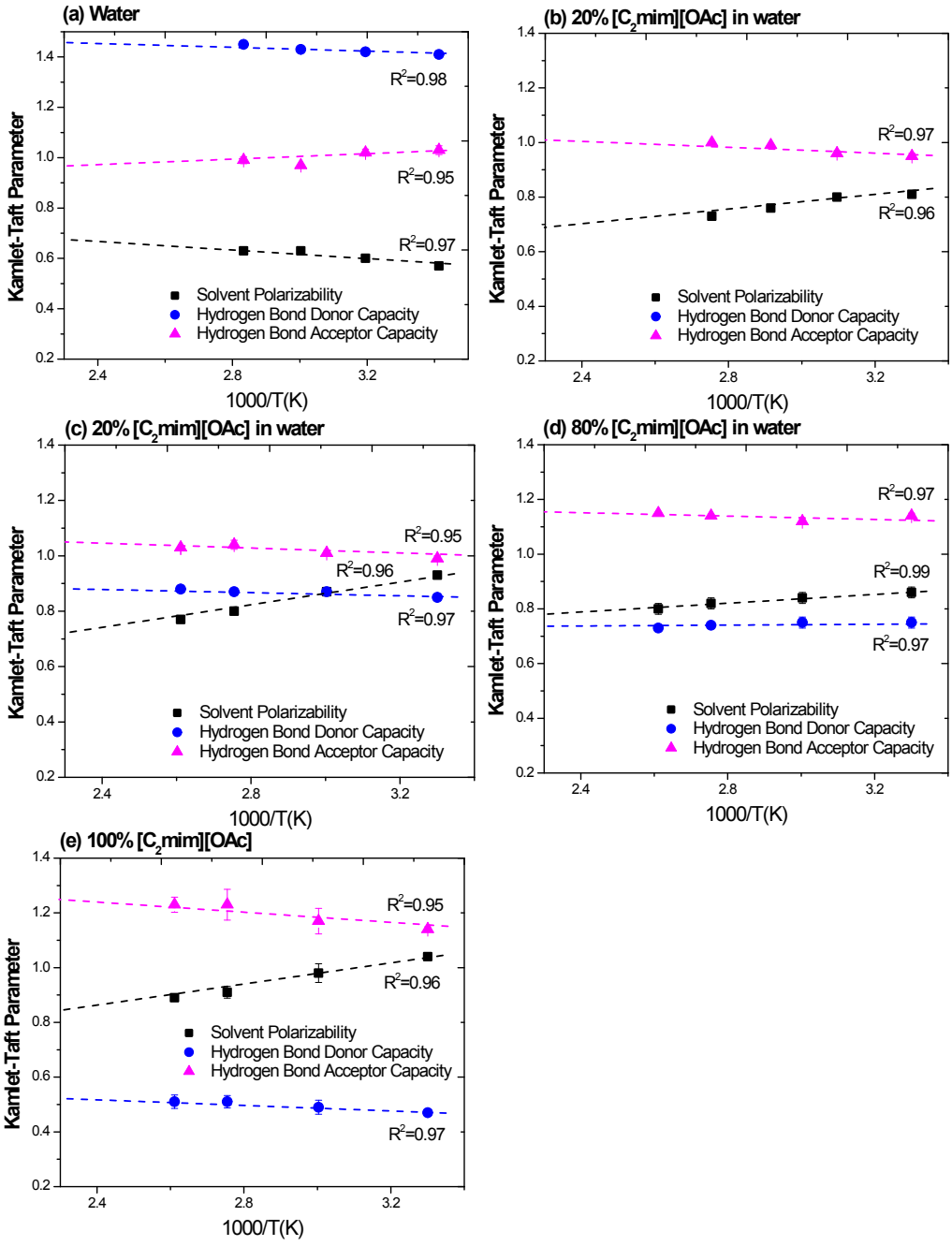

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