Combining random walk and regression models to understand solvation in multi-component solvent systems (Electronic Supplentary Information)

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S1 Supplementary Information

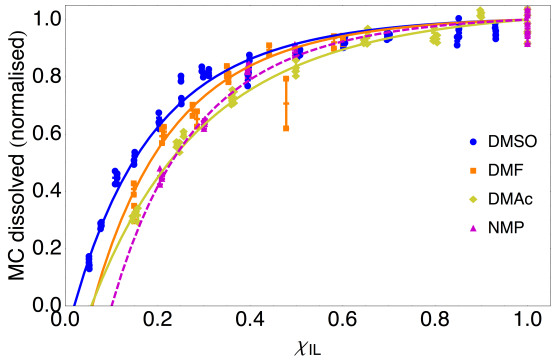

Figure S1: Typical dissolution profiles for selected organic electrolyte solutions (OES)s. Points are experimental data measured in pairs of over- and under-estimates of the maximum cellulose dissolvable, the lines are the 1-D random walk fits.

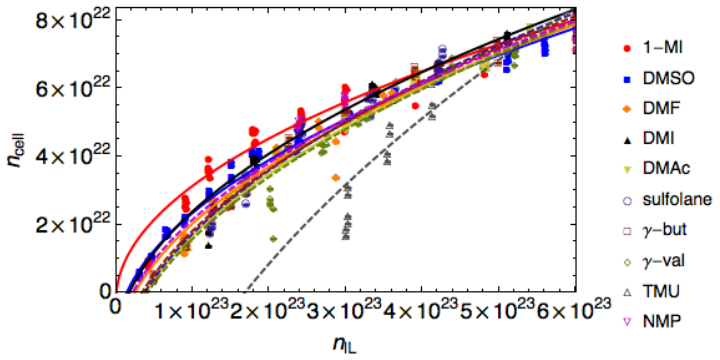

Figure S2: Number of cellobiose residues of cellulose, n_{cell} molecules (taken from molar fraction data) in a mole of mixture against the number of IL pairs. The fit is $n_{cell} = d + \sqrt{m\, n_{IL}}$. Points are experimental data measured in pairs of over- and under-estimates of the maximum cellulose dissolvable, the lines are the 1-D random walk fits.

Table S1: Coefficients for the $n_{cell} vs n_{IL}$ fits. The equation used was: $n_{cell} = d + m\sqrt{n_{IL}}$. The norm of the residuals is given by R^2.

Dataset	d	m	R^2
1-MI	-2.27001×10^{21}	1.06328×10^{11}	0.994499
DMSO	-1.40183×10^{22}	1.18428×10^{11}	0.997986
DMF	-2.01097×10^{22}	1.27692×10^{11}	0.997576
DMI	-1.70546×10^{22}	1.29415×10^{11}	0.998327
DMAc	-2.65143×10^{22}	1.37092×10^{11}	0.998610
sulfolane	-2.73645×10^{22}	1.41466×10^{11}	0.996042
γ-but	-2.53112×10^{22}	1.37517×10^{11}	0.996956
γ-val	-2.82255×10^{22}	1.39164×10^{11}	0.998441
TMU	-9.44975×10^{22}	2.30376×10^{11}	0.985068
NMP	-1.88558×10^{22}	1.27419×10^{11}	0.995587

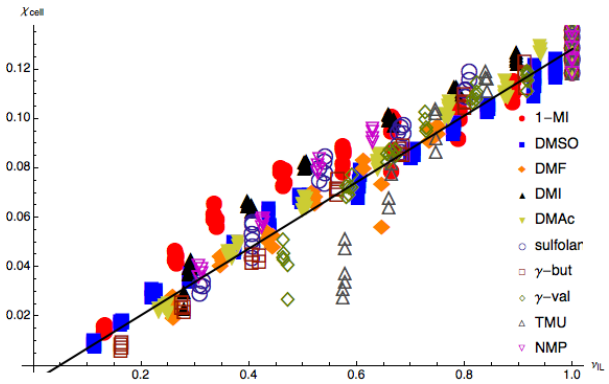

Figure S3: Molar fraction of cellobiose residues in dissolved cellulose versus volume fraction of ionic liquid (as calculated from molar volumes and molar fractions). The amount of cellulose dissolvable in a solution mixture is only related to the volume of IL available suggesting that a space-filling model of dissolution works. Fitted line equation given in Table 2 of the paper.

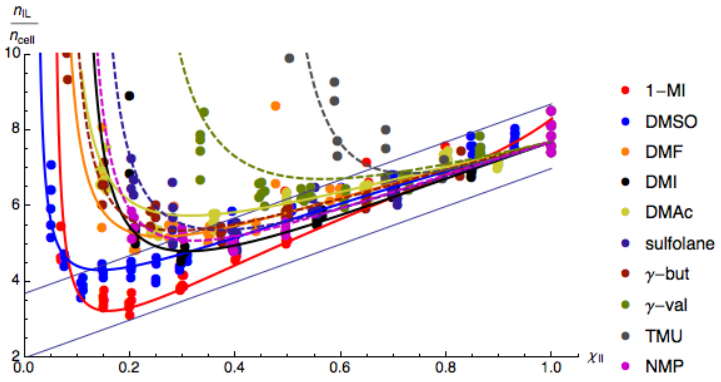

Figure S4: The number of ionic liquid pairs per cellobiose residue. Upper and lower boundaries (blue lines) are drawn at ${}^{n_{IL}}/_{n_{cell}} = 1.8{+}1{\cdot}5\chi_{IL}$ and ${}^{n_{IL}}/_{n_{cell}} = 3.7{+}1{\cdot}5\chi_{IL}$.

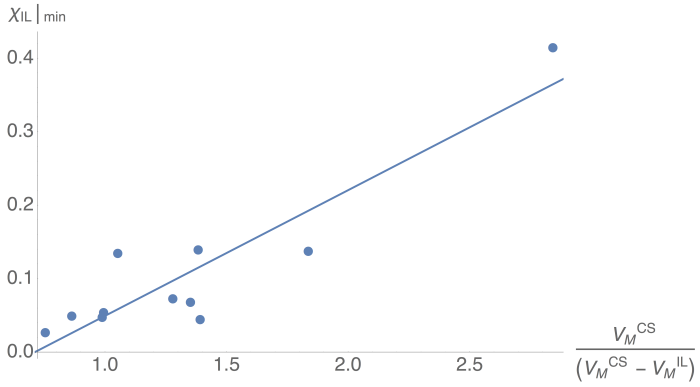

Figure S5: Linear fit of minimum χ_{IL} to linearized CS molar volume.

Table S2: Molar volumes of tested co-solvents and ionic liquid.

Name	Key	Molar volume cm^3mol^{-1}
1-methylimidazole	1-MI	82.4
dimethylsulfoxide	DMSO	71.3
n,n-dimethylformamide	DMF	82.628
1,3-dimethylimidazolidin-2-one	DMI	107.3
n,n-dimethylacetamide	DMAc	93.02
sulfolane	Sulfolane	95.27
gamm+B542a-butyrolactone	γ-But	76.8
gamma-valerolactone	γ-Val	96.2
1,1,3,3-tetramethylurea	TMU	122.6
n-methylpyrrolidine-2-one	NMP	96.44
1-Ethyl-3-methylimidazolium acetate	[EMim][OAc]	165.735

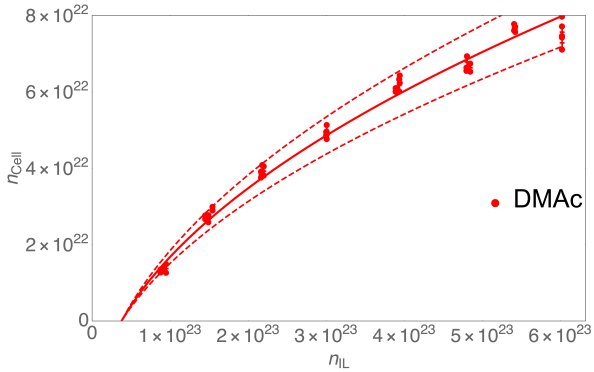

Figure S6: Sensitivity of the random walk model parameters. An example fitted model for DMAc is plotted with equations containing ± 10% of the fitted values. A small change in model parameters causes a small change in the model predictions

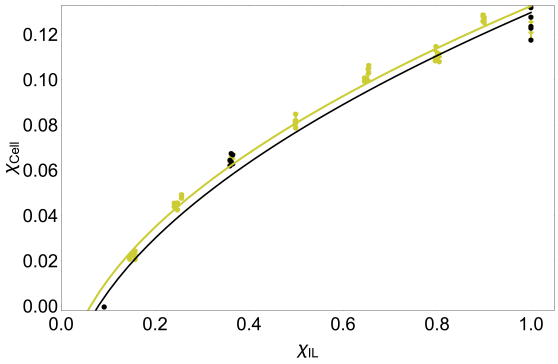

Figure S7: Using the random walk model for prediction of DMAc OES data. Yellow: fit (line) to all measured data (dots). Black: fit (line) to subset points (black dots). Only the measurement at around χ_{IL} =0.35 needs to be measured, the point at $\chi_{IL} = 1$ is known and the point at $\chi_{cell} = 0$ can be estimated from equation 8. The single measurement fit differs from the actual data by only 7.1% on average.

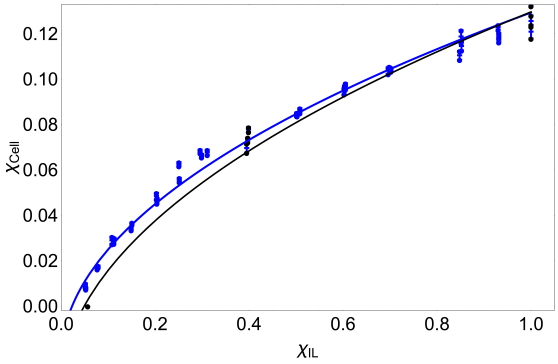

Figure S8: Using the random walk model for prediction of DMSO OES data. Blue: data (dotss) and fit (line) to all measured data. Black: fit (line) to measured or estimated points (dots). Only the measurement at around $\chi_{IL} = 0.4$ needs to be measured, the point at $\chi_{IL} = 1$ is known and the point at $\chi_{cell} = 0$ can be estimated from equation 8. The single measurement fit differs from the actual data by only 9.4% on average.