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Supporting Information for the Manuscript "Entropy of Cellulose Dissolution in Water and in the Ionic Liquid 1-Butyl-3-Methylimidazolim Chloride "

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Application of the Two-Phase Thermodynamic Model to Determine Cellulose Dissolution Entropy

The two-phase thermodynamic (2PT) method[1, 2] was used to calculate the entropy of water, BmimCl, and cellulose in order to determine the entropy of solution of cellulose in those two solvents. From previously conducted simulations,[3] 15 100 ps simulations were started and run from restarts at regularly spaced intervals of 1 ns for cellulose/water systems and 2 ns for cellulose/BmimCl systems. Position and velocity data was collected every 4 fs for analysis. The 2PT entropy of each component, solvent or cellulose, was then calculated in the following manner:

1. Calculation of the velocity time autocorrelation functions

The velocity of each atom at each time step was split up into translational, rotational, and intramolecular components

$$\vec{v}_i(t) = \vec{v}_i^{trans}(t) + \vec{v}_i^{rot}(t) + \vec{v}_i^{\text{intra}}(t)$$

where i refers to atom and t to time. The translational velocity is calculated as

$$\vec{v}_i^{trans}(t) = \frac{\sum_{j \in M} m_j \vec{v}_j(t)}{\sum_{j \in M} m_j}$$

where m_j refers to the mass of atom j, and the sum is over all atoms within a single molecule or body (each atom can only belong to one molecule). The translational velocity is the velocity of the center of mass of the body to which the selected atom belongs.

The rotational velocity of an atom is calculated with the following equations

$$\vec{L}_M(t) = \sum_{j \in M} m_j \left(\vec{r}_{jM}(t) \times \vec{v}_j(t) \right) = \underline{\underline{I_M(t)}} \vec{\omega}_M(t)$$

$$\vec{v}_i^{rot}(t) = \vec{\omega}_M(t) \times \vec{r}_{iM}(t)$$

L_M is the angular momentum of molecule M, to which atom i belongs, r_{jM} is the position vector between atom j and the center of mass of body M, I_M is the moment of inertia tensor of M, and ω_M the angular velocity of M. As in the case for the translational velocity, the summation is over all atoms that are part of the body M. In practice, the rotational velocity of atom i is found by inverting the moment of inertia tensor, and multiplying it with the angular momentum vector to calculate the angular velocity vector. The rotational velocity is the cross product of this with the position vector.

The intramolecular velocity is then the balance

$$\vec{v}_i^{\text{intra}}(t) = \vec{v}_i(t) - \vec{v}_i^{trans}(t) - \vec{v}_i^{rot}(t)$$

With the three velocities types calculated for all atoms at all time points, the velocity time autocorrelation functions of each atom type are calculated

$$C_j^x(t) = \left\langle v_j^x(\tau + t) \cdot v_j^x(\tau) \right\rangle$$

C is the autocorrelation function, j refers to a specific atom type, and x refers to type of motion or degree of freedom (translational, rotational, or intramolecular).

2. Calculation of the density of states functions

The density of states function of each molecular species for each degree of freedom type (translational, rotational, or intramolecular) is the mass weighted Fourier

transform of the velocity time autocorrelation function associated with that type of motion.[4]

$$\rho^x(\omega) = FT\left[C^x(t)\right] = FT\left[N_M \sum_{j\in M} m_j \left\langle v_j^x(\tau + t)\cdot v_j^x(\tau)\right\rangle\right]$$

N_M is the number of molecules of type M, x again refers to degree of freedom type, j refers to atom type, m_j is the mass of atom type j, ω is frequency, and the summation is over all atoms types that exist in molecule type M. Each molecule type will have its own density of states functions associated with it. FT stands for Fourier Transform.

After the density of state functions are calculated, they are split up according to the 2PT methodology. This is done via a fluidicity factor, which ranges from zero to one. Values closer to zero indicate a more solid-like system, while values near one a more fluid-like one.[2] The factor is a function of the thermodynamic state point of the system, as well as ρ(0), the zero frequency density of state.[1, 2] Once it is calculated, the density of states is split into two parts, one that represents a hard sphere gas, and one that represents an ideal, harmonic solid. This division of the density of states function is the key step in the 2PT methodology.

$$\rho_g^x(\omega) = \frac{\rho^x(0)}{1 + \left[\frac{\pi\rho^x(0)\omega}{6\mathrm{f}^x N}\right]^2}$$

$$\rho_s^x(\omega) = \rho^x(\omega) - \rho_g^x(\omega)$$

The subscript g and s denote either the gas or solid system, respectively, N is the number of that type of molecule, and f is the fluidicity factor. Note the following:

$$\rho_s^x(0) = 0$$
$$\rho_g^{\text{intra}}(\omega) = 0 \text{ for all } \omega$$

Also, integration of the density of states function gives the number of degrees of freedom associated with that type of motion.

3. Calculation of the Entropy

With the density of states functions known, the entropy of each molecule type can be calculated

$$S^x = k_b\left[\int \rho_s^x(\omega) S_{HO}(\omega) d\omega + \int \rho_g^x(\omega) S_{HS}^x d\omega\right]$$

$$S_{HO}(\omega) = \frac{\beta h\omega}{\exp(\beta h\omega) - 1} - \ln[1 - \exp(-\beta h\omega)]$$

$$S_{HS}^{trans} = \frac{5}{2} + \ln\left[\left(\frac{2\pi m k_b T}{h^2}\right)^{3/2} \frac{V}{\mathrm{f}^{trans}} z(y)\right] + \frac{y(3y-4)}{(1-y)^2}$$

$$S_{HS}^{rot} = \ln\left[\left(\frac{\pi^{1/2} e^{3/2}}{\sigma}\right)\left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}\right]$$

S^x is the translational, rotational, or intramolecular entropy, and is the sum of that of the ideal solid and hard sphere gas entropies. S_{HO} is the entropy of an ideal harmonic

oscillator as a function of frequency. S_{HS} is the entropy of the hard sphere gas, the exact formula of which depends on whether the translational or rotational entropy is being calculated. In the translational hard sphere entropy equation, f is the translational fluidicity factor, y is a function of the state point of the system as well as the zero frequency density of state, and z(y) is the Carnahan-Starling equation of state of a hard sphere gas.[2] In the rotational hard sphere entropy equation, the Θ's are the three rotational temperatures of the molecule type, and σ is the symmetry factor.[2, 5] Note that the intramolecular entropy only has contributions from the ideal solid term, as its gas density of states function is always zero.

After the translational, rotational, and intramolecular are calculated for each molecule type in the system, they are summed together to give the total system entropy. The entropy of dissolution of cellulose in either water or BmimCl is then calculated as the differences in entropy values between the dissociated and microfibril simulations (dissociated – microfibril). The values presented here are the results of 15 simulations for each solvent/cellulose conformation combination and temperature choice.

Microfibril Degree of Freedom Partition and Entropy

The translational, rotational, and intramolecular time autocorrelation functions must be calculated as part of the 2PT analysis. Embedded in this process is the choice of what collection of sites constitutes an independent body. For instance, the translational velocities of each body are calculated as the mass-weighted sum of the velocities of each atom within that body. The rotational velocities are calculated according to the formulas for rigid-body rotation.[2, 5] For a small molecule like water or $Bmim^+$, the choice of what

sites should define each body is obvious, a set of atoms connected by covalent bonds to each other, but not connected to any other atoms by such bonds, i.e. all the atoms in a single molecule. The oxygen and two hydrogens of each water would constitute one such body. This definition is readily extended to the dissociated chain conformation of cellulose. However, for the microfibril, the case is not so simple. It can be viewed either as a collection of 36 individual chains, each with its own independent translational, rotational, and intramolecular DOF, or, as one collective body, wherein movement of one chain relative to another is considered internal motion. The decision of how to partition the microfibril's DOF will affect the absolute entropy values calculated for these DOF of the microfibril. In Table S1A-B, we compare the microfibril entropies calculated using both approaches. As expected, considering each chain as its own, independent entity (as done in the main text) yields a higher absolute entropy value for the microfibril's translational and rotational entropies compared to treating the microfibril as one collective body, as in the former method, cellulose has more DOF associated with these types of motion. The same reasoning explains why this first approach gives a lower intramolecular entropy compared to the second. Once relative motion between chains is considered intramolecular motion, and not translational or rotational motion, more DOF become associated with the intramolecular term. However, when considering the net entropy, both approaches are equivalent, and give the same total entropy for the microfibril. The choice of using the chain-by-chain approach was made for consistency with the dissociated state, which used that basis for calculating the glucan entropy.

Comparison of Water Entropy from the Cellulose Simulations with Neat Water Entropy

In Table S2A, we show the entropy of water from the dissociated and microfibril simulations, while in Table S2B, we show the entropy of neat water at 300. In either simulation, the effect of cellulose is to decrease the entropy of water relative to the neat case. Essentially, the entirety of the change occurs with translational entropy, which decreases by 0.4 cal/K/mol, while the rotational entropy is basically unchanged. The combination of the glucan chains' many OH groups along with its extended structure serve to bind nearby waters in a collective manner and limit their freedom more severely compared to the more localized, short range structure of pure water.

Pressure-Volume Contribution to the Free Energy Change of Cellulose Dissolution

In Table S3, we show the pV-work term associated with cellulose dissolution in water and BmimCl from our MD simulations. The $p\Delta V$ values are negligible, at least 5 orders of magnitude smaller than the calculated Helmholtz free energy terms shown in Fig 4 of the main text. Thus the Helmholtz and Gibbs free energy changes for this process are equivalent.

Internal Energy Change as a Predictor of the Sign of Free Energy Change for Cellulose Dissolution

In Table S4A-B we show the values of ΔE, ΔS, and ΔA of cellulose dissolution in either water or BmimCl calculated from our MD simulations. In all cases except for cellulose in water at 300 K and in BmimCl at 500 K, $|\Delta E|>T\Delta S|$, and energy change

determines the sign of the free energy change. For those two simulations where $|\Delta E|<T\Delta S|$, ΔE still has the same sign as ΔA. Thus, energy of solution could be a good predictor for the sign of the free energy change. This is beneficial, as energy of solution is both quicker and simpler to calculate than entropy of solution, and could be used as an *in silico* test to screen potential cellulose solvents. In future work, this will be investigated to test whether this result extends to other solvents, IL or otherwise.

References:

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Table S1A. Comparison of 2PT entropies calculated for the cellulose microfibril in water using either the whole microfibril or each individual chain as the basis for the DOF decomposition of the glucans.

Temp (K)	300		325		350	
Basis	Whole Microfibril	Chain-by-Chain	Whole Microfibril	Chain-by-Chain	Whole Microfibril	Chain-by-Chain
Trans Entropy[a]	0.04	0.93	0.04	0.96	0.04	1.00
Rot Entropy[a]	0.04	0.81	0.04	0.84	0.04	0.88
Intra Entropy[a]	41.60	39.94	45.47	43.75	49.37	47.57
Total Entropy[a]	41.68	41.68	45.54	45.55	49.45	49.45

[a] cal/K/mol-gluc

Table S1B. Comparison of 2PT entropies calculated for the cellulose microfibril in BmimCl using either the whole microfibril or each individual chain as the basis for the DOF decomposition of the glucans.

Temp (K)	425		450		500	
Basis	Whole Microfibril	Chain-by-Chain	Whole Microfibril	Chain-by-Chain	Whole Microfibril	Chain-by-Chain
Trans Entropy[a]	0.04	1.06	0.04	1.08	0.04	1.13
Rot Entropy[a]	0.04	0.93	0.04	0.95	0.04	1.01
Intra Entropy[a]	59.50	57.59	63.00	61.05	70.04	67.98
Total Entropy[a]	59.58	59.58	63.07	63.08	70.12	70.13

[a] cal/K/mol-gluc

Table S2A. Entropy of water from the dissociated chain and microfibril simulations

Temp (K)	300		325		350	
Simulation	Dissociated	Microfibril	Dissociated	Microfibril	Dissociated	Microfibril
Trans Entropy[a]	13.419 ± 0.003	13.585 ± 0.002	14.245 ± 0.002	14.380 ± 0.001	14.991 ± 0.003	15.091 ± 0.003
Rot Entropy[a]	3.163 ± 0001	3.181 ± 0.001	3.667 ± 0.001	3.685 ± 0.000	4.166 ± 0.001	40181 ± 0.001
Total Entropy[a]	16.582 ± 0.003	16.766 ± 0.002	17.912 ± 0.003	18.065 ± 0.002	19.157 ± 0.004	19.272 ± 0.004

[a] cal/K/mol

Table S2B. Entropy of neat water at 300 K

Trans Entropy[a]	13.834
Rot Entropy[a]	3.160
Total Entropy[a]	16.994

[a] cal/K/mol

Table S3. Pressure-volume contribution to the free energy change of cellulose dissolution.

Solvent	Temp (K)	ΔV (Å^3)	pΔV (kcal/mol-gluc)
Water	300	-544.1	-1.38E-05
Water	325	-79.9	-2.02E-06
Water	350	215.8	5.46E-06
BmimCl	425	227.3	5.76E-06
BmimCl	450	869.0	2.20E-05
BmimCl	500	1533.8	3.88E-05

Table S4A. Energy, entropy and Helmholtz free energy change of dissolution of cellulose in water.

Temp (K)	300			325			350		
ΔE (kcal/mol-glucan)	0.057	±	0.037	0.769	±	0.029	1.183	±	0.031
TΔS (kcal/mol-glucan)	-0.383	±	0.059	0.146	±	0.057	0.899	±	0.095
ΔA (kcal/mol-glucan)	0.440	±	0.070	0.623	±	0.064	0.283	±	0.100

Table S4B. Energy, entropy and Helmholtz free energy change of dissolution of cellulose in BmimCl.

Temp (K)	425			450			500		
ΔE (kcal/mol-glucan)	-1.726	±	0.111	-1.195	±	0.102	-0.669	±	0.069
TΔS (kcal/mol-glucan)	0.947	±	0.252	0.967	±	0.286	1.390	±	0.284
ΔA (kcal/mol-glucan)	-2.673	±	0.276	-2.163	±	0.304	-2.059	±	0.292