Supporting Materials

Molecular insight into the cosolvent effect on the lignin-cellulose adhesion.

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Supporting Tables

Table S1. Configuration of simulated systems and equilibrium size of simulation boxes for lignin-cellulose complex studied in this work. The model consists of cellulose nanocrystal with 7 chains (8 glucose monomers per chain) and 4 lignin dimer.

Solvent system	Organic solvent fraction (wt%)	Number of organic solvent molecules	Number of water molecules	Cubic box side length (nm)
pure water	0	0	10370	6.886
ethanol-water	50	1725	4415	6.749
	75	2443	2084	6.749
acetonitrile-water	50	1760	4013	6.615
	75	2639	2006	6.746
pure ethanol	100	2985	0	6.711
pure acetonitrile	100	3442	0	6.813

Table S2. Average Lennard-Jones (LJ), Coulomb (Coul) and total (Total) lignin-cellulose energies with total standard deviation errors. Values are normalised by the number of lignin dimers and presented in kJ/mol. The large error bars are due to the mobility of two among the four lignin dimers, uncoordinated to cellulose (see main text and Table S3).

	Average Energies and standard deviation errors								
Solvent	LJ			Coul			Total		
100 wt% Water	-17.0	±	6.5	-11.2	±	5.5	-28.2	±	8.3
50 wt% Ethanol	-9.0	±	5.8	-4.8	±	4.8	-13.8	±	9.3
75 wt% Ethanol	-6.7	±	7.5	-4.7	±	6.6	-11.4	±	13.0
100 wt% Ethanol	-13.7	±	11.6	-10.9	±	10.7	-24.6	±	21.3
50 wt% Acetonitrile	-5.2	±	7.1	-3.0	±	5.0	-8.2	±	11.2
75 wt% Acetonitrile	-5.5	±	7.1	-6.1	±	9.1	-11.6	±	15.1
100 wt% Acetonitrile	-6.1	±	6.9	-7.4	±	8.2	-13.5	±	13.6
No Solvent	-65.1	±	4.0	-86.1	±	8.5	-151.2	±	9.4

Table S3. Average lignin-cellulose intermolecular energies in kJ/mol between each lignin dimer labelled as L1, L2, L3 and L4, and the hydrophilic (chains AF) or hydrophobic (chains BDEG) surface chains of cellulose, as a function of the organic cosolvent fraction (Xcosol). The four lignin dimers and cellulose chains (AFBDEG) are shown in Fig. 2, main text.

Solvent		**No Solvent**	**Water**	**Ethanol**			**Acetonitrile**		
Xcosol		**-**	**0**	**0.50**	**0.75**	**1**	**0.50**	**0.75**	**1**
Hydrophilic	**L1**	-132.0 ± 1.9	-1.6 ± 1.0	-3.9 ± 2.0	-6.5 ± 4.3	-13.0 ± 4.9	-2.5 ± 1.2	-4.2 ± 2.8	-0.5 ± 0.3
	L2	-7.6 ± 0.1	-1.1 ± 0.2	-1.0 ± 0.8	-0.4 ± 0.2	-0.9 ± 0.2	-0.2 ± 0.2	-0.3 ± 0.3	-12.8 ± 6.3
	L3	-61.5 ± 3.8	-3.9 ± 1.5	-4.0 ± 1.9	-1.6 ± 1.2	-0.1 ± 0.1	-1.2 ± 0.6	-6.9 ± 3.9	-2.4 ± 1.5
	L4	-4.4 ± 0.2	-1.6 ± 0.8	-1.8 ± 0.9	0.0 ± 0.0	-1.0 ± 0.1	-2.2 ± 1.1	-15.7 ± 5.9	-8.1 ± 4.4
Hydrophobic	**L1**	-42.0 ± 0.2	-1.0 ± 0.7	-2.6 ± 1.8	-2.6 ± 1.2	-1.8 ± 0.8	-2.1 ± 1.0	-1.5 ± 1.1	-3.7 ± 2.8
	L2	-137.5 ± 1.3	-75.7 ± 9.1	-2.7 ± 2.1	-31.0 ± 12.0	-32.5 ± 13.2	-5.9 ± 4.2	-5.8 ± 3.5	-17.4 ± 6.2
	L3	-92.5 ± 8.4	-4.6 ± 1.8	-12.6 ± 8.7	0.0 ± 0.0	-0.1 ± 0.1	-5.5 ± 3.8	-4.2 ± 1.6	-0.5 ± 0.3
	L4	-127.4 ± 2.0	-23.2 ± 9.5	-26.6 ± 7.9	-3.3 ± 2.4	-48.9 ± 14.3	-13.1 ± 4.0	-7.7 ± 3.0	-8.7 ± 4.6

Table S4. Average block analysis of the torsion angle ω (O5-C5-C6-O6) in cellulose chains.

Solvent		**Time Interval (ns)**			
	Xcosol	**5-10**	**10-15**	**15-20**	**5-20**
Water	**0**	57 ± 10	50 ± 8	53 ± 7	53 ± 9
Ethanol	**0.50**	84 ± 8	65 ± 11	64 ± 9	71 ± 13
	0.75	72 ± 11	58 ± 9	61 ± 8	64 ± 11
	1	75 ± 10	68 ± 8	79 ± 10	74 ± 10
Acetonitrile	**0.50**	78 ± 8	79 ± 8	72 ± 10	76 ± 9
	0.75	43 ± 10	43 ± 8	45 ± 7	44 ± 9
	1	85 ± 11	79 ± 10	80 ± 11	82 ± 11

Table S5. Average block analysis for RMSD of the positions of atoms in cellulose hydroxymethyl groups

Solvent		**Time Interval (ns)**				
	Xcosol	**0-5**	**5-10**	**10-15**	**15-20**	**5-20**
Water	**0**	0.19 ± 0.03	0.23 ± 0.02	0.24 ± 0.02	0.24 ± 0.02	0.23 ± 0.02
Ethanol	**0.50**	0.20 ± 0.03	0.21 ± 0.02	0.23 ± 0.02	0.24 ± 0.02	0.23 ± 0.02
	0.75	0.19 ± 0.02	0.23 ± 0.02	0.23 ± 0.02	0.25 ± 0.02	0.23 ± 0.02
	1	0.21 ± 0.03	0.21 ± 0.02	0.22 ± 0.02	0.23 ± 0.02	0.22 ± 0.02
Acetonitrile	**0.50**	0.20 ± 0.03	0.24 ± 0.03	0.24 ± 0.03	0.22 ± 0.02	0.23 ± 0.03
	0.75	0.18 ± 0.04	0.30 ± 0.02	0.29 ± 0.03	0.25 ± 0.02	0.28 ± 0.03
	1	0.18 ± 0.03	0.20 ± 0.02	0.21 ± 0.02	0.22 ± 0.02	0.21 ± 0.02

Table S6. H-bond lifetimes for the cellulose-water (C-W) and cellulose-cosolvent (C-Cosol), interaction types, obtained from the H-bond autocorrelation functions of each H-bond type, for the hydrophobic (chains BDEG) and the hydrophilic (chains AF) cellulose surfaces, respectively.

	HB lifetimes (ps)							
Solvent mixture	**Water-EtOH**				**Water-ACN**			
	Hydrophilic		**Hydrophobic**		**Hydrophilic**		**Hydrophobic**	
X_{cosol}	C-W	C-Cosol	C-W	C-Cosol	C-W	C-Cosol	C-W	C-Cosol
0	9.8	-	12.3	-	9.8	-	12.3	-
0.25	18.6	21.5	23.6	34.5	17.6	9.7	22.6	28.6
0.50	32.2	30.3	32.6	30.3	20.3	9.9	30.7	22.1
0.75	49.0	44.0	57.9	57.4	20.7	10.4	24.7	27.2
1	-	43.8	-	94.5	-	12.0	-	41.7

Supporting Figures

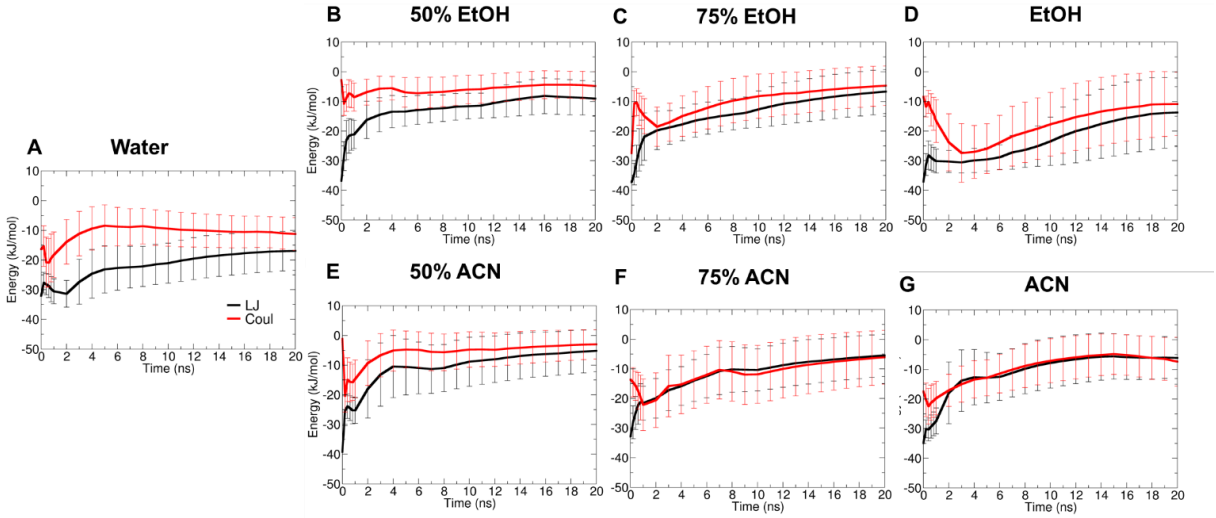

Figure S1. Lennard-Jones (LJ, black) and Coulomb (Coul, red) average lignin-cellulose energies along the 20-ns MD normalised by the number of lignin dimers in water, ethanol (EtOH) and acetonitrile (ACN) pure solvents and the respective water-organic (EtOH and ACN) binary mixtures

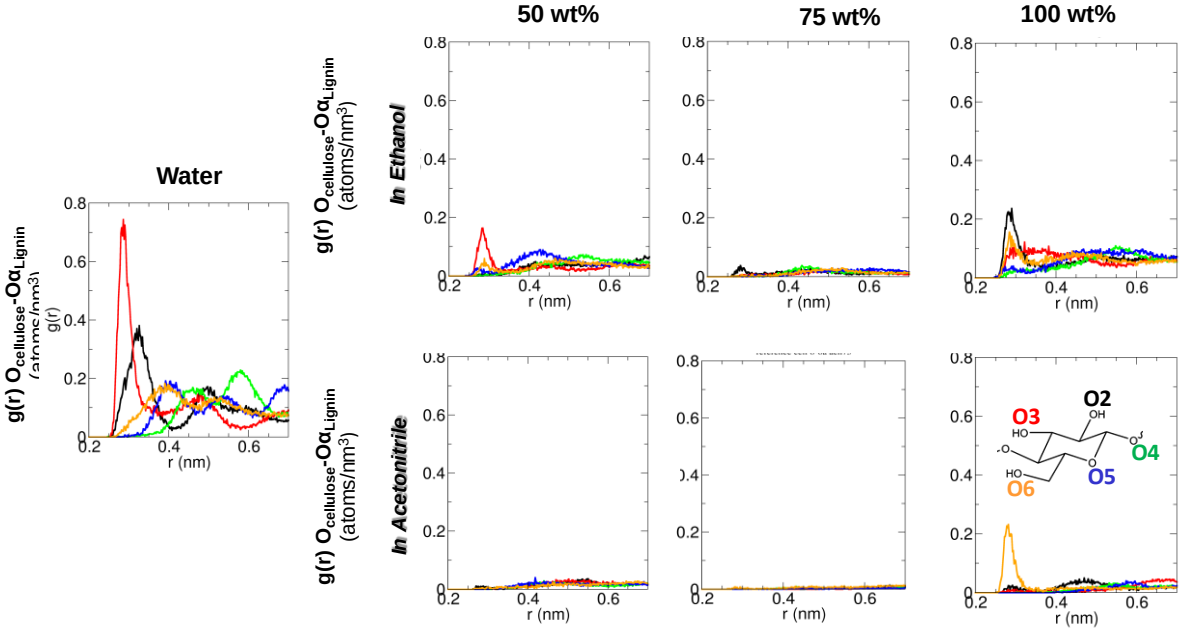

Figure S2. $O_{cellulose}$-$O\alpha_{lignin}$ radial distribution functions in water-organic solvents at 50 and 75wt% concentration of the organic compound, and in their mono-component counterparts for direct comparison.

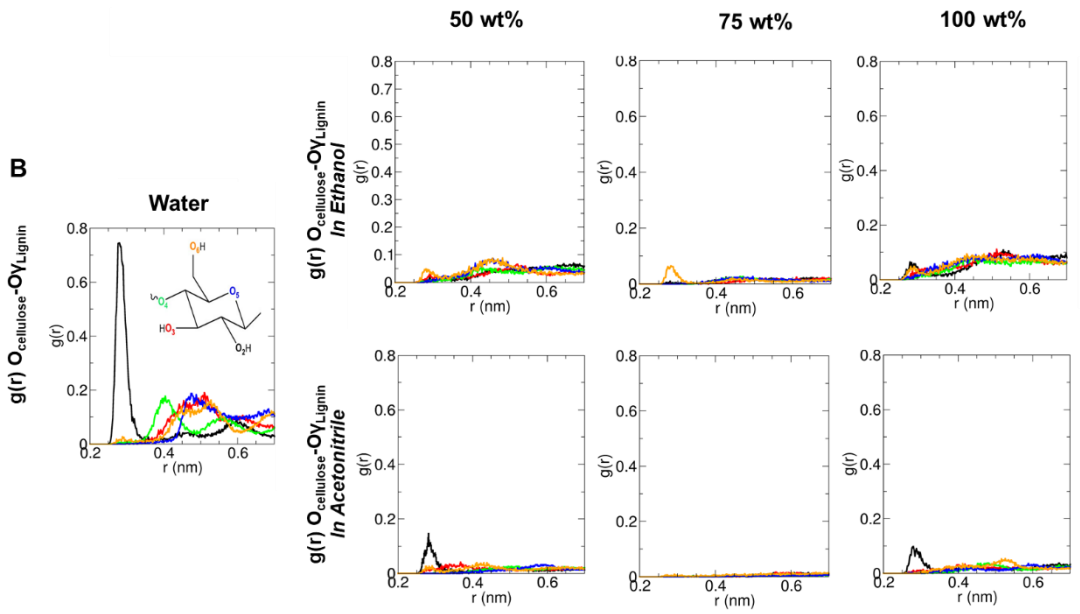

Figure S3. $O_{cellulose}$-$O\gamma_{lignin}$ radial distribution functions in water-organic solvents at 50 and 75 wt% concentration of the organic compound, and in their mono-component counterparts.

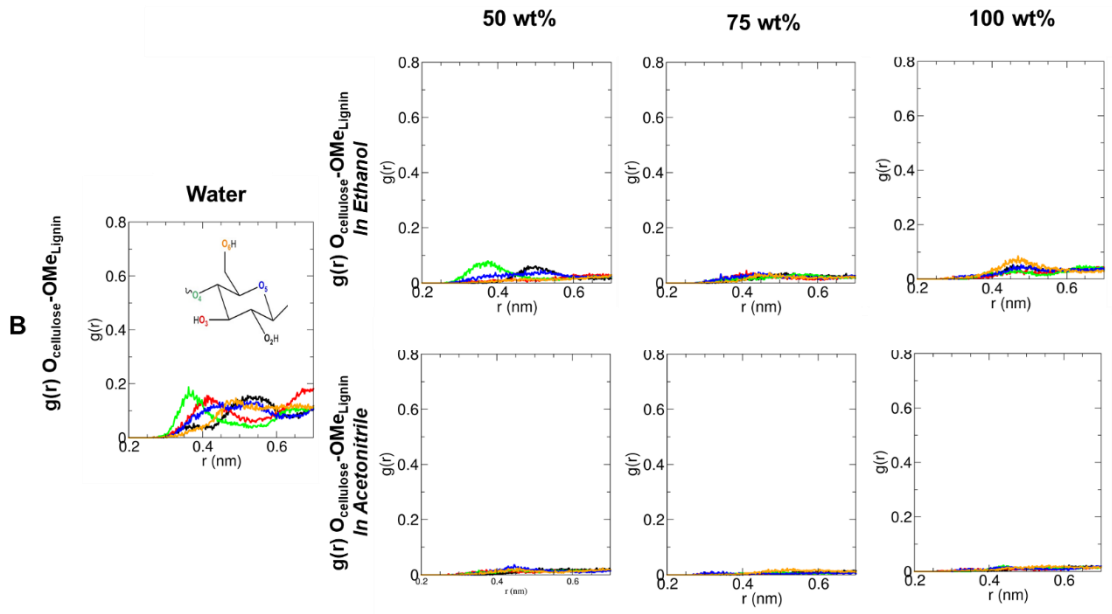

Figure S4. $O_{cellulose}$-$OMe_{liginin}$ radial distribution functions in water-organic solvents at 50 and 75% concentration of the organic compound, and in their mono-component counterparts.

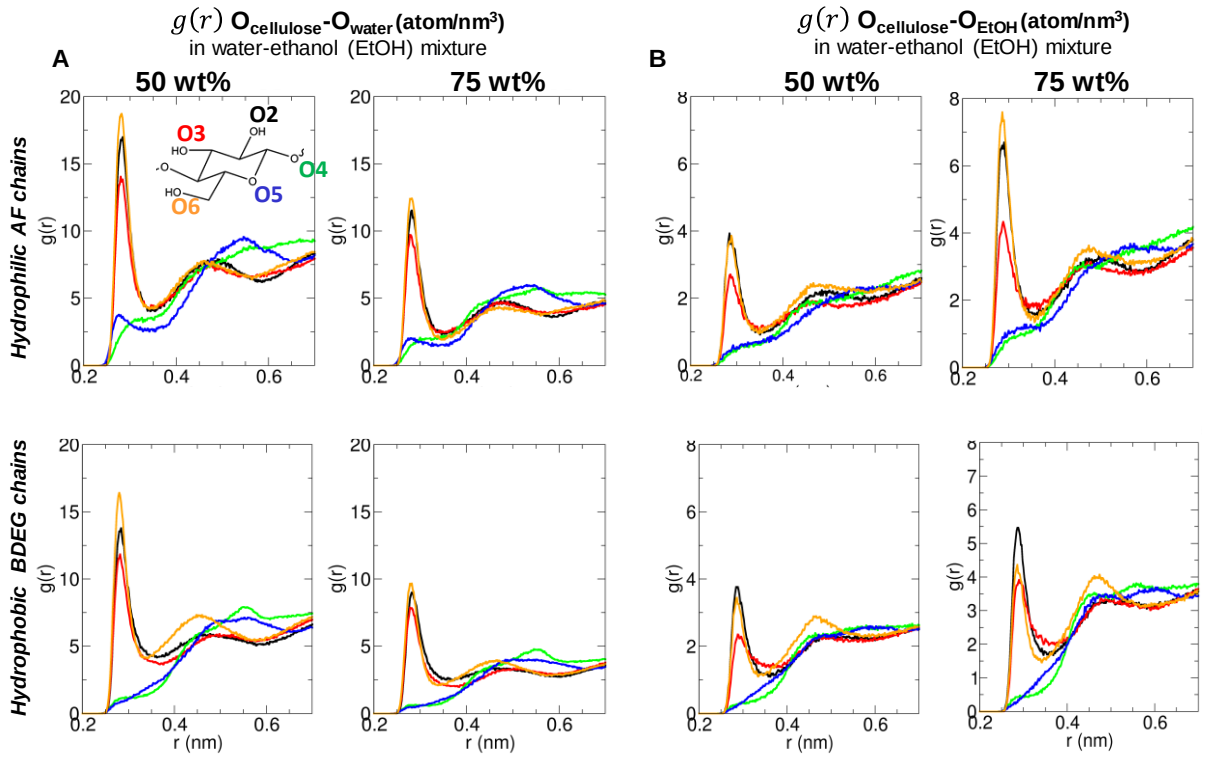

Figure S5. $O_{cellulose}$-O_{water} (A) and $O_{cellulose}$-O_{EtOH} (B) $g(r)$s in water-ethanol (EtOH) mixtures

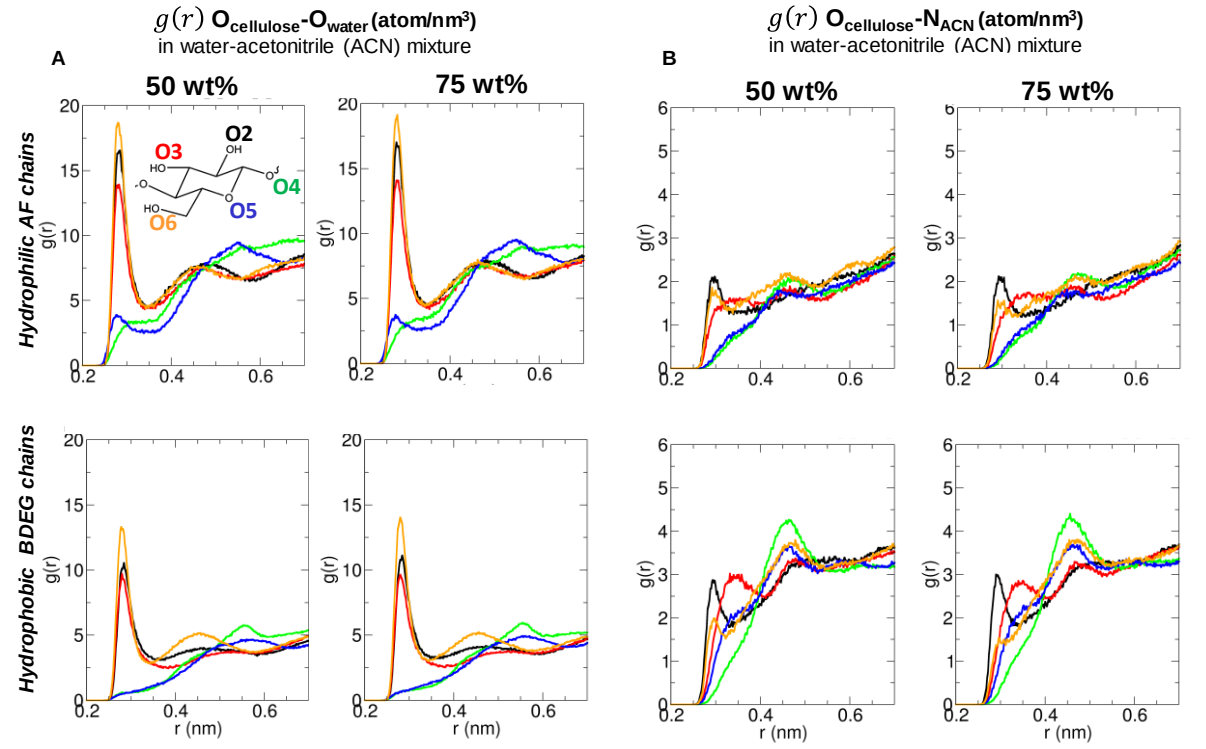

Figure S6. Ocellulose-Owater(A) and Ocellulose-N_{ACN} (B) $g(r)$s in water- acetonitrile (ACN) mixtures

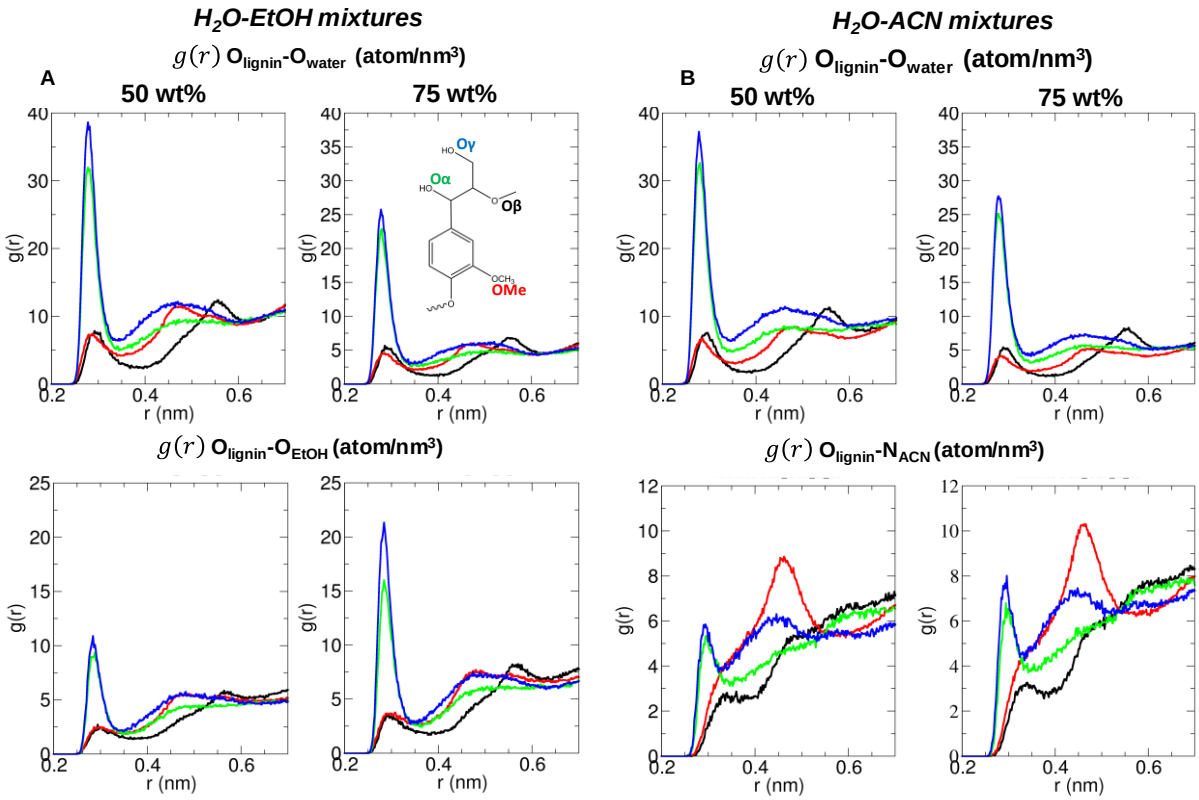

Figure S7. O_{lignin}-O_{water}, O_{lignin}-O_{EtOH}, O_{lignin}-N_{ACN} radial distribution functions, $g(r)$, in (A) water-ethanol (EtOH) and (B) water-acetonitrile (ACN) mixtures.

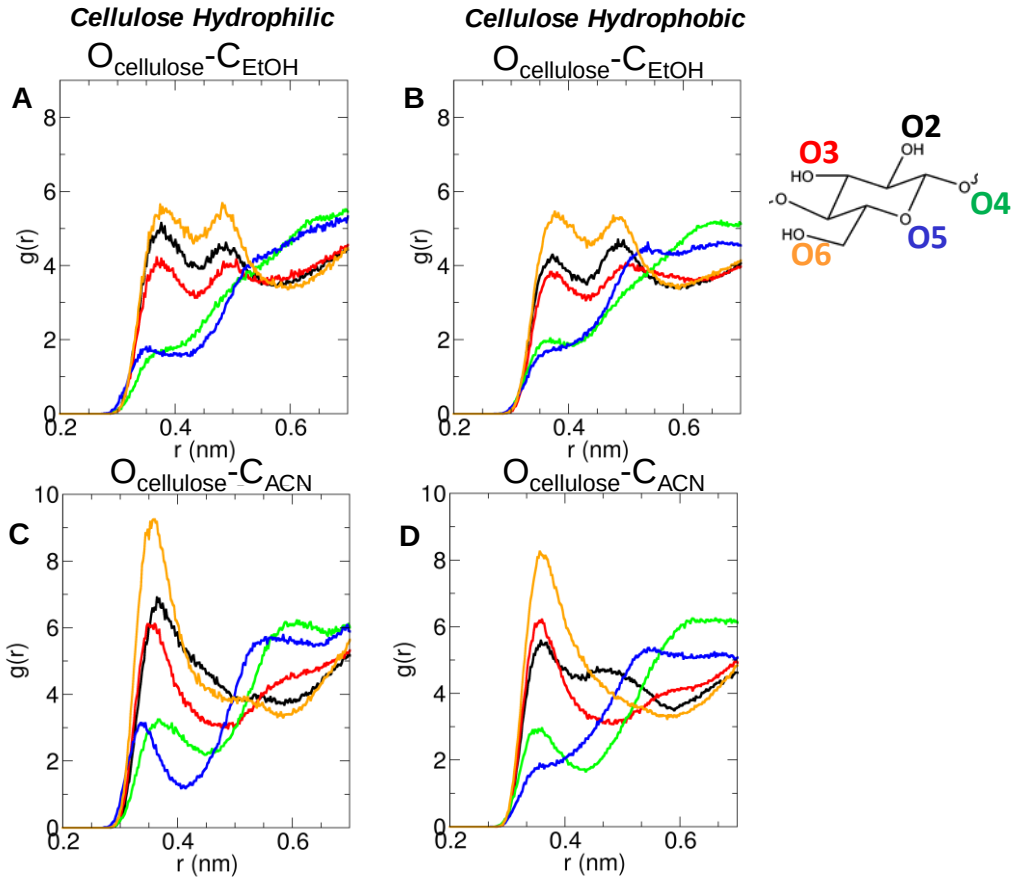

Figure S8. $O_{cellulose}$-$C_{EtOH\ /\ ACN}$ radial distribution functions, $g(r)$, between the cellulose oxygens in hydrophilic and hydrophobic surfaces, and methyl carbons of the (A, B) ethanol (EtOH) and (C, D) acetonitrile (ACN) in 100 wt% organic solvents.

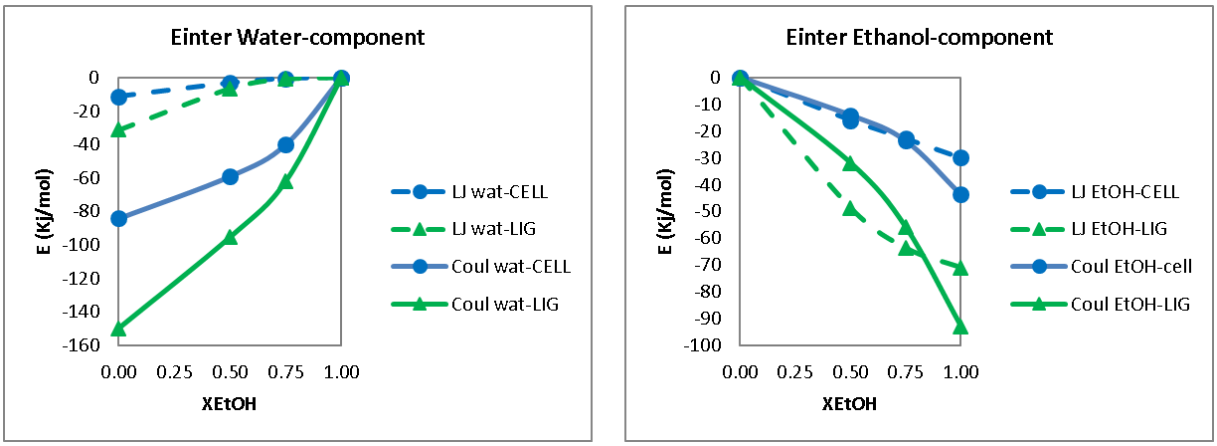

Figure S9. Interaction energies between water and cellulose (wat-CELL), and water and lignin (wat-LIG) (left pannel), and between ethanol and cellulose (EtOH-CELL), and ethanol and lignin (EtOH-LIG) (right panel). The interaction energies are decomposed in Lennard-Jones (LJ) and Coulomb (Coul) energies and are normalized by number of glucose or lignin monomers, as function of EtOH content (X_{EtOH})

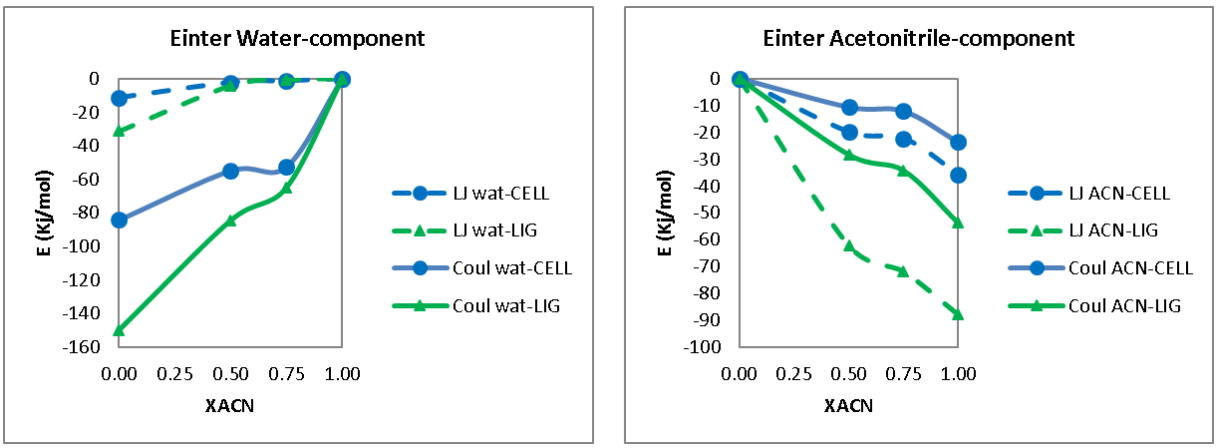

Figure S10. Interaction energies between water and cellulose (wat-CELL), and water and lignin (wat-LIG) (left panel), and between acetonitrile and cellulose (ACN-CELL), and acetonitrile and lignin (ACN-LIG) (right panel). The interaction energies are decomposed in Lennard-Jones (LJ) and Coulomb (Coul) energies and are normalized by number of glucose or lignin monomers, as function of ACN content (X_{ACN})