Electronic Supplementary Information

Why are some cyano-based ionic liquids better glucose solvents than water?

Marta L. S. Batista[1], Helena Passos[1], Bruno J. M. Henriques[1], Edward J. Maginn[2], Simão P. Pinho[3], Mara G. Freire[1], José R. B. Gomes*[1], João A. P. Coutinho[1]*

[1]Departamento de Química, CICECO, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

[2] Department of Chemical and Biomolecular Engineering, 182 Fitzpatrick Hall, University of Notre Dame, Notre Dame, Indiana 46556, United States

[3]Associate Laboratory LSRE-LCM, Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, 5301-857 Bragança, Portugal.

***** Corresponding author

Tel: +351 234 370 200; E-mail addresses: maragfreire@ua.pt; jrgomes@ua.pt

The solution standard molar functions were determined using the following equations:

$$\Delta_{sol}G_m^0 = -RT\ln(x_2)_p \quad \text{S1}$$

$$\frac{\Delta_{sol}H_m^0}{RT^2} = \left(\frac{\partial \ln x_2}{\partial T}\right)_p \quad \text{S2}$$

$$\Delta_{sol}S_m^0 = R\left(\frac{\partial T \ln x_2}{\partial T}\right)_p \quad \text{S3}$$

where x_2 is the mole fraction solubility of glucose in the ionic liquids, R is the ideal gas constant, T is the absolute temperature, subscript p indicates isobaric condition and the subscript m refers to molar quantity.[1,2]

Table S1 – Interaction parameters for $[C_2C_1im][SCN]$. The CHelpG atomic charges were calculated at the B3LYP/6-311+G(d,p) level of theory.

$[C_2C_1im][SCN]$			
atom	**σ / nm**	**ε / kJ·mol^{-1}**	**charge / *e***
N1	0.3926	0.8368	0.09864
C2	0.3207	0.2092	0.08288
N3	0.3926	0.8368	-0.05516
C4	0.3207	0.2092	-0.17967
C5	0.3207	0.2092	-0.12135
C6	0.4054	0.0837	-0.04704
C7	0.4054	0.0837	0.25101
C8	0.3875	0.2301	0.04155
H1	0.1604	0.1925	0.14445
H2	0.2616	0.0326	0.17728
H3	0.2616	0.0326	0.18593
H4	0.2351	0.0920	0.07377
H5	0.2351	0.0920	0.07377
H6	0.2351	0.0920	0.07377
H7	0.2351	0.0920	-0.00559
H8	0.2351	0.0920	-0.00559
H9	0.2351	0.0920	-0.00445
H10	0.2351	0.0920	-0.00445
H11	0.2351	0.0920	-0.00445
S	0.3550	1.0460	-0.53746
C	0.3750	0.4393	0.42796
N	0.3250	0.7113	-0.66580

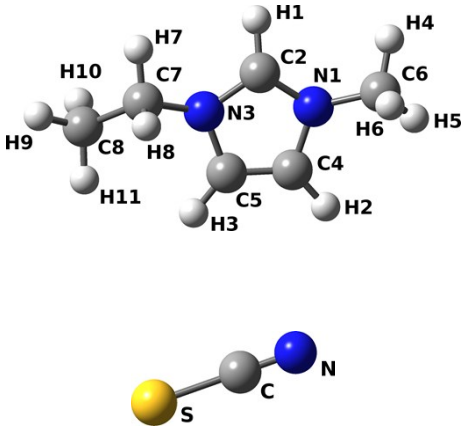
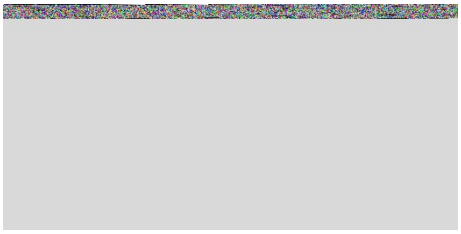


Table S2 – Interaction parameters for $[C_2C_1im][N(CN)_2]$. The CHelpG atomic charges were calculated at the B3LYP/6-311+G(d,p) level of theory.

$[C_2C_1im][N(CN)_2]$			
atom	**σ / nm**	**ε / kJ·mol^{-1}**	**charge / *e***
N1	0.3926	0.8368	0.08405
C2	0.3207	0.2092	0.04292
N3	0.3926	0.8368	-0.00529
C4	0.3207	0.2092	-0.13321
C5	0.3207	0.2092	-0.14042
C6	0.4054	0.0837	-0.09034
C7	0.4054	0.0837	0.23065
C8	0.3875	0.2301	-0.10889
H1	0.1604	0.1925	0.15955
H2	0.2616	0.0326	0.18286
H3	0.2616	0.0326	0.18509
H4	0.2351	0.0920	0.09453
H5	0.2351	0.0920	0.09453
H6	0.2351	0.0920	0.09453
H7	0.2351	0.0920	0.01502
H8	0.2351	0.0920	0.01502
H9	0.2351	0.0920	0.03440
H10	0.2351	0.0920	0.03440
H11	0.2351	0.0920	0.03440
N'	0.3250	0.7113	-0.68818
C	0.3300	0.2761	0.65334
N	0.3200	0.7113	-0.72115



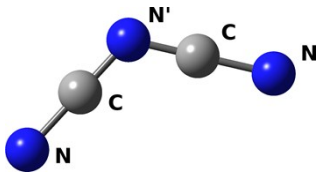
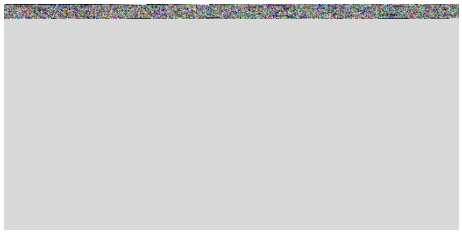


Table S3 – Interaction parameters for $[C_2C_1im][C(CN)_3]$. The CHelpG atomic charges were calculated at the B3LYP/6-311+G(d,p) level of theory.

$[C_2C_1im][C(CN)_3]$			
atom	**σ / nm**	**ε / kJ·mol^{-1}**	**charge / *e***
N1	0.3926	0.8368	0.16614
C2	0.3207	0.2092	-0.08743
N3	0.3926	0.8368	0.06418
C4	0.3207	0.2092	-0.15202
C5	0.3207	0.2092	-0.14453
C6	0.4054	0.0837	-0.1517
C7	0.4054	0.0837	0.08452
C8	0.3875	0.2301	-0.03404
H1	0.1604	0.1925	0.21125
H2	0.2616	0.0326	0.18617
H3	0.2616	0.0326	0.19177
H4	0.2351	0.0920	0.11338
H5	0.2351	0.0920	0.11338
H6	0.2351	0.0920	0.11338
H7	0.2351	0.0920	0.04461
H8	0.2351	0.0920	0.04461
H9	0.2351	0.0920	0.03131
H10	0.2351	0.0920	0.03131
H11	0.2351	0.0920	0.03131
C'	0.3431	0.4396	-0.69743
C	0.3431	0.4396	0.58754
N	0.3261	0.2889	-0.64093



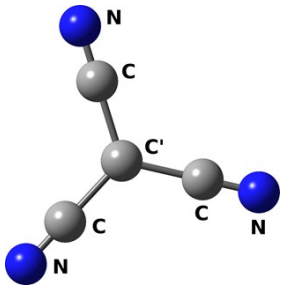
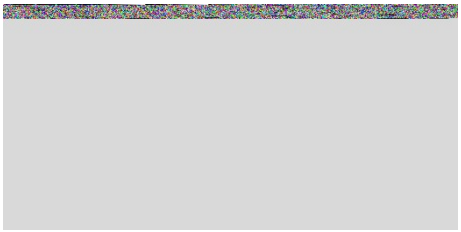


Table S4 – Interaction parameters for $[C_2C_1im][B(CN)_4]$. The CHelpG atomic charges were calculated at the B3LYP/6-311+G(d,p) level of theory.

$[C_2C_1im][B(CN)_4]$			
atom	**σ / nm**	**ε / kJ·mol^{-1}**	**charge / *e***
N1	0.3926	0.8368	0.10915
C2	0.3207	0.2092	-0.09005
N3	0.3926	0.8368	0.12574
C4	0.3207	0.2092	-0.11805
C5	0.3207	0.2092	-0.16698
C6	0.4054	0.0837	-0.05765
C7	0.4054	0.0837	0.11606
C8	0.3875	0.2301	-0.18562
H1	0.1604	0.1925	0.20803
H2	0.2616	0.0326	0.18534
H3	0.2616	0.0326	0.20587
H4	0.2351	0.0920	0.08597
H5	0.2351	0.0920	0.08597
H6	0.2351	0.0920	0.08597
H7	0.2351	0.0920	0.06102
H8	0.2351	0.0920	0.06102
H9	0.2351	0.0920	0.05837
H10	0.2351	0.0920	0.05837
H11	0.2351	0.0920	0.05837
B	0.3581	0.3975	**0.14410**
C	0.3300	0.2761	**0.22857**
N	0.3200	0.7113	**-0.48632**



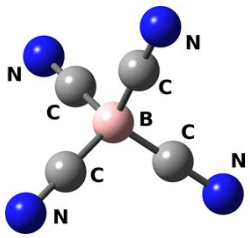


Table S5 – Experimental and computational density values for each pure IL addressed in this study, at 298.15 K. Values in parentheses denote the uncertainties of experimental measurements and relative deviations of simulated values from experimental values, respectively.

IL	**ρ_{exp} / kg·m^{-3}**	**ρ_{sim} / kg·m^{-3}**	**AAD×100**
$[C_2C_1im][SCN]$	1117.0[a] (±0.5)	1071.2 (±0.1)	4.1
$[C_2C_1im][N(CN)_2]$	1104.0[a] (±0.5)	1061.4 (±0.2)	3.8
$[C_2C_1im][C(CN)_3]$	1081.9[a] (±0.5)	1059.5 (±0.1)	2.1
$[C_2C_1im][B(CN)_4]$	1036.1[a] (±0.5)	1062.4 (±0.4)	2.5

AAD = ABS((ρexp – ρsim) / ρexp)

[a] Taken from Neves et al., *J. Phys. Chem. B*, 2013, **117**, 10271–10283.

Table S6 – Experimental values for glucose solubility in different ILs and water, in a temperature range of (283.15 – 333.15) K.

	T / K	(1000/T) / K^{-1}	x_{glu}	ln(x_{glu})	σ(x_{glu})	σ[ln(x_{glu})]
[C_2C_1im][SCN]	288.25	3.4692	0.1717	-1.7619	0.0039	0.0224
	298.15	3.3540	0.1954	-1.6329	0.0116	0.0592
	318.15	3.1432	0.2390	-1.4315	0.0024	0.0100
	328.15	3.0474	0.2615	-1.3415	0.0046	0.0176
[C_2C_1im][$N(CN)_2$]	288.15	3.4692	0.1452	-1.9299	0.0060	0.0412
	298.15	3.3540	0.1832	-1.6971	0.0126	0.0685
	318.15	3.1432	0.2697	-1.3105	0.0040	0.0148
	328.15	3.0474	0.2983	-1.2096	0.0022	0.0072
[C_2C_1im][$C(CN)_3$]	288.15	3.4692	0.0301	-3.5026	0.0018	0.0592
	298.15	3.3540	0.0375	-3.2831	0.0044	0.1172
	318.15	3.1432	0.0524	-2.9494	0.0039	0.0740
	328.15	3.0474	0.0621	-2.7789	0.0004	0.0069
[C_2C_1im][$B(CN)_4$]	288.15	3.4692	0.0029	-5.8540	0.0004	0.1389
	298.15	3.3540	0.0034	-5.6761	0.0005	0.1370
	318.15	3.1432	0.0042	-5.4821	0.0008	0.1802
	328.15	3.0474	0.0042	-5.4699	0.0006	0.1351
Water[a]	273.15	3.6610	0.0628	-2.7677		
	283.15	3.5317	0.0648	-2.7370		
	293.15	3.4112	0.0843	-2.4736		
	303.15	3.2987	0.1075	-2.2300		
	333.15	3.0017	0.2188	-1.5198		
	353.15	2.8317	0.3056	-1.1855		
Methanol[b]	298.15	3.3540	0.0042	-5.4822		
	308.15	3.2452	0.0062	-5.0820		
	323.15	3.0945	0.0091	-4.7038		
	349.25	2.8633	0.0193	-3.9501		
	360.65	2.7728	0.0311	-3.4718		
[C_4C_1im][SCN]	288.15	3.4692	0.1455	-1.9278	0.0028	0.0189
	298.15	3.3540	0.1696	-1.7744	0.0048	0.0282
	318.15	3.1432	0.2086	-1.5673	0.0150	0.0721
	328.15	3.0474	0.2164	-1.5307	0.0014	0.0063
[C_4C_1im][$N(CN)_2$]	288.15	3.4692	0.1215	-2.1079	0.0090	0.0740
	298.15	3.3540	0.1473	-1.9156	0.0079	0.0534
	318.15	3.1432	0.2201	-1.5135	0.0028	0.0126
	328.15	3.0474	0.2413	-1.4219	0.0174	0.0721

[a]Data taken from Yalkowsky, S. H.; He, Y.; Jain, P. *Handbook of Aqueous Solubility Data*; Second Ed.; CRC Press, 2010.

[b]Data taken from Stephen, H.; Stephen, T. *Solubilities of Inorganic and Organic Compounds*, Vol. 1, Part 2 (Binary systems), Pergamon Press Ltd., Oxford, England, 1963.

Table S7 – Experimental and computational values of density for the mixtures composed of glucose and ionic liquids, at 313.15 K. Values in parentheses denote uncertainty related to the experimental measurements and computational estimation.

$[C_2C_1im][SCN]$+Glucose

$x_{glucose}$	ρ_{exp} / kg·m^{-3}	ρ_{sim} / kg·m^{-3}	AAD×100
0.004	1110.6 (±0.5)	1057.1 (±0.2)	4.82
0.034	1119.7 (±0.5)	1068.6 (±0.1)	4.56
0.06	1127.3 (±0.5)	1078.8 (±0.8)	4.30
0.1	1143.1 (±0.5)	1095.8 (±0.4)	4.14

$[C_2C_1im][N(CN)_2]$+Glucose

$x_{glucose}$	ρ_{exp} / kg·m^{-3}	ρ_{sim} / kg·m^{-3}	AAD×100
0.004	1081.0 (±0.5)	1049.0 (±0.1)	2.96
0.034	1090.3 (±0.5)	1060.3 (±0.4)	2.75
0.06	1109.4 (±0.5)	1071.2 (±0.3)	3.44
0.1	1125.2 (±0.5)	1089.0 (±0.2)	3.22

$[C_2C_1im][C(CN)_3]$+Glucose

$x_{glucose}$	ρ_{exp} / kg·m^{-3}	ρ_{sim} / kg·m^{-3}	AAD×100
0.004		1048.6 (±0.1)	

$[C_2C_1im][B(CN)_4]$+Glucose

$x_{glucose}$	ρ_{exp} / kg·m^{-3}	ρ_{sim} / kg·m^{-3}	AAD×100
0.004		1046.2 (±0.3)	

$AAD = ABS((\rho_{exp} - \rho_{sim}) / \rho_{exp})$

Table S8 – Experimental and computational values of viscosity for the mixtures composed of glucose and ionic liquids, at 313.15 K. Values in parentheses denote uncertainty related to the experimental measurements and computational estimation.

[C_2C_1im][SCN]+Glucose			
$x_{glucose}$	η_{exp} / mPa·s	η_{sim} / mPa·s	AAD
0.004	15.065	8.377 (±0.455)	0.44
0.034	18.667	12.400 (±0.650)	0.34
0.06	24.132	16.874 (±0.876)	0.30
0.1	34.482	30.662 (±0.458)	0.11
[C_2C_1im][$N(CN)_2$]+Glucose			
$x_{glucose}$	η_{exp} / mPa·s	η_{sim} / mPa·s	AAD
0.004	5.396	8.291 (±0.549)	0.54
0.034	6.232	11.990 (±0.586)	0.92
0.06	13.964	13.755 (±0.547)	0.01
0.1	19.107	17.973 (±0.462)	0.06

$AAD = ABS((\eta_{exp} - \eta_{sim}) / \eta_{exp})$

Table S9 – Fitting parameters and decay times obtained using equation 2.

		[C_2C_1im][SCN]+Glucose		
$x_{glucose}$	A	α	τ_1	τ_2
0.004	170.46	1.26E-01	7.82E-02	4.50E-02
0.034	519.63	1.58E-01	1.00E-01	9.49E-03
0.06	433.69	1.27E-01	1.82E-01	1.82E-02
0.1	440.34	1.64E-01	2.87E-01	2.73E-02
		[C_2C_1im][$N(CN)_2$]+Glucose		
$x_{glucose}$	A	α	τ_1	τ_2
0.004	439.44	1.15E-01	9.25E-02	9.97E-03
0.034	279.01	2.88E-02	4.68E-01	3.06E-02
0.06	585.59	1.68E-01	1.00E-01	7.99E-03
0.1	610.15	2.01E-01	1.07E-01	9.83E-03

Table S10 – Coordination numbers (Z) for the systems composed of glucose and water, of glucose and $[C_2C_1im][SCN]$, and of glucose and $[C_2C_1im][N(CN)_2]$.

$x_{glucose}$=0.034				$x_{glucose}$=0.060				$x_{glucose}$=0.100			
WATER (H-bond acceptor)											
Water	Water	Z	r_Z	Water	Water	Z	r_Z	Water	Water	Z	r_Z
O_W	H_W	1.75	0.25	**O_W**	H_W	1.63	0.25	**O_W**	H_W	1.48	0.25
WATER (H-bond donor)											
Water	Glucose	Z	r_Z	Water	Glucose	Z	r_Z	Water	Glucose	Z	r_Z
H_W	OS_5	–	0.25	**H_W**	OS_5	–	0.25	**H_W**	OS_5	–	0.25
	OH_1	1.13	0.25		OH_1	0.99	0.25		OH_1	0.85	0.25
	OH_2	1.16	0.25		OH_2	1.06	0.25		OH_2	0.90	0.25
	OH_3	1.19	0.25		OH_3	1.09	0.25		OH_3	0.95	0.25
	OH_4	1.02	0.25		OH_4	0.93	0.25		OH_4	0.83	0.25
	OH_6	1.35	0.25		OH_6	1.22	0.25		OH_6	1.06	0.25
$[C_2C_1im][SCN]$											
Anion	Cation	Z	r_Z	Anion	Cation	Z	r_Z	Anion	Cation	Z	r_Z
N	H_1	1.22	0.4	**N**	H_1	1.18	0.4	**N**	H_1	1.13	0.4
Cation	Glucose	Z	r_Z	Cation	Glucose	Z	r_Z	Cation	Glucose	Z	r_Z
H_1	OS_5	0.49	0.32	**H_1**	OS_5	0.46	0.32	**H_1**	OS_5	0.44	0.32
	OH_1	–	0.32		OH_1	–	0.32		OH_1	–	0.32
	OH_2	0.48	0.32		OH_2	0.50	0.32		OH_2	0.44	0.32
	OH_3	0.62	0.32		OH_3	0.59	0.32		OH_3	0.55	0.32
	OH_4	0.38	0.32		OH_4	0.35	0.32		OH_4	0.33	0.32
	OH_6	0.53	0.32		OH_6	0.51	0.32		OH_6	0.49	0.32
$[C_2C_1im][N(CN)_2]$											
Anion	Cation	Z	r_Z	Anion	Cation	Z	r_Z	Anion	Cation	Z	r_Z
N	H_1	1.95	0.4	**N**	H_1	1.89	0.4	**N**	H_1	1.83	0.4
Cation	Glucose	Z	r_Z	Cation	Glucose	Z	r_Z	Cation	Glucose	Z	r_Z
H_1	OS_5	0.48	0.32	**H_1**	OS_5	0.50	0.32	**H_1**	OS_5	0.46	0.32
	OH_1	–	0.32		OH_1	–	0.32		OH_1	–	0.32
	OH_2	0.54	0.32		OH_2	0.52	0.32		OH_2	0.50	0.32
	OH_3	0.65	0.32		OH_3	0.61	0.32		OH_3	0.56	0.32
	OH_4	0.35	0.32		OH_4	0.36	0.32		OH_4	0.31	0.32
	OH_6	0.51	0.32		OH_6	0.51	0.32		OH_6	0.49	0.32

Table S11 – Number of molecules of each species in the simulation boxes for systems composed of glucose and ionic liquids.

$x_{glucose}$ in ILs	Number of molecules		
	Glucose	Cation	Anion
0.004 (“infinite dilution”)	1	250	250
0.034	6	170	170
0.060	11	170	170
0.100	20	170	170

Table S12 – Number of molecules of each species in the simulation boxes for systems composed of glucose and water.

$x_{glucose}$ in water	Number of molecules	
	Glucose	Water
0.034	18	510
0.060	33	510
0.100	60	510

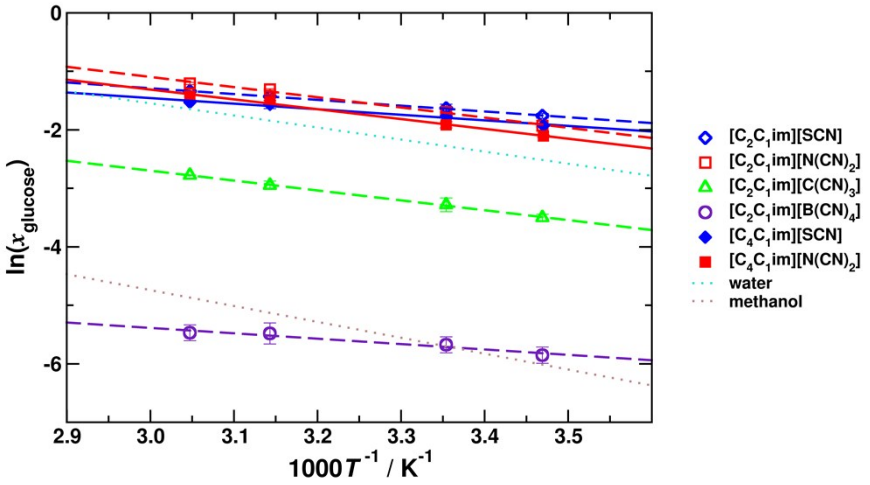


Figure S1 – Glucose solubility as function of 1/T on $[C_2C_1im][N(CN)_2]$, $[C_2C_1im][SCN]$, $[C_4C_1im][N(CN)_2]$, $[C_4C_1im][SCN]$, $[C_2C_1im][C(CN)_3]$, $[C_2C_1im][B(CN)_4]$, water and methanol.

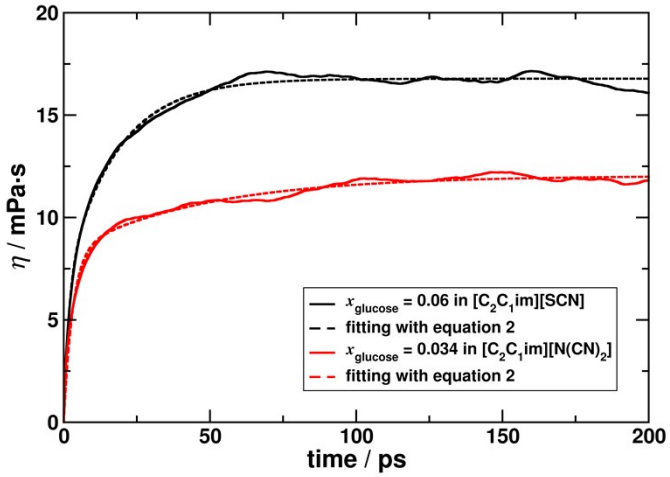


Figure S2 – Viscosities obtained with equation 1 for two glucose molar fractions in $[C_2C_1im][SCN]$ and $[C_2C_1im][N(CN)_2]$ ionic liquids and corresponding fittings obtained with equation 2.

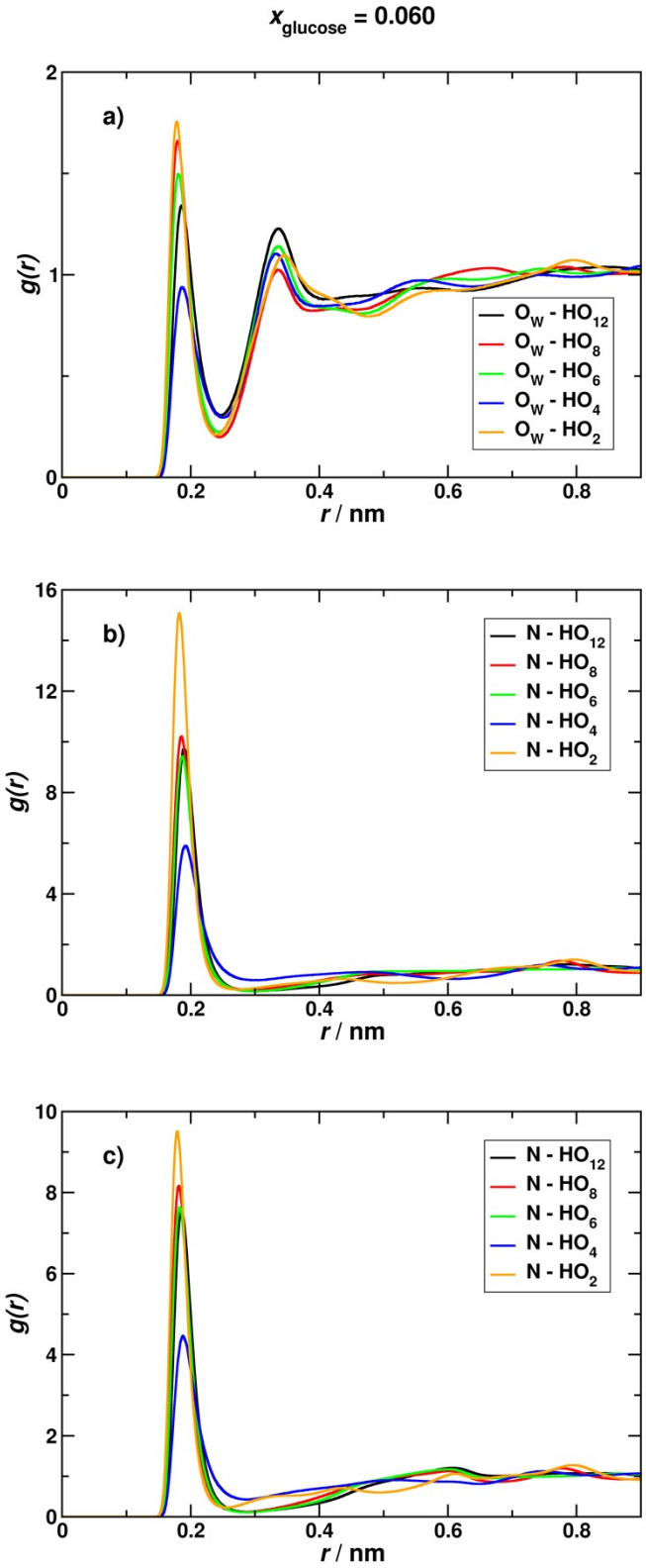
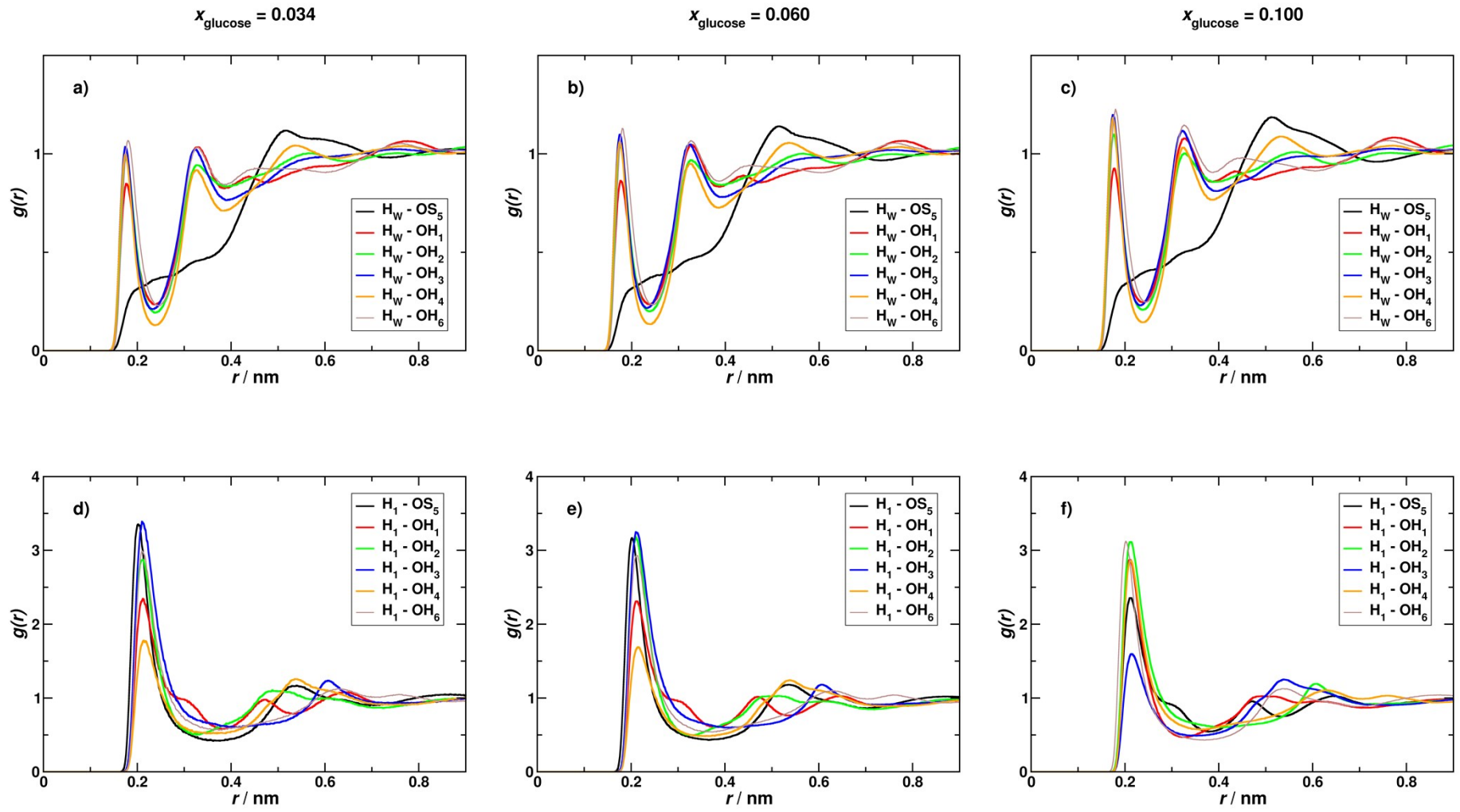


Figure S3 – Radial distributions functions (RDFs) for glucose-water (panel a), glucose-$[C_2C_1im][SCN]$ (panel b) and glucose-$[C_2C_1im][N(CN)_2]$ (panel c) interactions at glucose mole fraction of 0.06, and a temperature of 313.15 K. RDFs for interaction between O_W/N-HO_{12}(—), O_W/N-HO_8(—), O_W/N-HO_6(—), O_W/N-HO_{im}—), O_W/N-HO_2 (—) are represented in this figure.


$x_{glucose}$ = 0.034
$x_{glucose}$ = 0.060
$x_{glucose}$ = 0.100
a)
b)
c)
d)
e)
f)
g(r)
r / nm
H_W - OS_5
H_W - OH_1
H_W - OH_2
H_W - OH_3
H_W - OH_4
H_W - OH_6
H_1 - OS_5
H_1 - OH_1
H_1 - OH_2
H_1 - OH_3
H_1 - OH_4
H_1 - OH_6

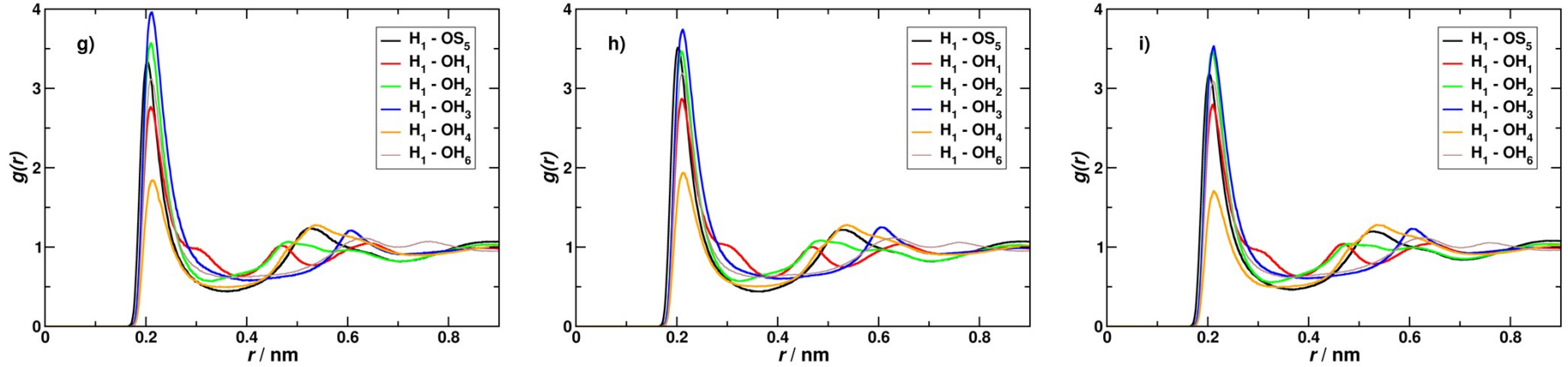


Figure S4 – Radial distributions functions (RDFs) for glucose-water (panels a-c), glucose-[C_2C_1im][SCN] (panels d-f) and glucose-[C_2C_1im][$N(CN)_2$] (panels g-i) interactions at three different glucose concentrations and a temperature of 313.15 K. RDFs for interaction between H_W/H_1-OS_5(—), H_W/H_1-OH_1(—), H_W/H_1-OH_2(—), H_W/H_1-OH_3(—), H_W/H_1-OH_4(—), H_W/H_1-OH_4(—) are represented in this figure.

References

(1) Freire, M. G.; Carvalho, P. J.; Gardas, R. L.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. Mutual Solubilities of Water and the [C N mim][Tf 2 N] Hydrophobic Ionic Liquids. *J. Phys. Chem. B* **2008**, *112* (6), 1604–1610.

(2) Freire, M. G.; Carvalho, P. J.; Gardas, R. L.; Santos, L. M. N. B. F.; Marrucho, I. M.; Coutinho, J. A. P. Solubility of Water in Tetradecyltrihexylphosphonium-Based Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53* (10), 2378–2382.