Electronic Supplementary Information

Solubility and solvation of monosaccharides in ionic liquids

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Table S1. Weight percentage (wt%) of water in the studied monosaccharides and ionic liquids.

Compound	Water Content (wt%)
D-(+)-glucose	0.598
D-(+)-mannose	0.654
D-(-)-fructose	0.080
D-(+)-galactose	0.373
D-(+)-xylose	0.142
L-(+)-arabinose	0.510
$[C_4C_1im][N(CN)_2]$	0.010
$[C_4C_1im][(OCH_3)_2PO_4]$	0.078
$[P_{6\,6\,6\,14}][N(CN)_2]$	0.033
$[P_{6\,6\,6\,14}]Cl$	0.163

Table S2. Mole fraction solubility of monosaccharides in [C_4C_1im][$N(CN)_2$] at different temperatures, and comparison with data from the literature.

	D-(+)-glucose				**D-(-)-fructose**		
	$x_{Glucose}$ (±σ)				$x_{Frustose}$ (±σ)		
***T* / K**	This work	Carneiro *et al.*[1]	Paduszynski *et al.*[2]	Liu *et al.*[3]	This work	Carneiro *et al.*[1]	Paduszynski *et al.*[2]
288	0.142 (±0.007)	0.133			0.132 (±0.005)	0.281	
298	0.170 (±0.009)	0.165		0.146	0.153 (±0.004)	0.310	0.11
308	0.191 (±0.006)	0.192	0.186	0.210	0.178 (±0.004)	0.340	
318	0.229 (±0.010)	0.210	0.217		0.201 (±0.005)	0.378	0.174
328	0.250 (±0.007)	0.236	0.276		0.220 (±0.006)	0.410	0.202
338	0.280 (±0.004)		0.335		0.245 (±0.008)		0.257
345			0.391				0.344
348	0.319 (±0.005)		0.441	0.398	0.275 (±0.009)		0.402
355			0.496				0.465
358			0.542				
361			0.606				0.541
366			0.766				0.648
368							0.749

Table S3. Mole fraction solubility of D-(+)-glucose in $[P_{6,6,6,14}][N(CN)_2]$ at different temperatures, and comparison with data from the literature.

Monosaccharide	**D-(+)-glucose**		
***T* / K**	$x_{Glucose}$ **(±σ)**		
	This work	Carneiro *et al.*[1]	Rosatella *et al.*[4]
288	0.007 (±0.001)	0.0018	
298	0.009 (±0.002)	0.0024	
308	0.012 (±0.001)	0.0037	0.0151
318	0.013 (±0.001)	0.0048	
328	0.018 (±0.001)		
338	0.027 (±0.003)		
348	0.029 (±0.002)		

Table S4. Fitting parameters of the linear function corresponding to the solubility of monosaccharides, as the natural logarithm of the mole fraction, $\ln x_{Glucose}$, in the studied ILs, *versus* the reciprocal temperature (1/*T*).

Monosaccharide	**Linear equation**	R^2
	[C_4C_1im][$N(CN)_2$]	
D-(+)-glucose	$\ln x = -1331.6 \cdot 1/T + 2.680$	0.9978
D-(+)-mannose	$\ln x = -1353.6 \cdot 1/T + 2.920$	0.9965
D-(-)-fructose	$\ln x = -1203.1 \cdot 1/T + 2.164$	0.9967
D-(+)-galactose	$\ln x = -1240.8 \cdot 1/T + 2.368$	0.9952
D-(+)-xylose	$\ln x = -1327.4 \cdot 1/T + 2.896$	0.9974
L-(+)-arabinose	$\ln x = -1260.3 \cdot 1/T + 2.423$	0.9979
	[C_4C_1im][$(OCH_3)_2PO_4$]	
D-(+)-glucose	$\ln x = -3872.2 \cdot 1/T + 10.006$	0.9837
D-(+)-mannose	$\ln x = -4084.5 \cdot 1/T + 10.672$	0.9956
D-(-)-fructose	$\ln x = -4112.2 \cdot 1/T + 10.138$	0.9885
D-(+)-galactose	$\ln x = -3490.3 \cdot 1/T + 9.511$	0.9849
D-(+)-xylose	$\ln x = -3779.1 \cdot 1/T + 10.632$	0.9838
L-(+)-arabinose	$\ln x = -3729.2 \cdot 1/T + 9.949$	0.9986
	[$P_{6,6,6,14}$][$N(CN)_2$]	
D-(+)-glucose	$\ln x = -2434.9 \cdot 1/T + 3.455$	0.9803
	[$P_{6,6,6,14}$]Cl	
D-(+)-glucose	$\ln x = -3984.1 \cdot 1/T + 8.838$	0.9727

Table S5. Melting temperature, T_m (in K), and thermodynamic solution properties (in kJ·mol^{-1}) of monosaccharides in water and methanol at 298 K: enthalpy of melting, ΔH_m, enthalpy of solution, ΔH_{sol}, entropy of solution, $T\Delta S_{sol}$, Gibbs free energy of solution, G_{sol}, and respective uncertainties (within brackets).

Monosaccharide	ΔH_m	T_m (K)	ΔH_{sol}	$T\Delta S_{sol}$	ΔG_{sol}	ΔH_{sol}	$T\Delta S_{sol}$	ΔG_{sol}
			Water			Methanol		
D-(+)-glucose	32.3[20]	423.2[21]	19.41	13.61	5.80	28.08	14.05	14.03
D-(+)-mannose	24.7[20]	407.2[20]	---[a]	---[a]	---[a]	34.15	22.19	11.96
D-(-)-fructose	26.0[22]	378.2[23]	11.32	8.24	3.09	47.51	37.83	9.68
D-(+)-galactose	43.8[20]	436.2[20]	17.07	9.72	7.35	33.99	16.96	17.02
D-(+)-xylose	31.7[20]	423.2[21]	13.51	8.42	5.09	38.64	25.50	13.14
L-(+)-arabinose	35.8[20]	428.7[22]	11.31	3.99	7.32	36.78	21.85	14.93

[a]Insufficient available data for a coherent analysis

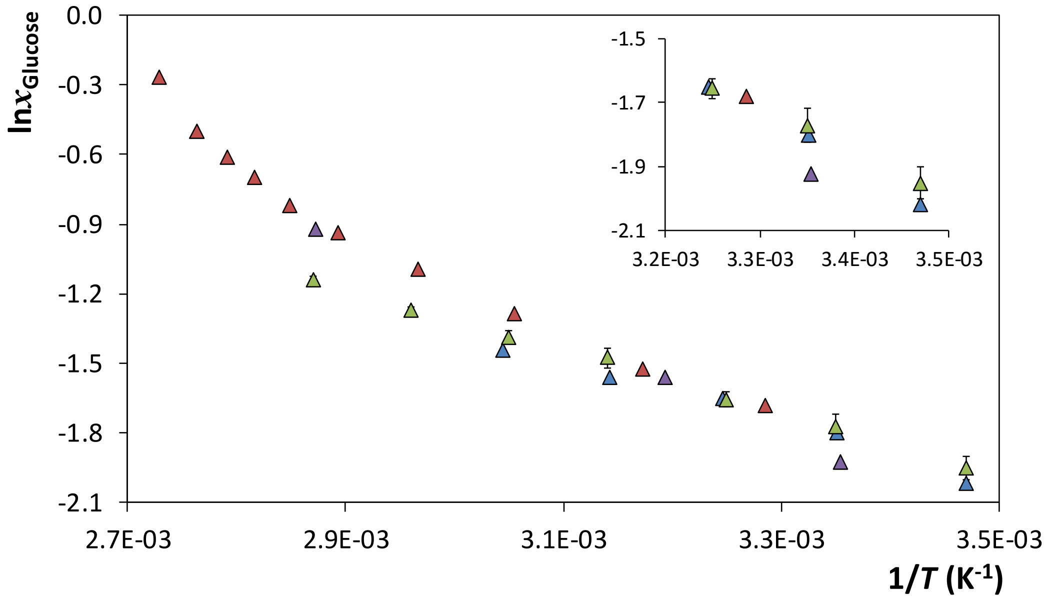

Figure S1. Solubility of D-(+)-glucose, as the natural logarithm of the mole fraction ($\ln x_{Glucose}$), in $[C_4C_1im][N(CN)_2]$, *versus* the reciprocal temperature (1/*T*): ▲, This work; ▲, Carneiro *et al.*;[1] ▲, Paduszynski *et al.*;[2] and ▲, Liu *et al.*[3]

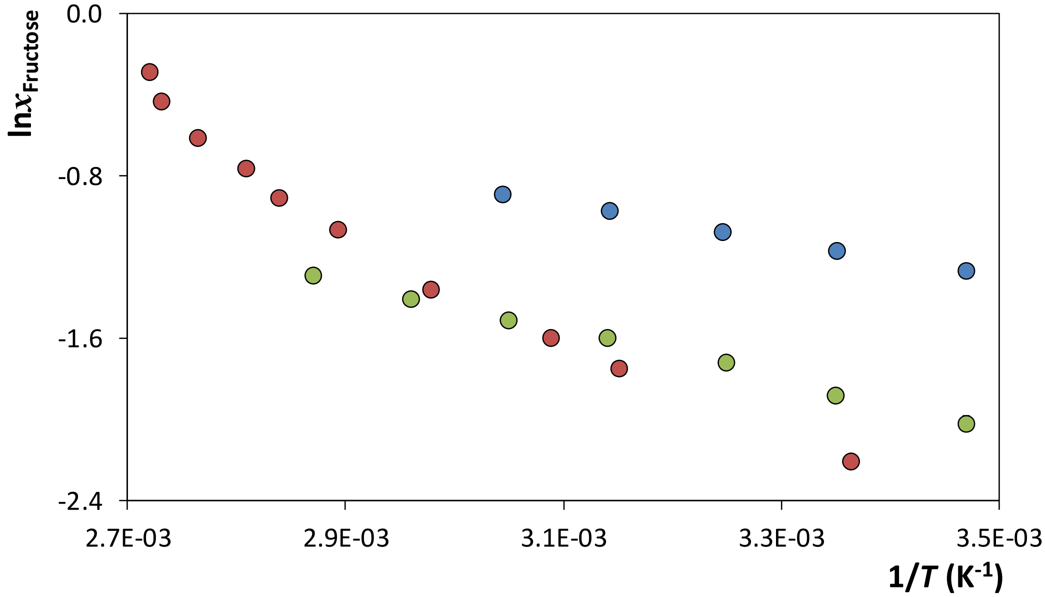

Figure S2. Solubility of D-(-)-fructose, as the natural logarithm of the mole fraction ($\ln x_{\text{Fructose}}$), in $[C_4C_1\text{im}][N(CN)_2]$, *versus* the reciprocal temperature ($1/T$): ●, This work; ●, Carneiro *et al.*;[1] and ●, Paduszynski *et al.*[2]

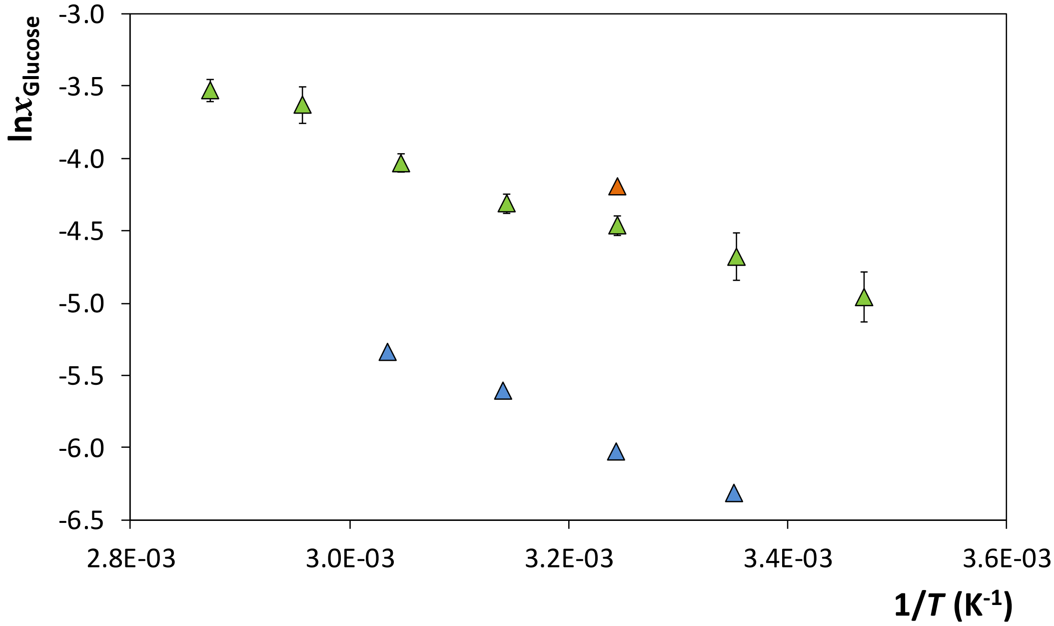

Figure S3. Solubility of D-(+)-glucose, as the natural logarithm of the mole fraction ($\ln x_{\mathrm{Glucose}}$), in $[P_{6,6,6,14}][N(CN)_2]$, *versus* the reciprocal temperature (1/*T*): ▲, This work; ▲, Carneiro *et al.*;[1] and ▲, Rosatella *et al.*[4]

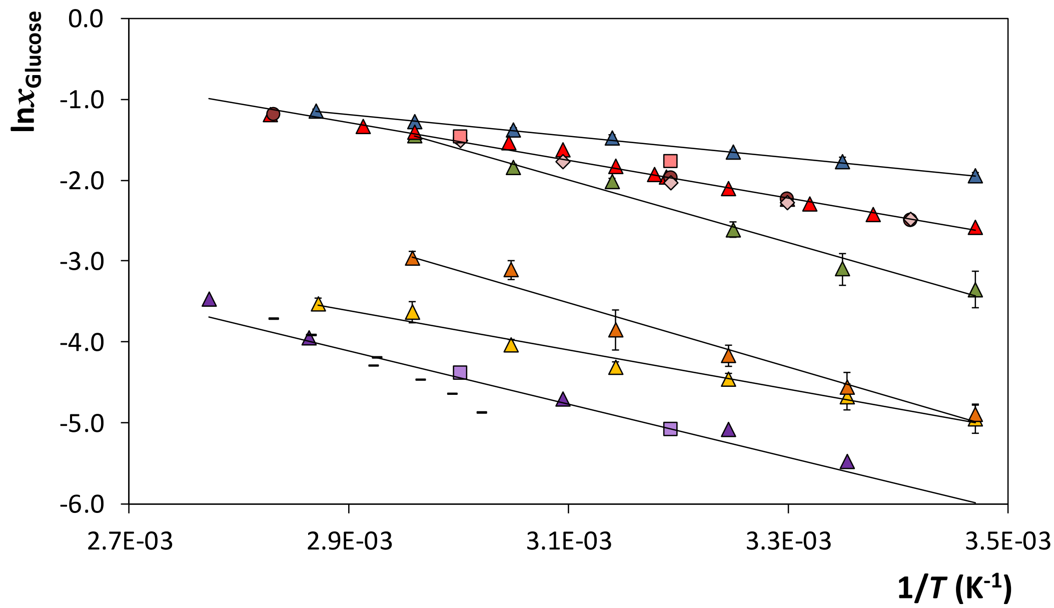

Figure S4. Solubility of D-(+)-glucose, as the natural logarithm of the mole fraction ($\ln x_{Glucose}$), in the studied ionic liquids, water and methanol, *versus* the reciprocal temperature (1/*T*): ▲, $[C_4C_1im][N(CN)_2]$; ▲, $[C_4C_1im][(OCH_3)_2PO_2]$; ▲, $[P_{66614}]Cl$; ▲, $[P_{66614}][N(CN)_2]$; ▲, water from Stephen and Stephen;[5] ●, water from Mullin;[6] ◆, water from Alves *et al.*;[7] ■, water from Peres and Macedo;[8] ▲, methanol from Stephen and Stephen;[5] ■, methanol from Peres and Macedo;[8] and ▪, methanol from Putten *et al.*[9]

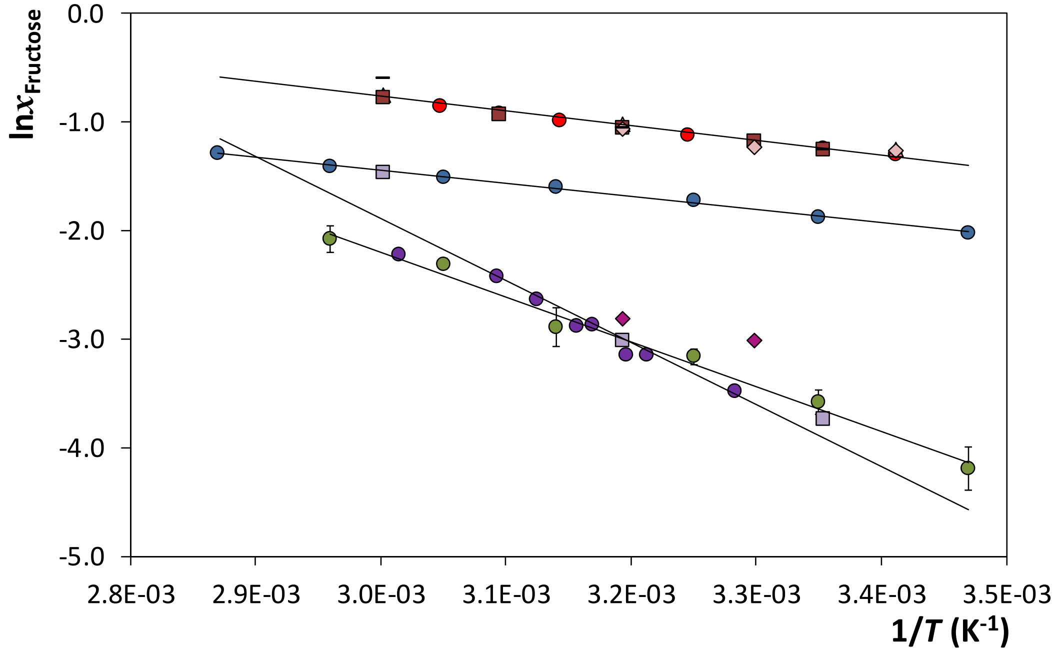

Figure S5. Solubility of D-(-)-fructose, as the natural logarithm of the mole fraction ($\ln x_{Fructose}$) in the studied ionic liquids, water and methanol, *versus* the reciprocal temperature (1/*T*): ●, $[C_4C_1im][N(CN)_2]$; ●, $[C_4C_1im][(OCH_3)_2PO_2]$; ▲, water from Mullin;[6] ●, water from Jackson *et al.*;[10] ■, water from Crestani *et al.*;[11] ◆, water from Alavi *et al.*;[12] ●, methanol from Putten *et al.*;[9] ■, methanol from Peres and Macedo;[13] and ◆, methanol from Montañés *et al.*[14]

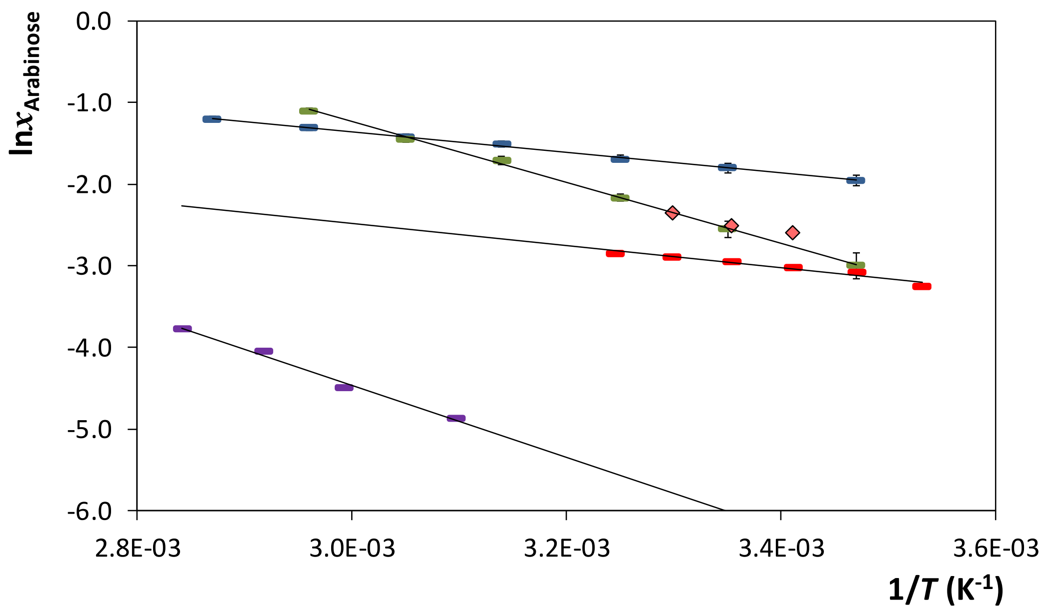

Figure S6. Solubility of L-(+)-arabinose, as the natural logarithm of the mole fraction (ln$x_{Arabinose}$) in the studied ionic liquids, water and methanol, *versus* the reciprocal temperature (1/*T*): -, $[C_4C_1im][N(CN)_2]$; -,$[C_4C_1im][(OCH_3)_2PO_2]$; -, water from Jiang *et al.*;[15] ◆, water from Gray *et al*;[16] and -, methanol from Putten *et al.*[9]

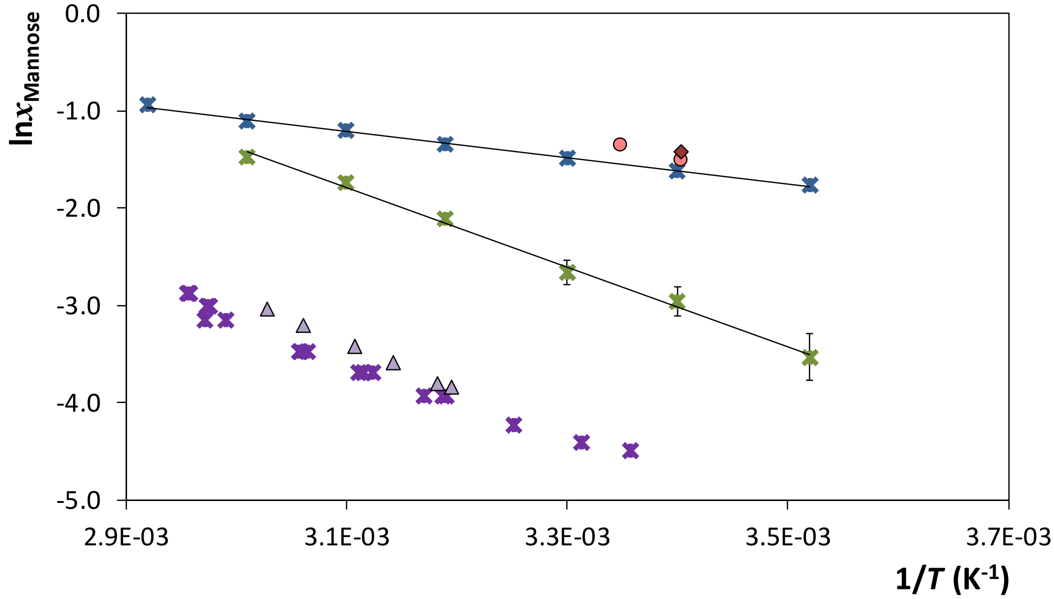

Figure S7. Solubility of D-(+)-mannose, as the natural logarithm of the mole fraction ($\ln x_{\text{Mannose}}$) in the studied ionic liquids and water, *versus* the reciprocal temperature ($1/T$): ✱, $[C_4C_1im][N(CN)_2]$; ✱, $[C_4C_1im][(OCH_3)_2PO_2]$; ▲, methanol from Stephen and Stephen;[5] and ✱, methanol from Putten *et al.*[9]

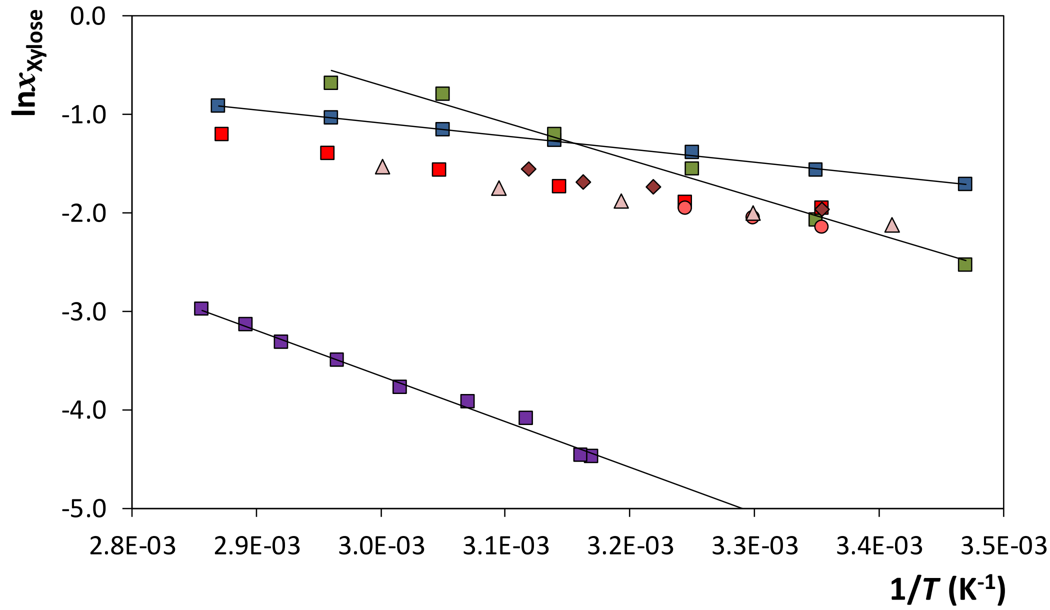

Figure S8. Solubility of D-(+)-xylose, as the natural logarithm of the mole fraction ($\ln x_{\mathrm{Xylose}}$) in the studied ionic liquids, water and methanol, *versus* the reciprocal temperature ($1/T$): ■, $[C_4C_1im][N(CN)_2]$; ■,$[C_4C_1im][(OCH_3)_2PO_2]$; ●, water from Gray *et al*;[16] ■, water from Jónsdóttir *et al.*;[17] ◆, water from Goldberg *et al.*;[18] ▲, water from Martínez *et al.*;[19] and ■, methanol from Putten *et al.*[9]

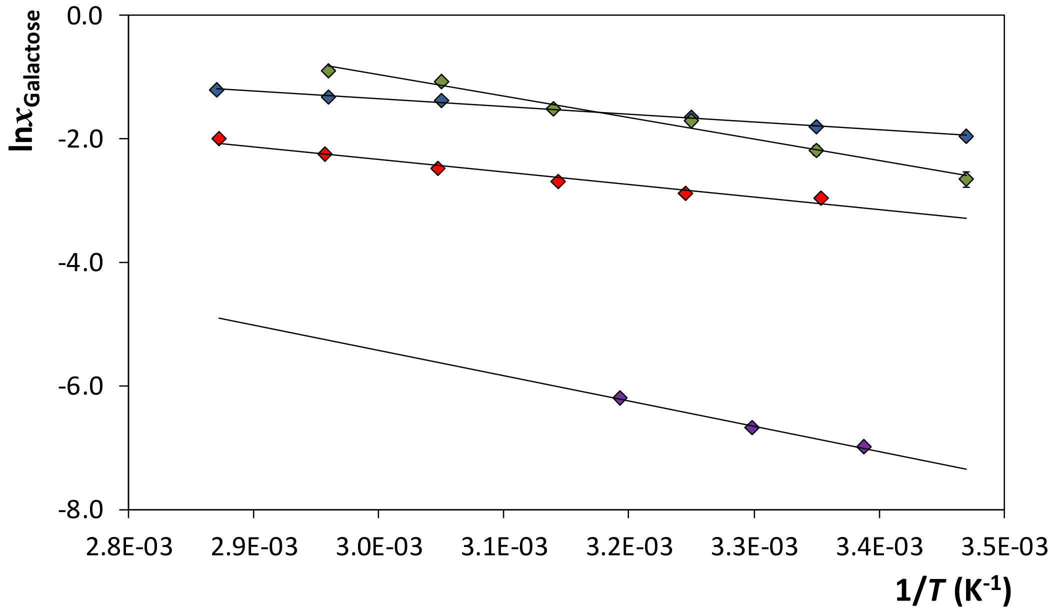

Figure S9. Solubility of D-(+)-galactose, as the natural logarithm of the mole fraction ($\ln x_{\text{Galactose}}$) in the studied ionic liquids, water and methanol, *versus* the reciprocal temperature ($1/T$): ◆, [C_4C_1im][$N(CN)_2$]; ◆, [C_4C_1im][$(OCH_3)_2PO_2$]; ◆, water from Jónsdóttir *et al.*;[17] and ◆, methanol from Montañés *et al.*[14]

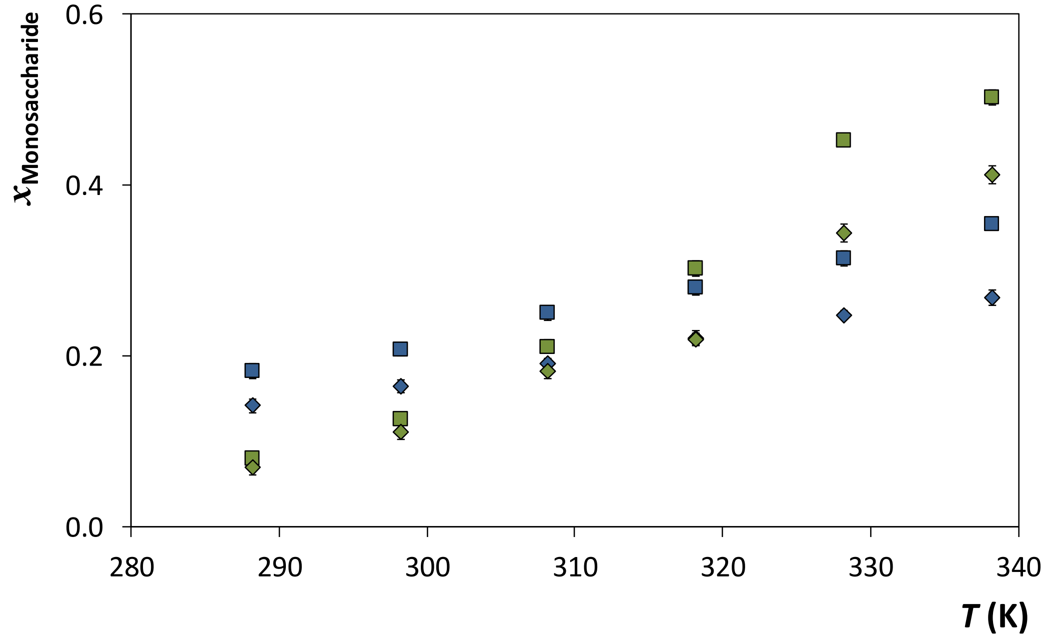

Figure S10. Mole fraction solubility of D-(+)-xylose (square dots) and D-(+)-galactose (diamond dots) in ionic liquids: ■, $[C_4C_1im][N(CN)_2]$; ■, $[C_4C_1im][(OCH_3)_2PO_2]$; ◆, $[C_4C_1im][N(CN)_2]$; and ◆, $[C_4C_1im][(OCH_3)_2PO_2]$.

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