Molecular Dynamics Simulation Studies of the Interactions between Ionic Liquids and Amino Acids in Aqueous Solution

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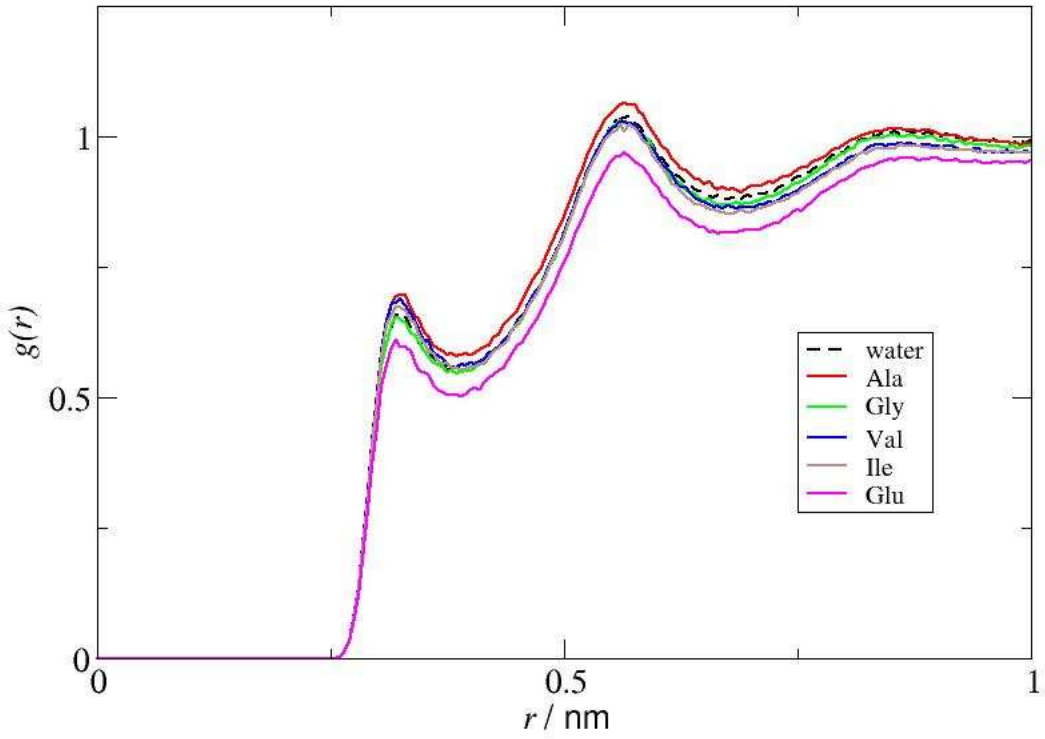
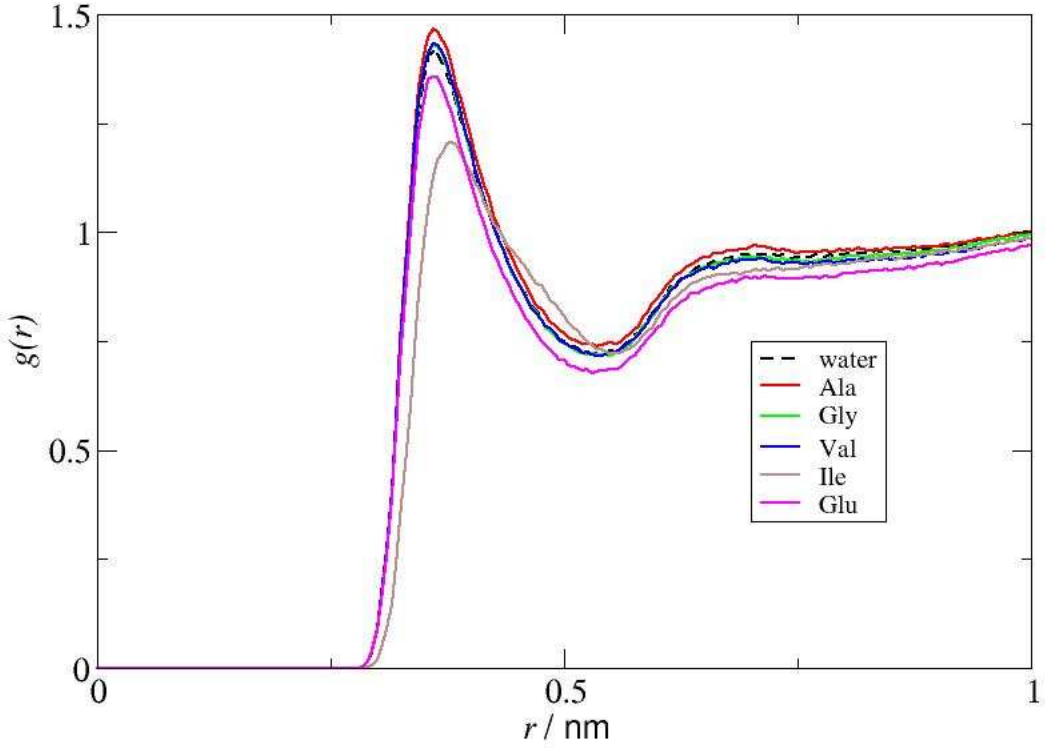
This Supporting Information contains: additional RDFs that emphasize the discussion in the main paper; a snapshot from a simulation of Ile mixtures; full set of electrostatic charges for the IL model; values of *r* (nm) at which the corresponding RDFs were truncated to calculate the coordination numbers presented in Tables 2 and 3 of the main paper.

C_3 (cation)_O (H_2O)



Ct_m (cation)_O (H_2O)



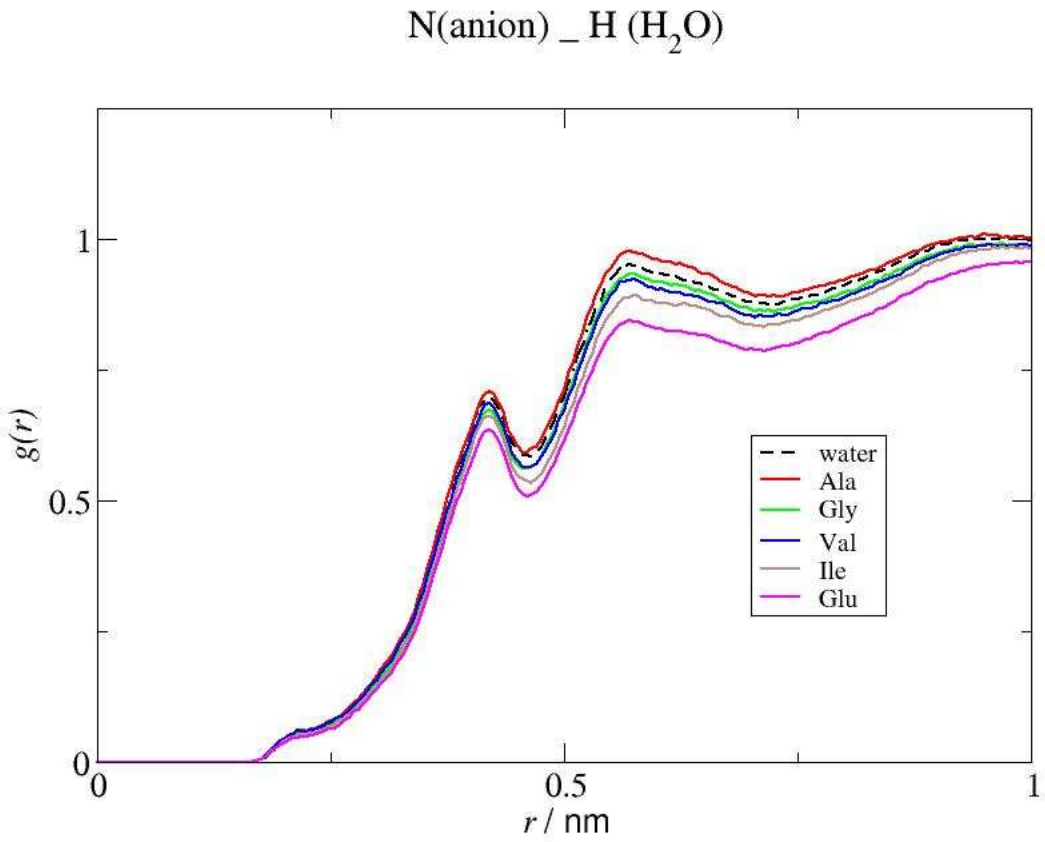


Figure S1. Radial distribution functions of the water oxygen atoms around the C_3 and Ct_m atoms of the IL cation and of the water hydrogen atoms around the N atom of the IL anion, in the IL+water binary system or in the IL+water+amino acid ternary systems.

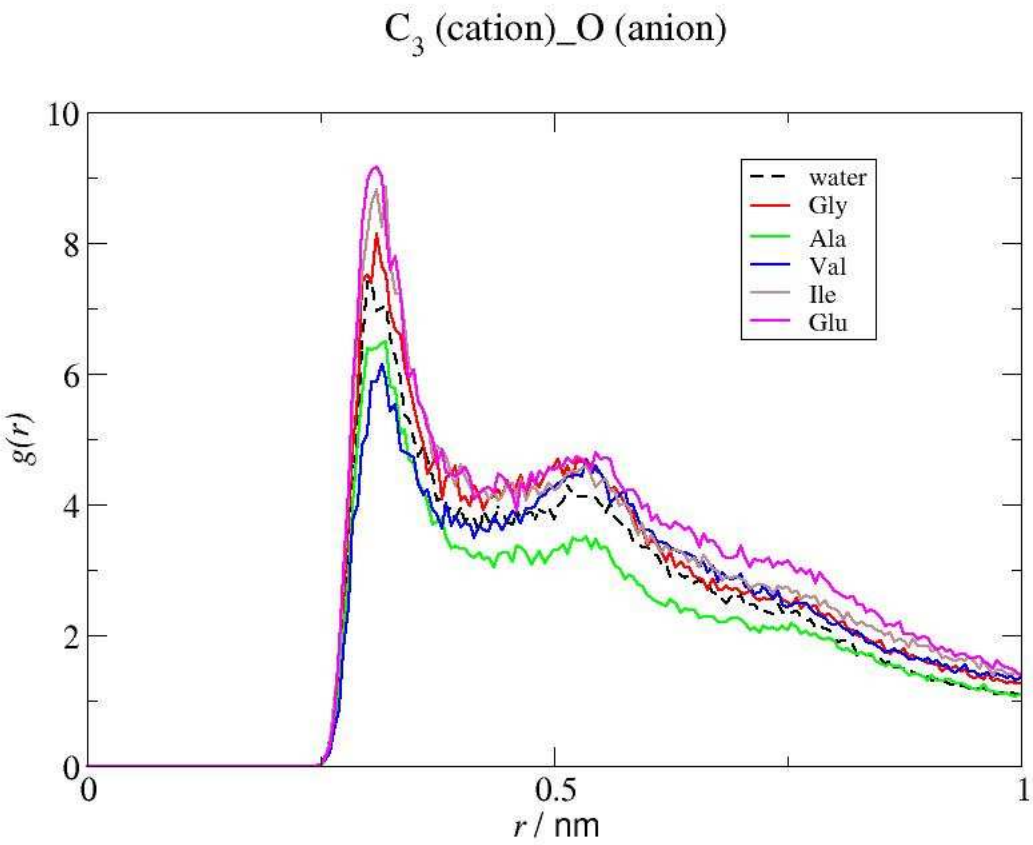


Figure S2. Radial distribution functions for the interactions between the C_3 atom of the IL cation and the oxygen atom of the IL anion, in the IL+water binary system or in the IL+water+amino acid ternary systems.

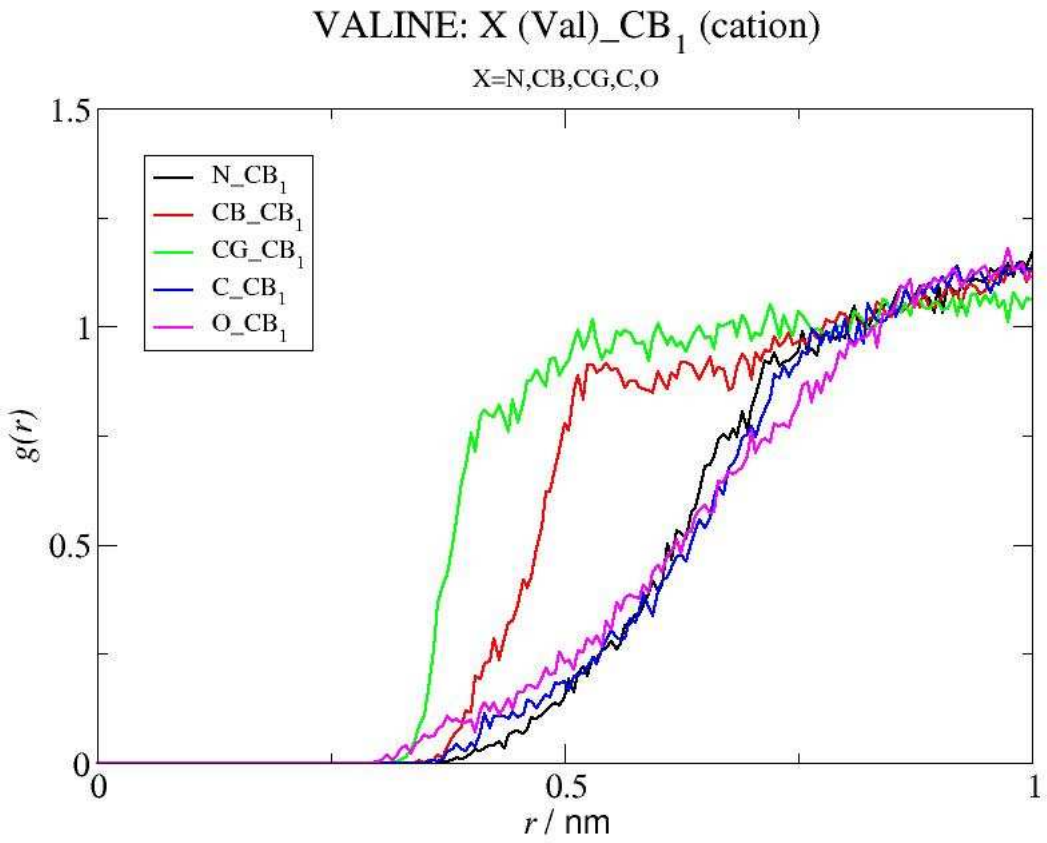


Figure S3. Radial distribution functions between different molecular regions of Val and the CB_1 atom of the IL cation.

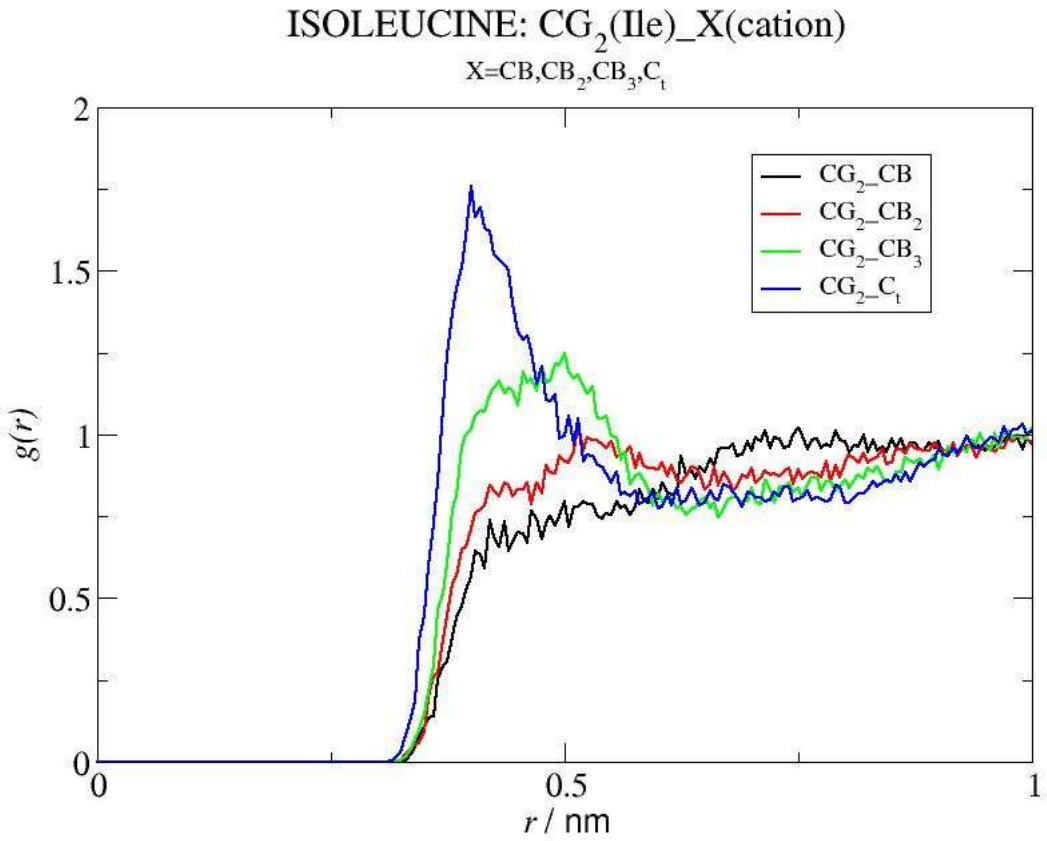


Figure S4. Radial distribution functions of the carbon atoms of the alkyl chain of the IL cation (Ct_b and CB_x) around the CG_2 atom of Ile.

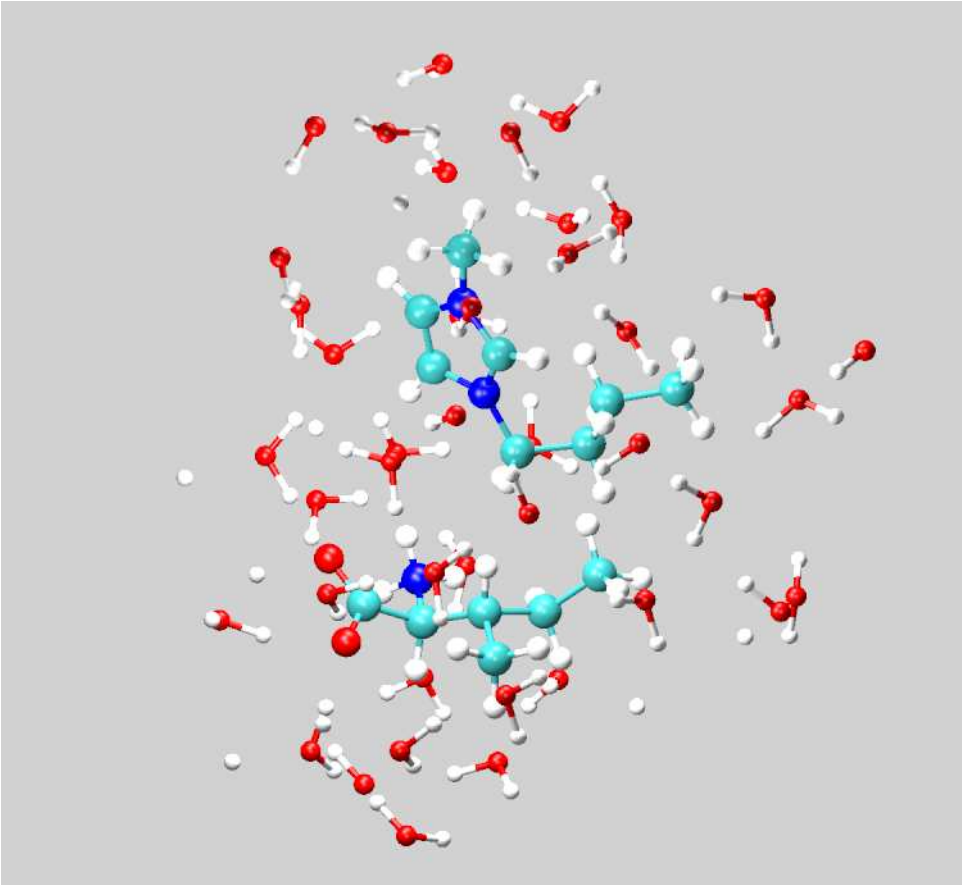


Figure S5. Snapshots from a simulation of Ile mixtures. Only water molecules that are within a distance of 4Å from either [C4mim] or Ile are displayed. The distances (Å) between the CG atoms of Ile and the carbon atoms of the cation's alkyl chain are the following: (CG_1···CB_1), 4.74; (CG_2···CB_1), 4.15; (CG_2···CB_2), 3.82; (CG_2···CB_3), 3.98; (CG_2···C_t), 4.60.

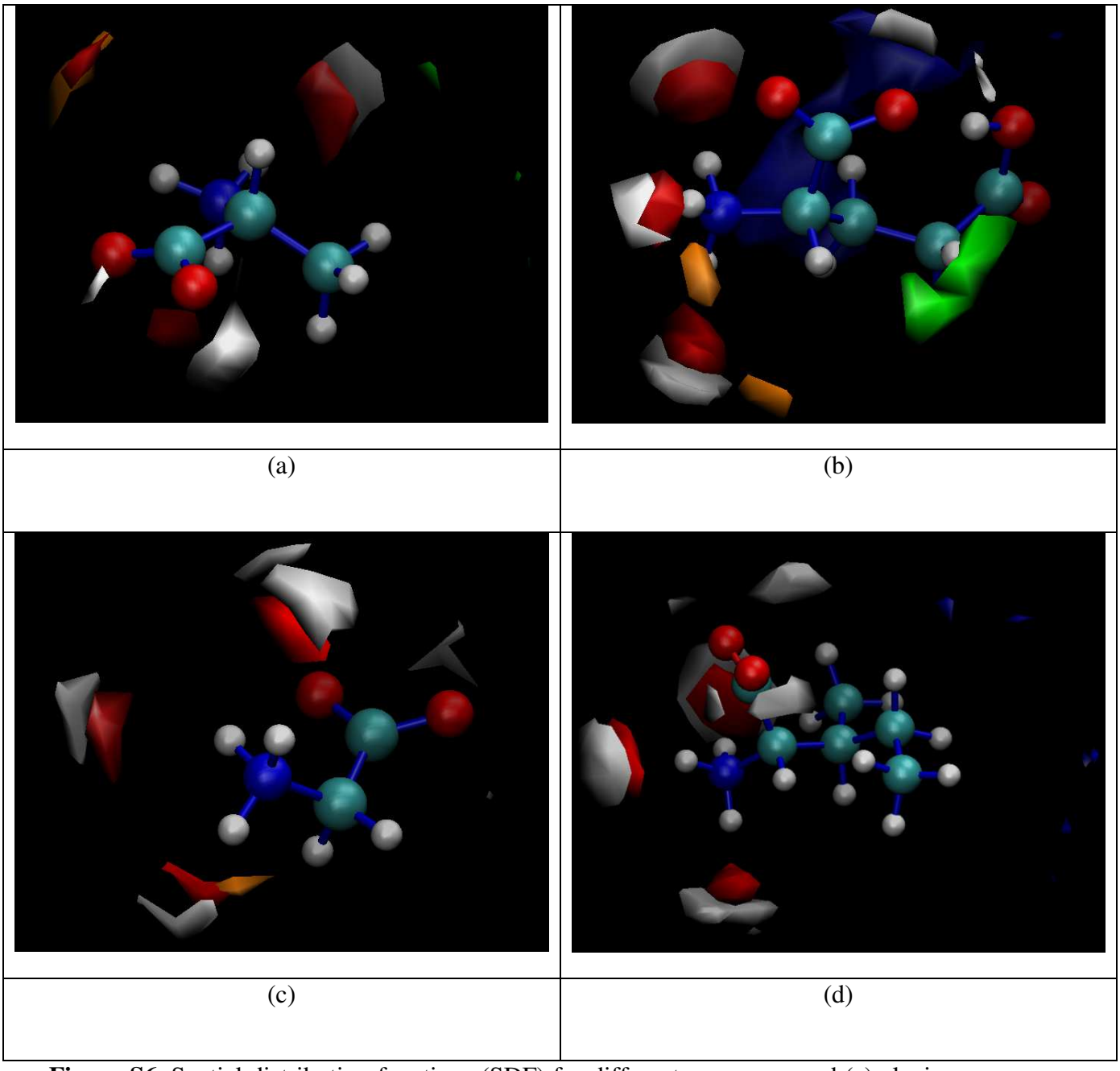


Figure S6. Spatial distribution functions (SDF) for different groups around (a) alanine, (b) glutamic acid, (c) glycine and (d) isoleucine amino acids. Orange: O atoms of the IL anion; blue: Ct_b atom of the IL cation; green: F atoms of the IL anion; red: O atoms of water; white: H atoms of water.

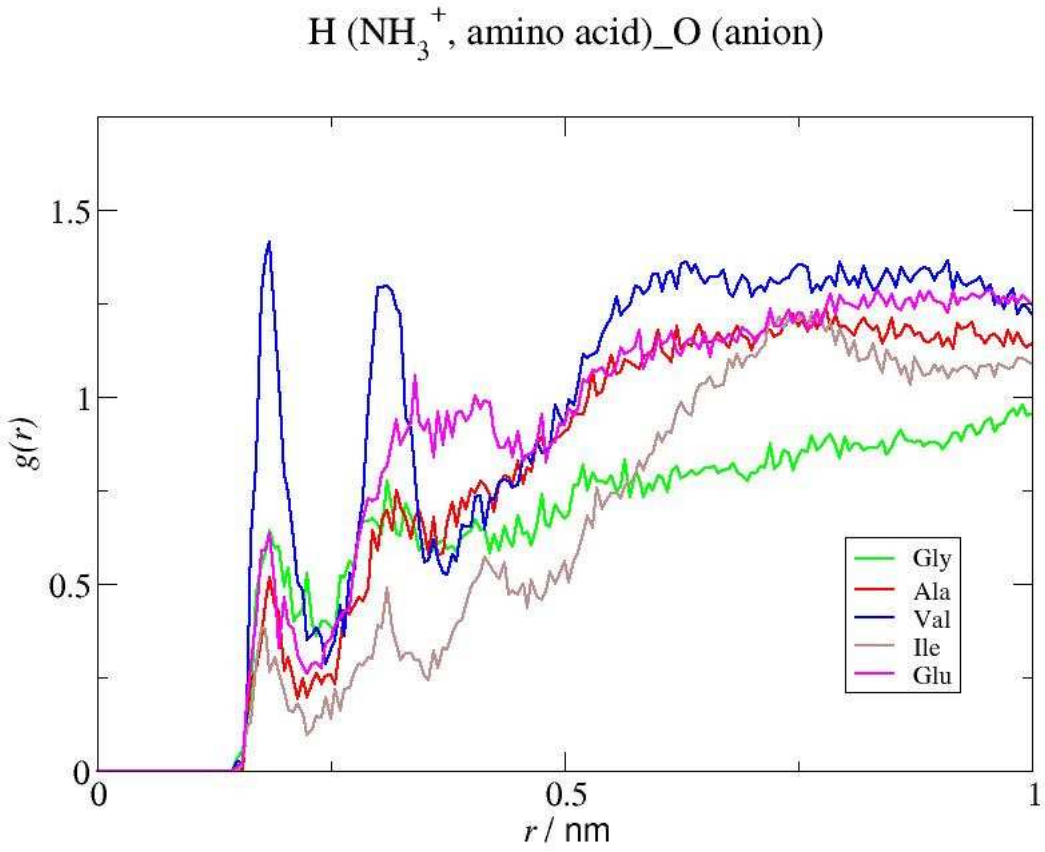


Figure S7. Radial distribution functions for the interactions between the amino hydrogen atoms of the amino acids and the oxygen atom of the IL anion, in the IL+water+amino acids ternary systems.

Table S1. Electrostatic Charges for [C4mim][NTf_2]. Atom numbering corresponds to the adjacent diagram.

1 C	0.532410
2 F	-0.157342
3 S	1.004848
4 O	-0.572554
5 N	-0.620594
6 S	0.999532
7 O	-0.512814
8 O	-0.507261
9 F	-0.192904
10 F	-0.211239
11 C	0.537681
12 F	-0.158906
13 O	-0.544733
14 F	-0.193540
15 F	-0.224617
16 C	0.082606
17 N	0.090388
18 C	-0.148077
19 C	-0.198418
20 N	0.099140
21 C	-0.132946
22 C	-0.033804
23 C	0.091484
24 C	0.224910
25 C	-0.291828
26 H	0.093276
27 H	0.185123
28 H	0.207250
29 H	0.094969
30 H	0.148320
31 H	0.092489
32 H	0.067348
33 H	0.054838
34 H	-0.037601
35 H	-0.013229
36 H	-0.009512
37 H	-0.047412
38 H	0.059390
39 H	0.070012
40 H	0.073316

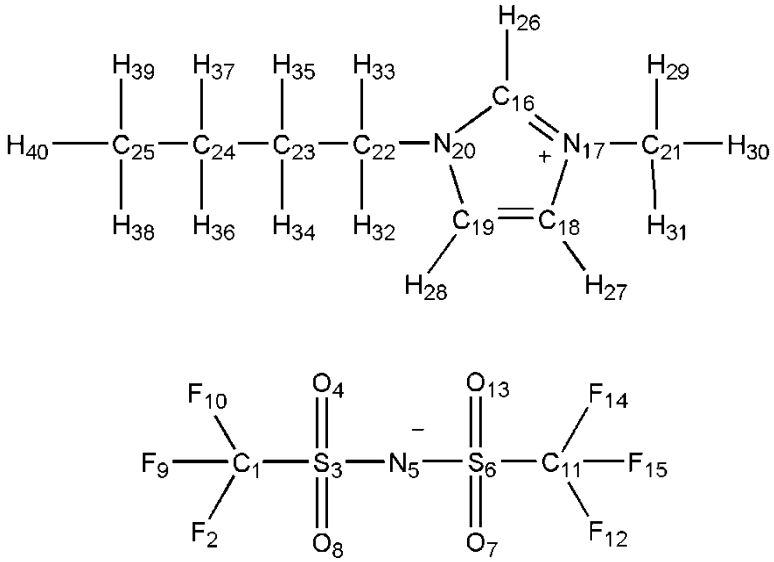


Table S2. Position and intensities of the RDF peak maxima corresponding to the interactions of selected groups of Gly with water and with selected groups of the IL cation and IL anion.

Gly	**O(H_2O)**		**H(H_2O)**		**O(anion)**		**F(anion)**		**Ct_b(cation)**	
	r / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*
N(NH_3^+)					0.280	1.495				
					0.520	0.878				
H(NH_3^+)	0.175	1.778			0.185	0.637				
	0.320	1.280			0.310	0.770				
O(COO^-)			0.165	3.250						
			0.310	1.313						
$C_{terminal}$ (CA)							0.360	0.880	0.405	0.459
							0.535	0.837		

Table S3. Position and intensities of the RDF peak maxima corresponding to the interactions of selected groups of Ala with water and with selected groups of the IL cation and IL anion.

Ala	**O(H_2O)**		**H(H_2O)**		**O(anion)**		**F(anion)**		**Ct_b(cation)**	
	r / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*
N(NH_3^+)					0.280	1.533				
					0.530	1.265				
H(NH_3^+)	0.175	1.777			0.185	0.513				
	0.320	1.196			0.320	0.743				
O(COO^-)			0.165	3.020						
			0.310	1.201						
$C_{terminal}$ (CB)							0.340	1.635	0.395	0.881
							0.545	1.143		

Table S4. Position and intensities of the RDF peak maxima corresponding to the interactions of selected groups of Val with water and with selected groups of the IL cation and IL anion.

Val	O(H_2O)		H(H_2O)		O(anion)		F(anion)		Ct_b(cation)	
	r / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*
N(NH_3^+)					0.281	3.180	0.630	1.626	0.661	1.082
					0.515	1.329				
H(NH_3^+)	0.175	1.830			0.185	1.410	0.600	1.411		
	0.315	1.154			0.300	1.291				
C(COO^-)					0.690	1.328	0.866	1.438	0.720	1.213
O(COO^-)			0.165	2.987	0.790	1.282	0.805	1.423	0.776	1.151
			0.310	1.202						
$C_{terminal}$ (CG)					0.360	2.657	0.340	2.184	0.405	2.062
							0.535	1.697		
$C_{terminal}$ (CB)					0.465	2.261	0.460	2.005	0.500	1.798

Table S5. Position and intensities of the RDF peak maxima corresponding to the interactions of selected groups of Ile with water and with selected groups of the IL cation and IL anion.

Ile	O(H_2O)		H(H_2O)		O(anion)		F(anion)		Ct_b(cation)	
	r / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*
N(NH_3^+)					0.280	0.841				
					0.510	0.860				
H(NH_3^+)	0.175	1.929			0.175	0.379				
	0.315	1.205			0.310	0.487				
O(COO^-)			0.165	3.226						
			0.310	1.265						
$C_{terminal}$ (CG2)							0.359	1.540	0.400	1.753
							0.520	1.331		
$C_{terminal}$ (CD)							0.355	1.775	0.395	2.255
							0.535	1.605		

Table S6. Position and intensities of the RDF peak maxima corresponding to the interactions of selected groups of Glu with water and with selected groups of the IL cation and IL anion.

Glu	O(H_2O)		H(H_2O)		O(anion)		F(anion)		Ct_b(cation)		C_3(cation)	
	r / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*
N(NH_3^+)					0.177	1.989						
					0.505	1.434						
H(NH_3^+)	0.175	1.958			0.185	0.626						
	0.320	1.206			0.340	1.050						
O(COO^-)			0.165	2.976								
			0.310	1.175								
$C_{terminal}$ (CG)							0.350	2.438	0.425	2.077		
							0.520	1.995				
$C_{terminal}$ (CD)							0.380	2.357	0.450	2.963		
							0.470	2.087				
CD(COOH)	0.350	1.149	0.418	1.009	0.417	2.232	0.380	2.381	0.450	2.966	0.385	3.031
											0.581	2.117
OE_1(COOH)	0.285	0.800	0.186	0.643	0.350	2.055	0.345	2.035	0.380	2.657	0.310	3.124
			0.533	0.900			0.516	2.148			0.530	2.147
OE_2(COOH)	0.265	1.239	0.193	0.239	0.510	2.094	0.335	2.265	0.375	3.013	0.310	3.628
							0.505	2.267			0.540	2.249
HE_2(COOH)	0.170	2.552	0.240	1.042	0.405	2.070	0.400	2.097	0.410	2.634	0.380	2.539
			0.461	0.905							0.551	2.063

Table S7. Position and intensities of the RDF peak maxima corresponding to the interactions of selected groups of the IL cation and of the IL anion with water and to cation-cation interactions, in the IL+water binary system or in the IL+water+amino acid ternary systems.

	water		**Gly**		**Ala**		**Val**		**Ile**		**Glu**	
	r / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*	*r* / nm	*g(r)*
Ct_b(cation)···O(H_2O)	0.375	1.249	0.378	1.240	0.378	1.285	0.378	1.199	0.379	1.203	0.380	1.137
C(anion)···O(H_2O)	0.416	1.074	0.420	1.062	0.425	1.086	0.415	0.988	0.420	1.003	0.420	0.946
Ct_b(cation)···Ct_b(cation)	0.405	1.598	0.390	2.223	0.400	2.287	0.405	2.764	0.395	1.650	0.400	3.635
									0.765	8.196		
C_3(cation)···O(H_2O)	0.320	0.658	0.320	0.651	0.325	0.696	0.325	0.688	0.320	0.673	0.320	0.608
	0.570	1.038	0.560	1.029	0.565	1.063	0.565	1.028	0.560	1.023	0.585	0.970
N(anion)···H(H_2O)	0.420	0.700	0.420	0.673	0.420	0.708	0.420	0.686	0.420	0.660	0.420	0.635
	0.570	0.951	0.574	0.932	0.570	0.977	0.574	0.922	0.574	0.890	0.571	0.842

Table S8. Values of *r* (nm) at which the RDFs used for the calculation of the coordination numbers for the Interactions between Selected Atoms in IL/water/amino acid Ternary Systems were truncated.

Interaction	**Gly**	**Ala**	**Glu**	**Val**	**Ile**	**Water**
H(NH_3^+)-O(H_2O) [b]	0.235	0.240	0.240	0.240	0.240	-
O(COO^-)-H(H_2O) [c]	0.235	0.235	0.235	0.235	0.235	-
Ct_b(cation)-O(H_2O) [d]	0.545	0.548	0.545	0.550	0.550	0.570
C(anion)-O(H_2O) [e]	0.580	0.578	0.570	0.580	0.575	0.575
Ct_b(cation)-Ct_b(cation) [f]	0.615	0.630	0.675	0.610	0.600	0.585
$C_{terminal}$(aa)-Ct_b(cation) [g]	0.480	0.580	0.660	0.635	0.600	-
O(COO^-)-C_3(cation) [h]	NP	NP	NP	NP	NP	-
$C_{terminal}$(aa)-F(anion) [i]	0.435	0.442	NP	0.445	0.435	-
N(aa)-O(anion) [j]	0.345	0.338	0.360	0.350	0.350	-

Table S9. Values of *r* (nm) at which the RDFs used for the calculation of the coordination numbers for the Interactions between the CD, OE_1, OE_2 and HE_2 atoms of the carboxyl group of Glu and Selected Atoms in IL/water/amino acid Ternary Systems.

	O(anion)	F(anion)	Ct_b(cation)	C_3(cation)	O(H_2O)	H(H_2O)
CD	0.520	NP	0.660	0.495	0.430	0.315/0.480
OE_1	0.435	0.425	0.750	0.430	0.320	0.245
OE_2	0.400	0.425	0.750	0.435	0.295	0.230/0.375
HE_2	0.225	NP	0.715	0.465	0.235	0.295