Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Aqueous Ionic Liquids and Their Influence on Peptide Conformations: Denaturation and Dehydration Mechanisms

SUPPLEMENTARY MATERIAL

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1 Convergence of metadynamics simulations

The metadynamics simulations of the β-hairpin peptide in aqueous EMIM/ACE, EMIM/BF4 and EMIM/CL solution had a length of 100 ns, in contrast to pure water, which had a length of 45 ns. We verified the proper convergence of the resulting free energy landscapes by calculation of the free energy landscapes for the individual collective variables (RMSD and R_e) after 85%, 90%, 95% and 100% of simulation time.

1.1 Time evolution of free energy landscape for β-hairpin peptide in pure water

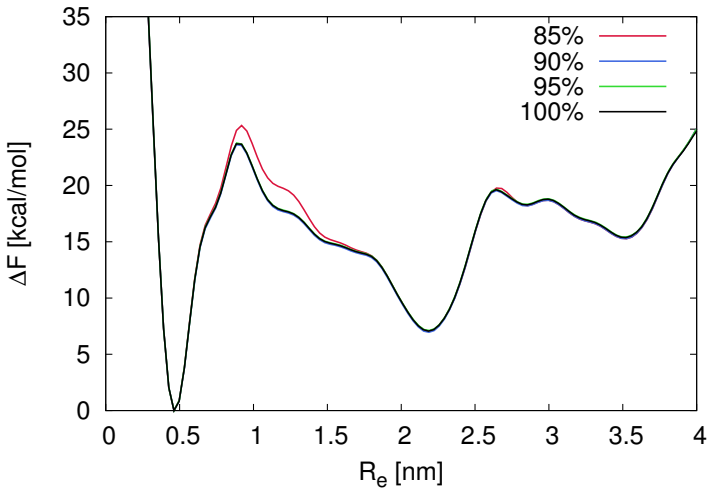

Figure 1: Time evolution of free energy landscape in pure water for collective variable R_e after 85%, 90%, 95% and 100% of simulation time.

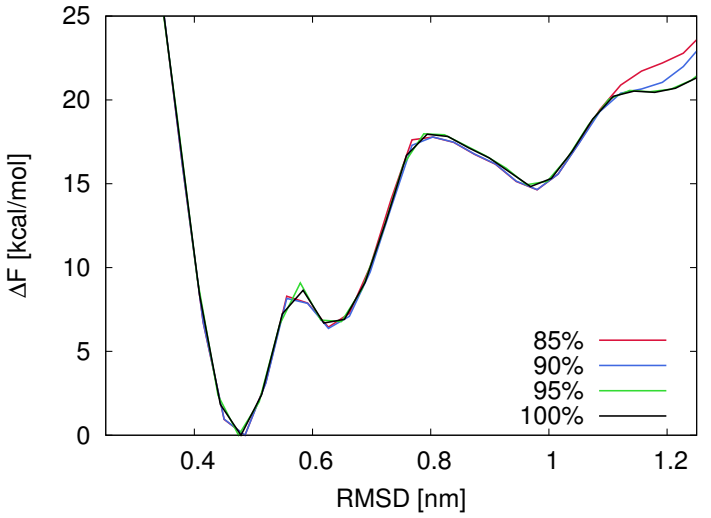

Figure 2: Time evolution of free energy landscape in pure water for collective variable RMSD after 85%, 90%, 95% and 100% of simulation time.

1.2 Time evolution of free energy landscape for β-hairpin peptide in aqueous EMIM/ACE

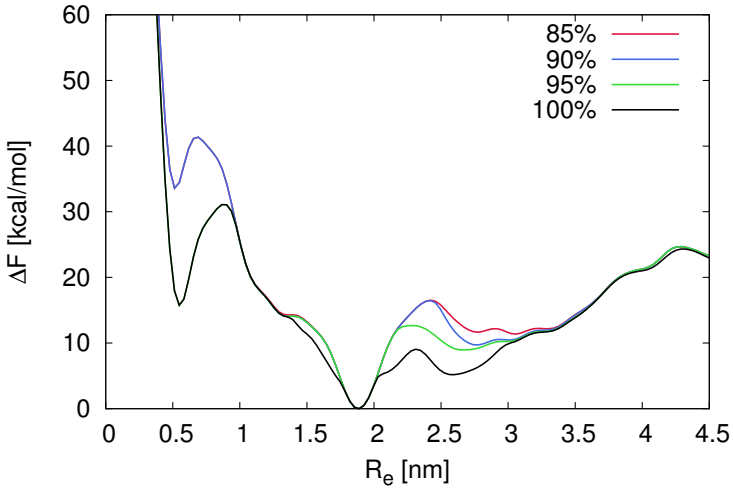

Figure 3: Time evolution of free energy landscape in aqueous EMIM/ACE for collective variable R_e after 85%, 90%, 95% and 100% of simulation time.

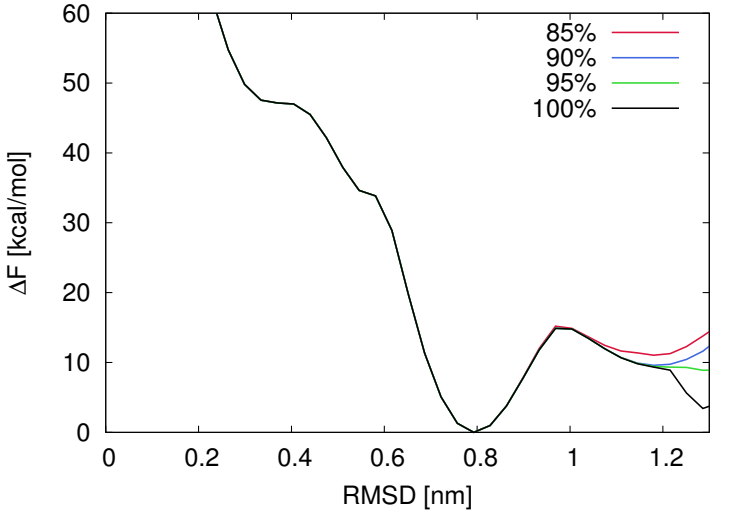

Figure 4: Time evolution of free energy landscape in aqueous EMIM/ACE for collective variable RMSD after 85%, 90%, 95% and 100% of simulation time.

1.3 Time evolution of free energy landscape for β-hairpin peptide in aqueous EMIM/BF4

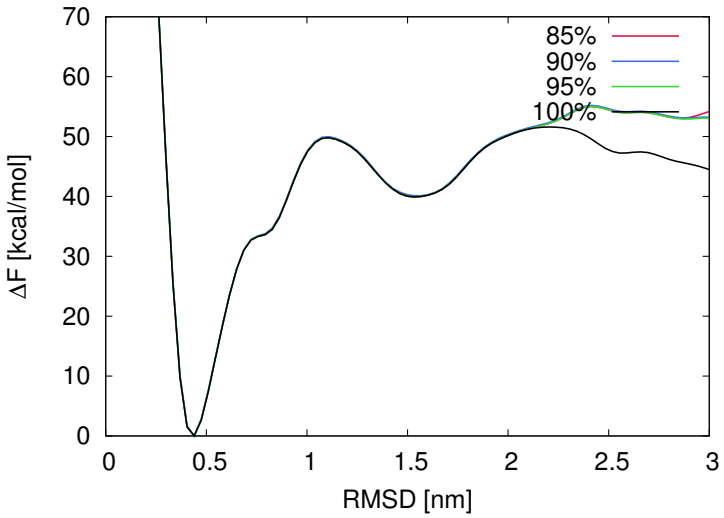

Figure 5: Time evolution of free energy landscape in aqueous EMIM/BF4 for collective variable R_e after 85%, 90%, 95% and 100% of simulation time.

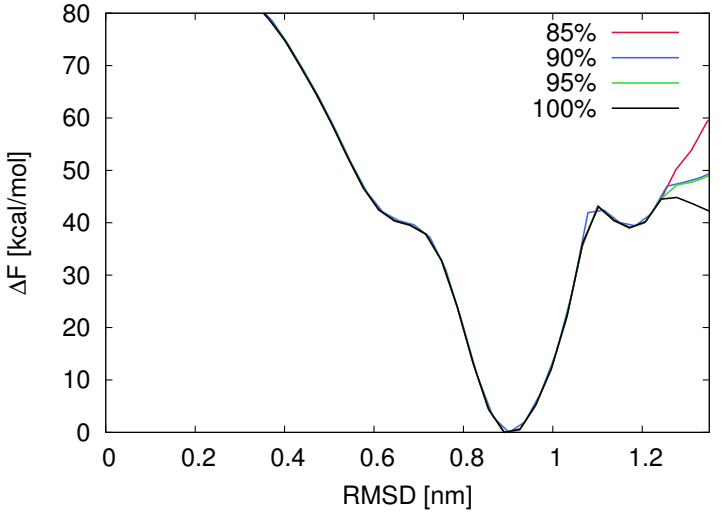

Figure 6: Time evolution of free energy landscape in aqueous EMIM/BF4 for collective variable RMSD after 85%, 90%, 95% and 100% of simulation time.

1.4 Time evolution of free energy landscape for β-hairpin peptide in aqueous EMIM/CL

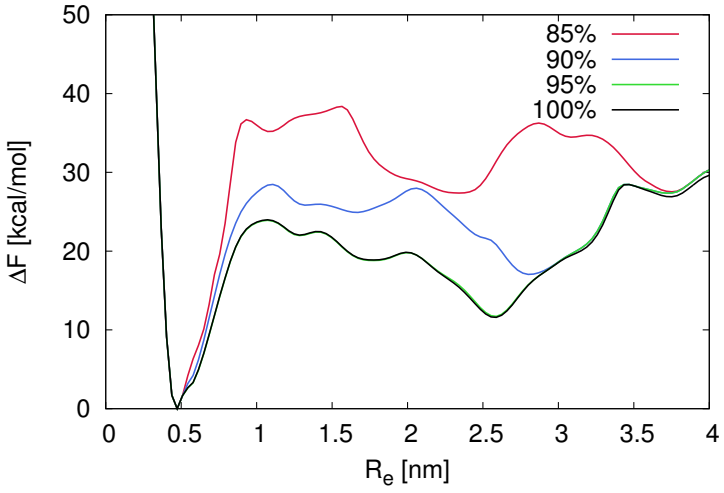

Figure 7: Time evolution of free energy landscape in aqueous EMIM/CL for collective variable R_e after 85%, 90%, 95% and 100% of simulation time.

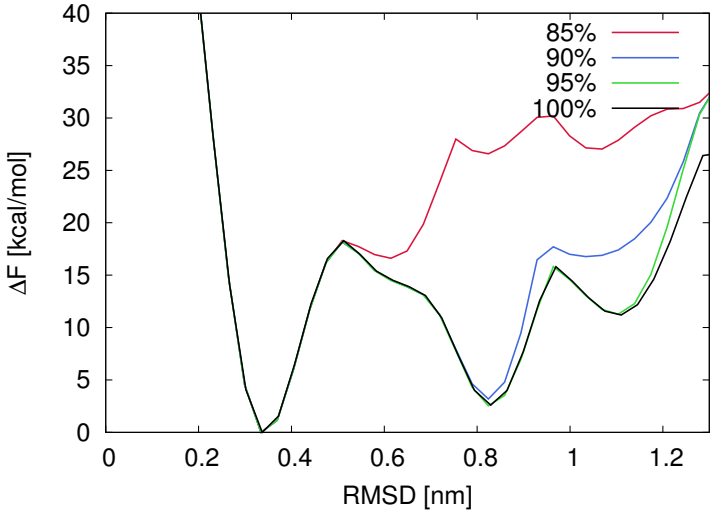

Figure 8: Time evolution of free energy landscape in aqueous EMIM/CL for collective variable RMSD after 85%, 90%, 95% and 100% of simulation time.

2 Trajectories of collective variables

In the following, we present the trajectories of the collective variables (RMSD and R_e) for the considered systems.

2.1 Trajectories of collective variables in pure water

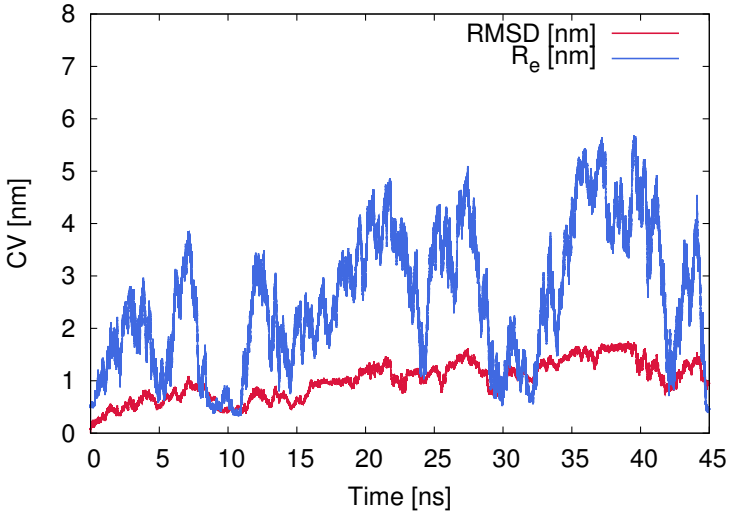

Figure 9: Trajectories of collective variables (CV) for R_e and RMSD in the metadynamics simulations of the β-hairpin peptide in pure water.

2.2 Trajectories of collective variables in aqueous EMIM/ACE

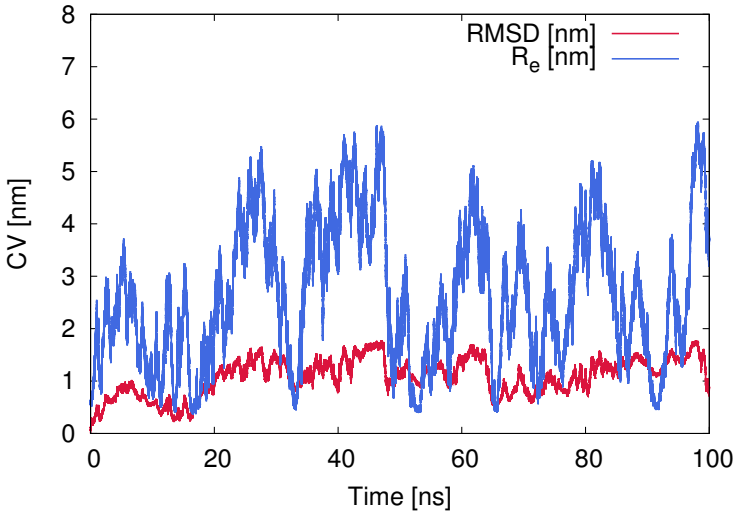

Figure 10: Trajectories of collective variables (CV) for R_e and RMSD in the metadynamics simulations of the β-hairpin peptide in aqueous EMIM/ACE.

2.3 Trajectories of collective variables in aqueous EMIM/BF4

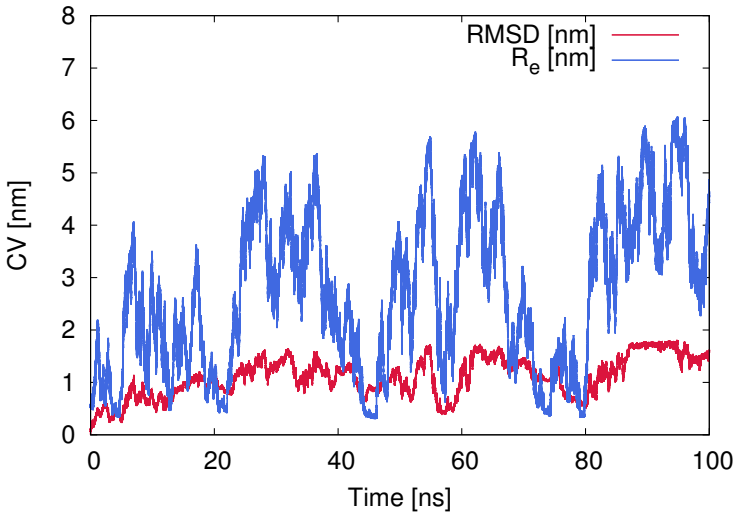

Figure 11: Trajectories of collective variable (CV) for R_e and RMSD in the metadynamics simulations of the β-hairpin peptide in aqueous EMIM/BF4.

2.4 Trajectories of collective variables in aqueous EMIM/CL

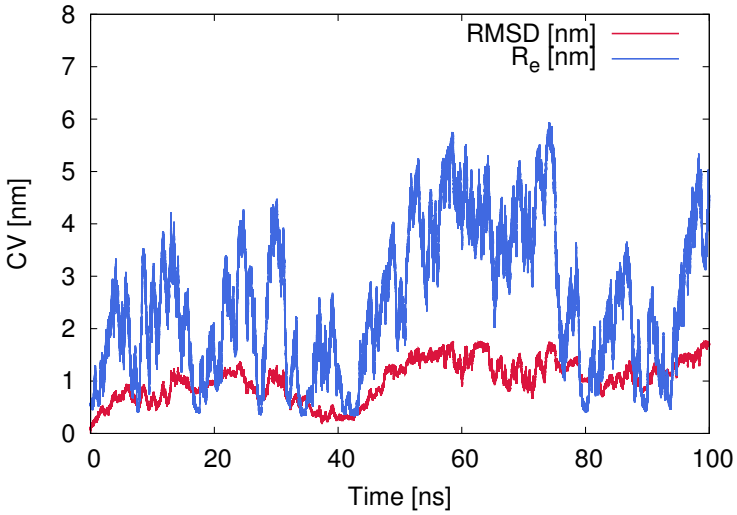

Figure 12: Trajectories of collective variables (CV) for R_e and RMSD in the metadynamics simulations of the β-hairpin peptide in aqueous EMIM/CL.

3 Detailed values and errors for non-bonded interactions between the IL species and the peptide

The following tables present the values and corresponding errors for the non-bonded interactions between the peptide and the IL species as shown in Fig. 5 in the main article. The errors were calculated by a jackknife analysis of ten blocks with equal length.

3.1 Total non-bonded interaction energies between peptide and IL species

Table 1: Nonbonded interaction energies (in kcal mol^{-1}) between the peptide and the IL ions. Only ions up to a radius of 1.2 nm to the peptide have been considered.

IL	Total	Cation	Anion
Denatured ($E_{(d)}$)			
EMIM ACE	-141.4990 ± 5.2360	-54.6590 ± 1.0823	-86.8400 ± 4.6697
EMIM BF4	-56.5142 ± 1.5888	-48.5939 ± 1.3152	-7.9203 ± 0.4285
EMIM Cl	-56.9382 ± 1.7616	-43.0703 ± 0.7816	-13.8679 ± 1.8235
Native ($E_{(n)}$)			
EMIM ACE	-72.1247 ± 3.4668	-40.4152 ± 1.0177	-31.7096 ± 2.8722
EMIM BF4	-38.7988 ± 1.4865	-32.0170 ± 1.0794	-6.7818 ± 0.4877
EMIM Cl	-50.8245 ± 2.4107	-35.8061 ± 0.8030	-15.0184 ± 2.1943
$\Delta E_{(d,n)} = E_{(d)} - E_{(n)}$			
EMIM ACE	-69.3743 ± 6.2797	-14.2438 ± 1.4856	-55.1304 ± 5.4823
EMIM BF4	-17.7154 ± 2.1758	-16.5769 ± 1.7014	-1.1385 ± 0.6492
EMIM Cl	-6.1137 ± 2.9858	-7.2642 ± 1.1206	1.1505 ± 2.8531

3.2 Coulomb interaction energies between peptide and IL species

Table 2: Coulomb energies (in kcal mol^{-1}) between the peptide and the IL ions. Only ions up to a radius of 1.2 nm to the peptide have been considered.

IL	Total	Cation	Anion
Denatured ($E_{(d)}$)			
EMIM ACE	-103.1621 ± 4.5951	-21.4123 ± 0.5011	-81.7498 ± 4.5677
EMIM BF4	-22.6745 ± 0.6201	-17.8855 ± 0.5093	-4.7890 ± 0.3538
EMIM Cl	-28.5064 ± 2.0796	-13.5401 ± 0.3259	-14.9663 ± 2.0539
Native ($E_{(n)}$)			
EMIM ACE	-45.3038 ± 3.1082	-16.1295 ± 0.5416	-29.1743 ± 3.0606
EMIM BF4	-15.9537 ± 0.5901	-11.8832 ± 0.4616	-4.0705 ± 0.3676
EMIM Cl	-29.4811 ± 2.5030	-13.1161 ± 0.4203	-16.3650 ± 2.4675
$\Delta E_{(d,n)} = E_{(d)} - E_{(n)}$			
EMIM ACE	-57.8583 ± 5.5476	-5.2828 ± 0.7379	-52.5755 ± 5.4983
EMIM BF4	-6.7208 ± 0.8561	-6.0023 ± 0.6874	-0.7185 ± 0.5102
EMIM Cl	0.9747 ± 3.2542	-0.4240 ± 0.5318	1.3987 ± 3.2105

3.3 Lennard-Jones interaction energies between peptide and IL species

Table 3: Lennard-Jones energies (in kcal mol^{-1}) between the peptide and the IL ions. Only ions up to a radius of 1.2 nm to the peptide have been considered.

IL	Total	Cation	Anion
Denatured ($E_{(d)}$)			
EMIM ACE	-38.3369 ± 0.6311	-33.2467 ± 0.6037	-5.0902 ± 0.1838
EMIM BF4	-33.8397 ± 0.8232	-30.7084 ± 0.8151	-3.1313 ± 0.1153
EMIM Cl	-28.4318 ± 0.5314	-29.5302 ± 0.4784	1.0984 ± 0.2313
Native ($E_{(n)}$)			
EMIM ACE	-26.8209 ± 0.5769	-24.2857 ± 0.5144	-2.5352 ± 0.2611
EMIM BF4	-22.8451 ± 0.6567	-20.1338 ± 0.6448	-2.7113 ± 0.1243
EMIM Cl	-21.3434 ± 0.4959	-22.6900 ± 0.4133	1.3466 ± 0.2741
$\Delta E_{(d,n)} = E_{(d)} - E_{(n)}$			
EMIM ACE	-11.5160 ± 0.7310	-8.9610 ± 0.7931	-2.5550 ± 0.3193
EMIM BF4	-10.9946 ± 1.0530	-10.5746 ± 1.0393	-0.4200 ± 0.1695
EMIM Cl	-7.0884 ± 0.7269	-6.8402 ± 0.6322	-0.2482 ± 0.3587