

SUPPORTING INFORMATION

Mixtures of 1-ethyl-3-methylimidazolium Acetate Ionic Liquid with Different Inorganic Salts: Insights into their Interactions.

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Table S1. ^1H NMR chemical shifts for the $[\text{C}_2\text{MIM}][\text{Ac}]^+$ IS systems at 298.15 K.

		$x[\text{NH}_4][\text{Ac}]$						
Position	0	0.0520	0.1000	0.1688	0.2466	0.3302	0.4346	
2	10.214	10.131	10.073	9.991	9.895	9.762	9.657	
4	8.114	8.062	8.024	7.972	7.913	7.833	7.774	
5	7.939	7.894	7.863	7.819	7.770	7.702	7.653	
6	3.627	3.619	3.610	3.600	3.597	3.587	3.593	
7	3.902	3.901	3.896	3.891	3.893	3.889	3.900	
8	0.891	0.900	0.903	0.909	0.928	0.946	0.984	
10/10'	1.128	1.143	1.147	1.155	1.176	1.193	1.225	
11	-	-	-	8.140	8.248	8.039	8.080	
		$x[\text{NH}_4]\text{Cl}$						
Position	0	0.0492	0.0988	0.1688	0.2479	0.3250	-	
2	10.214	10.094	10.016	9.874	9.705	9.534	-	
4	8.114	8.044	8.011	7.940	7.851	7.757	-	
5	7.939	7.876	7.848	7.786	7.706	7.621	-	
6	3.627	3.598	3.597	3.578	3.552	3.526	-	
7	3.902	3.879	3.882	3.868	3.847	3.827	-	
8	0.891	0.873	0.880	0.875	0.866	0.862	-	
10	1.128	1.110	1.115	1.106	1.092	1.086	-	
11	-	-	8.209	8.190	8.147	8.072	-	
		$x[\text{NH}_4][\text{SCN}]$						
Position	0	0.0494	0.0995	0.1610	0.2490	0.3298	-	
2	10.214	10.103	9.967	9.784	9.478	9.166	-	
4	8.114	8.028	7.928	7.804	7.628	7.484	-	
5	7.939	7.866	7.781	7.676	7.526	7.398	-	
6	3.627	3.611	3.588	3.567	3.543	3.526	-	
7	3.902	3.891	3.872	3.857	3.841	3.830	-	
8	0.891	0.902	0.906	0.919	0.946	0.973	-	
10	1.128	1.144	1.152	1.167	1.191	1.214	-	
11	-	8.525	8.447	8.339	8.204	7.996	-	
		$x[\text{NH}_4][\text{EtSO}_3]$						
Position	0	0.0503	0.1002	0.1702	0.2481	-	-	
2	10.214	10.084	9.955	9.765	9.541	-	-	
4	8.114	8.033	7.957	7.851	7.738	-	-	
5	7.939	7.868	7.802	7.711	7.612	-	-	
6	3.627	3.608	3.592	3.567	3.547	-	-	
7	3.902	3.890	3.880	3.861	3.847	-	-	
8	0.891	0.894	0.898	0.899	0.911	-	-	
10	1.128	1.137	1.145	1.147	1.156	-	-	
11	-	8.284	8.306	8.197	8.080	-	-	
12	-	2.000	2.008	2.016	2.035	-	-	
13	-	0.526	0.534	0.540	0.555	-	-	
		$x\text{Na}[\text{Ac}]$				$x\text{Na}[\text{SCN}]$		
Position	0	0.0493	0.1017	0.1406	0.0495	-	-	
2	10.214	10.162	10.110	10.075	10.098	-	-	
4	8.114	8.086	8.061	8.045	8.031	-	-	
5	7.939	7.916	7.896	7.884	7.868	-	-	
6	3.627	3.626	3.622	3.621	3.613	-	-	
7	3.902	3.909	3.912	3.915	3.897	-	-	
8	0.891	0.898	0.898	0.900	0.898	-	-	
10/10'	1.128	1.136	1.133	1.132	1.138	-	-	

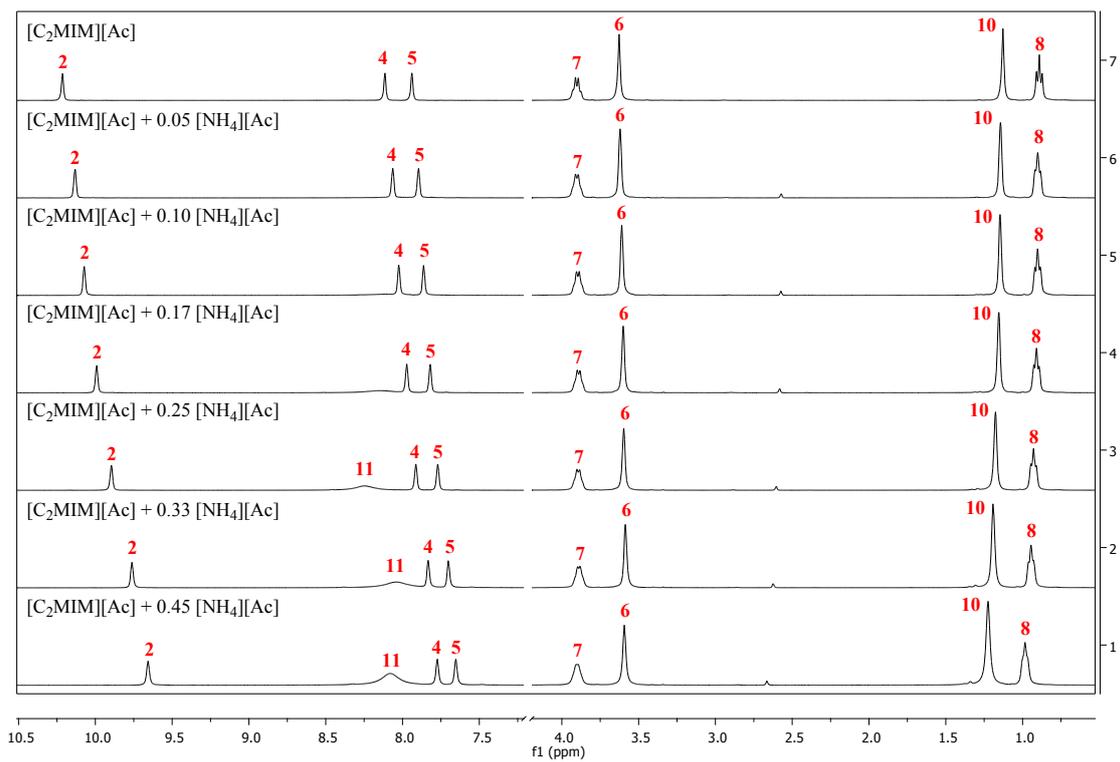


Figure S1. Effect of $[\text{NH}_4][\text{Ac}]$ concentration on the ^1H NMR spectrum of $[\text{C}_2\text{MIM}][\text{Ac}]$ at 298.15 K.

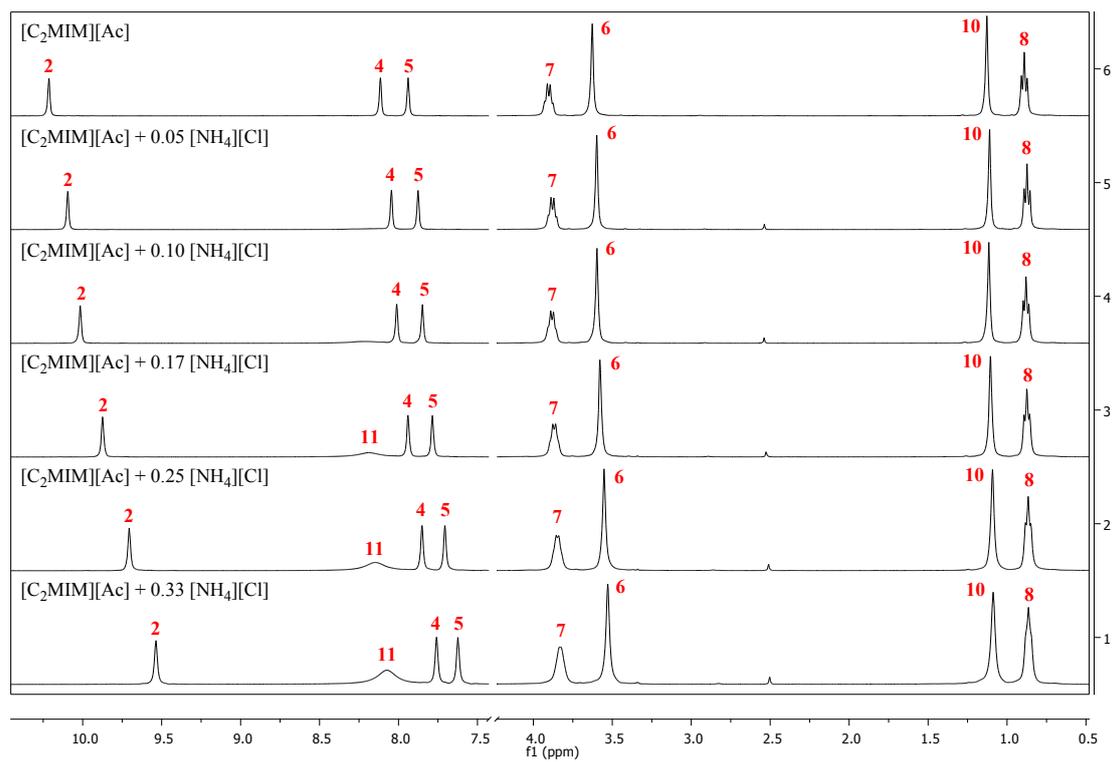


Figure S2. Effect of $[\text{NH}_4]\text{Cl}$ concentration on the ^1H NMR spectrum of $[\text{C}_2\text{MIM}][\text{Ac}]$ at 298.15 K.

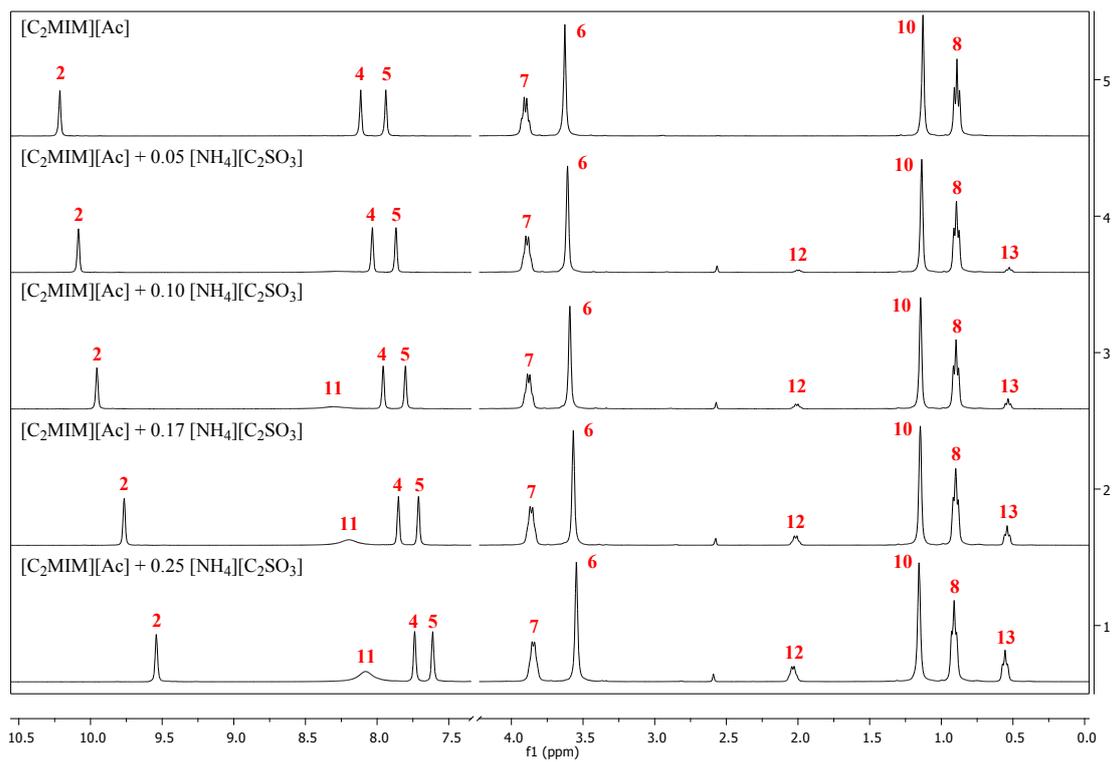


Figure S3. Effect of $[\text{NH}_4][\text{EtSO}_3]$ concentration on the ^1H NMR spectrum of $[\text{C}_2\text{MIM}][\text{Ac}]$ at 298.15 K.

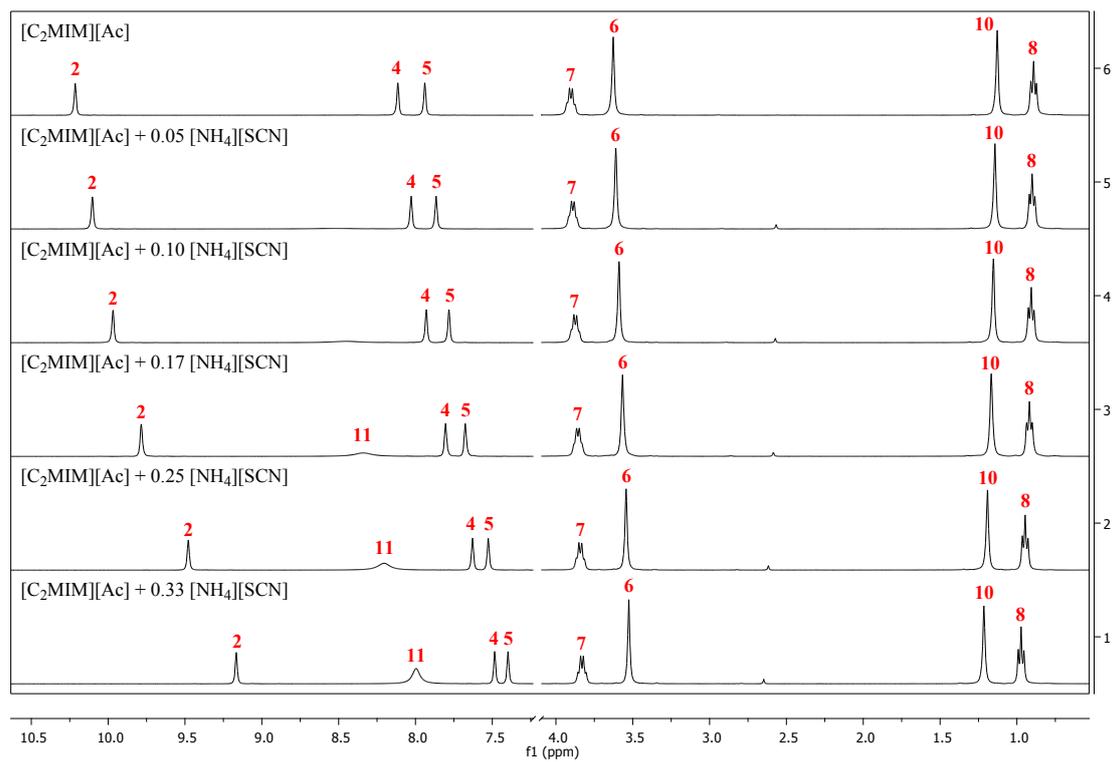


Figure S4. Effect of $[\text{NH}_4][\text{SCN}]$ concentration on the ^1H NMR spectrum of $[\text{C}_2\text{MIM}][\text{Ac}]$ at 298.15 K.

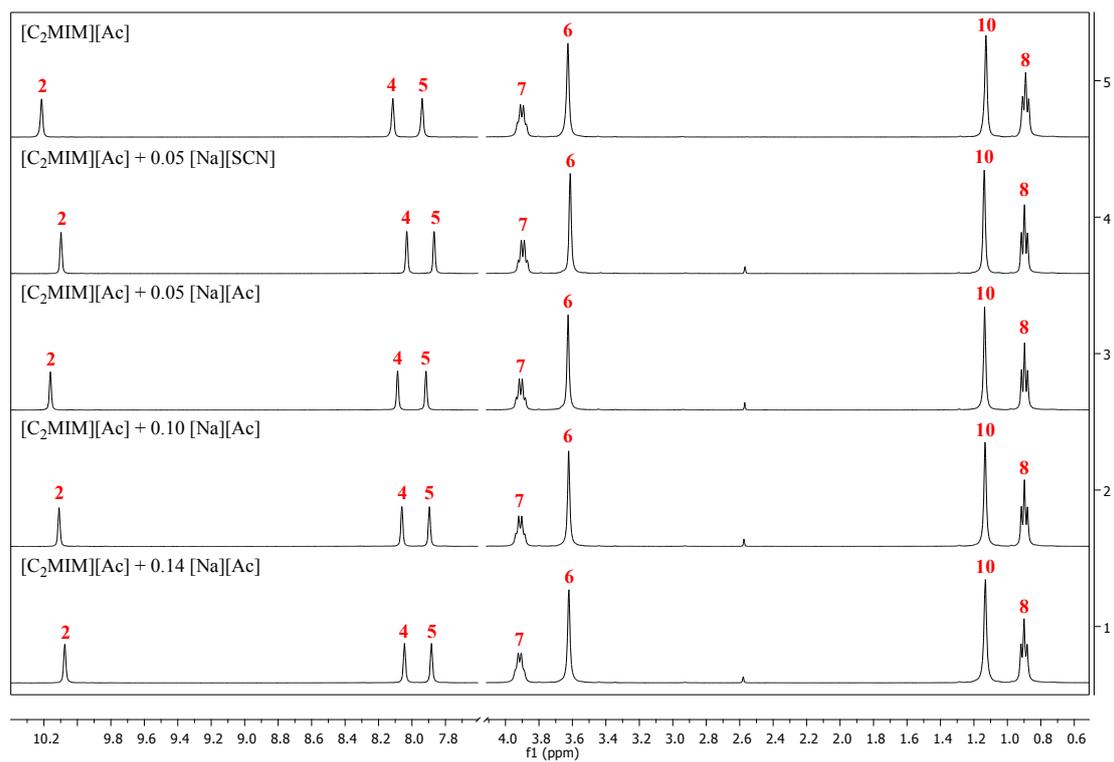


Figure S5. Effect of $[\text{Na}][\text{SCN}]$ and $[\text{Na}][\text{Ac}]$ concentration on the ^1H NMR spectrum of $[\text{C}_2\text{MIM}][\text{Ac}]$ at 298.15 K.

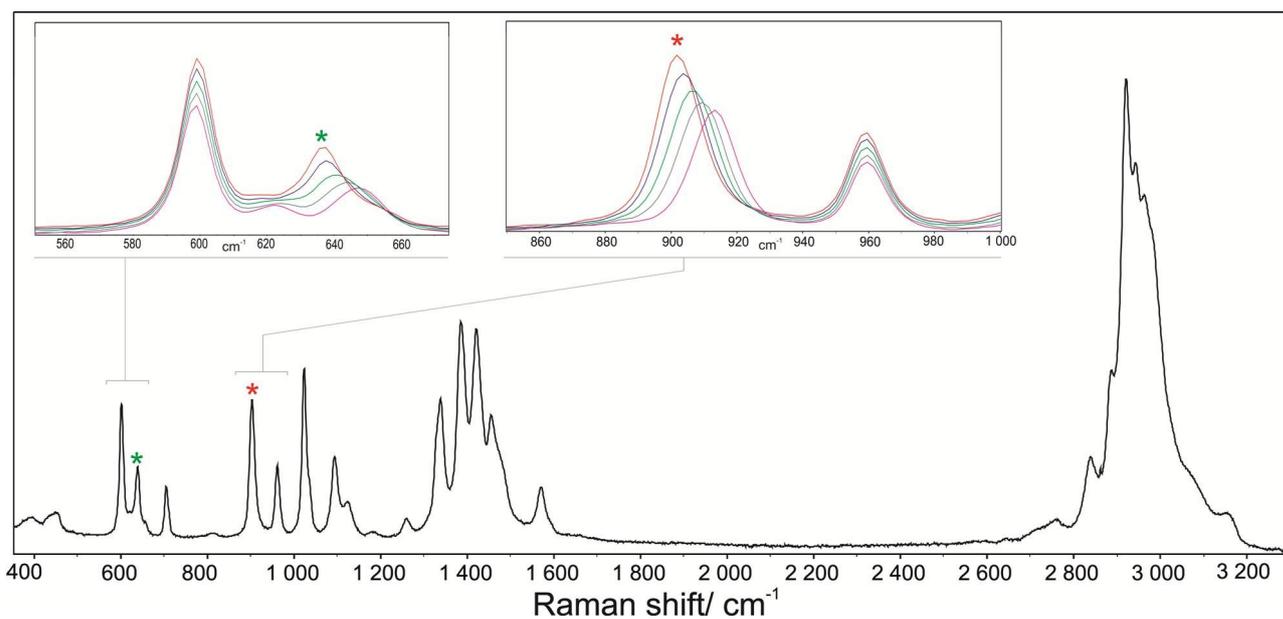


Figure S6. Raman spectrum of [C₂MIM][Ac] measured with 1064 nm excitation at 298.15 K; [Ac]⁻ vibrational modes are designated with asterisk (ν_{O-C=O} in green and ν_{C-COO} in red). Inset: The influence of [NH₄][SCN] with molar fraction, x_{IS} , of 0.05 (red), 0.10 (blue), 0.17 (green), 0.25 (gray) and 0.33 (magenta) on frequency and bandwidth of ν_{O-C=O} (left) and ν_{C-COO} (right).

Table S2. ^1H NMR self-diffusion coefficients of the different ions (D , in $10^{-11}\cdot\text{m}^2\cdot\text{s}^{-1}$) in the $[\text{C}_2\text{MIM}][\text{Ac}] + \text{IS}$ systems at 323.15 K.

x_{IS}	D_{IL^+}	D_{IL^-}	D_{IS^+}	D_{IS^-}
	[C ₂ MIM][Ac] + [NH ₄][Ac]			
0	4.42	3.84	-	3.84
0.0520	4.45	3.54	-	3.54
0.1000	4.09	3.01	-	3.01
0.1688	3.54	2.35	3.90	2.35
0.2466	3.09	1.88	3.21	1.88
0.3302	2.69	1.52	-	1.52
0.4361	1.93	1.03	1.69	1.03
	[C ₂ MIM][Ac] + [NH ₄]Cl			
0	4.42	3.84	-	-
0.0492	4.13	3.30	-	-
0.0988	3.56	2.64	-	-
0.1688	2.75	1.83	-	-
0.2479	2.02	1.22	2.03	-
0.3250	1.42	0.82	1.31	-
	[C ₂ MIM][Ac] + [NH ₄][SCN]			
0	4.42	3.84	-	-
0.0494	4.52	3.58	4.72	-
0.0995	4.43	3.19	5.04	-
0.1610	4.42	2.80	5.05	-
0.2490	4.52	2.45	4.83	-
0.3290	4.81	2.27	4.75	-
	[C ₂ MIM][Ac] + [NH ₄][EtSO ₃]			
0	4.42	3.84	-	-
0.0503	4.26	3.36	-	3.13
0.1002	3.89	2.84	4.33	2.77
0.1702	3.30	2.10	3.61	2.21
0.2481	2.74	1.56	2.54	1.73
	[C ₂ MIM][Ac] + Na[Ac]			
0	4.42	3.84	-	-
0.0493	3.93	3.14	-	3.14
0.1017	3.43	2.58	-	2.58
0.1406	3.03	2.16	-	2.16
	[C ₂ MIM][Ac] + Na[SCN]			
0	4.42	3.84	-	-
0.0495	4.23	3.41	-	-

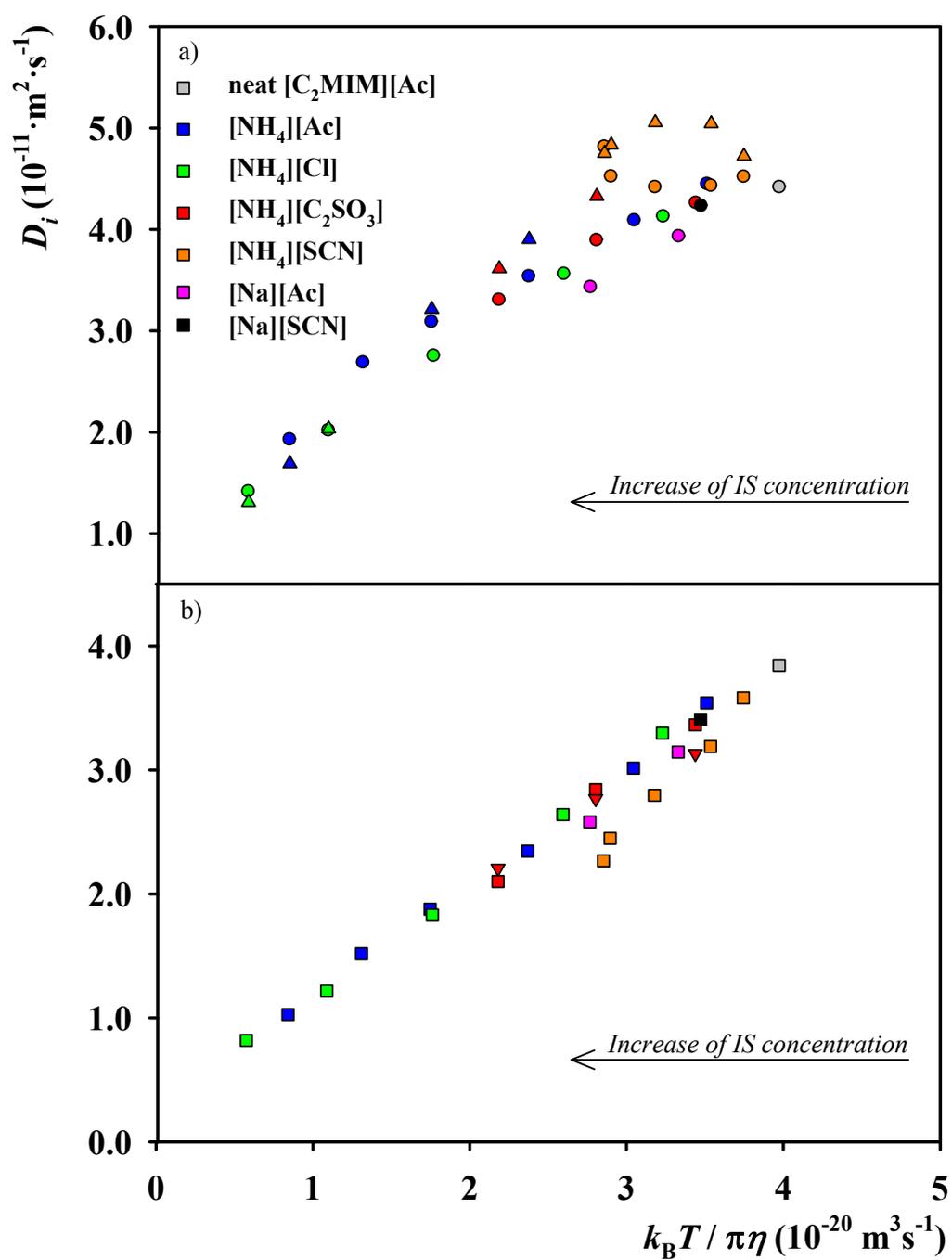


Figure S7. Ion self-diffusion coefficients plotted against $k_B T / \pi \eta$ in the $[\text{C}_2\text{MIM}][\text{Ac}] +$ IS systems at 323.15 K. Panel a) represents the cations of the system $[\text{C}_2\text{MIM}]^+$ (●) and $[\text{NH}_4]^+$ (▲) whereas panel b) represents the anions $[\text{Ac}]^-$ (■) and $[\text{EtSO}_3]^-$ (▼).

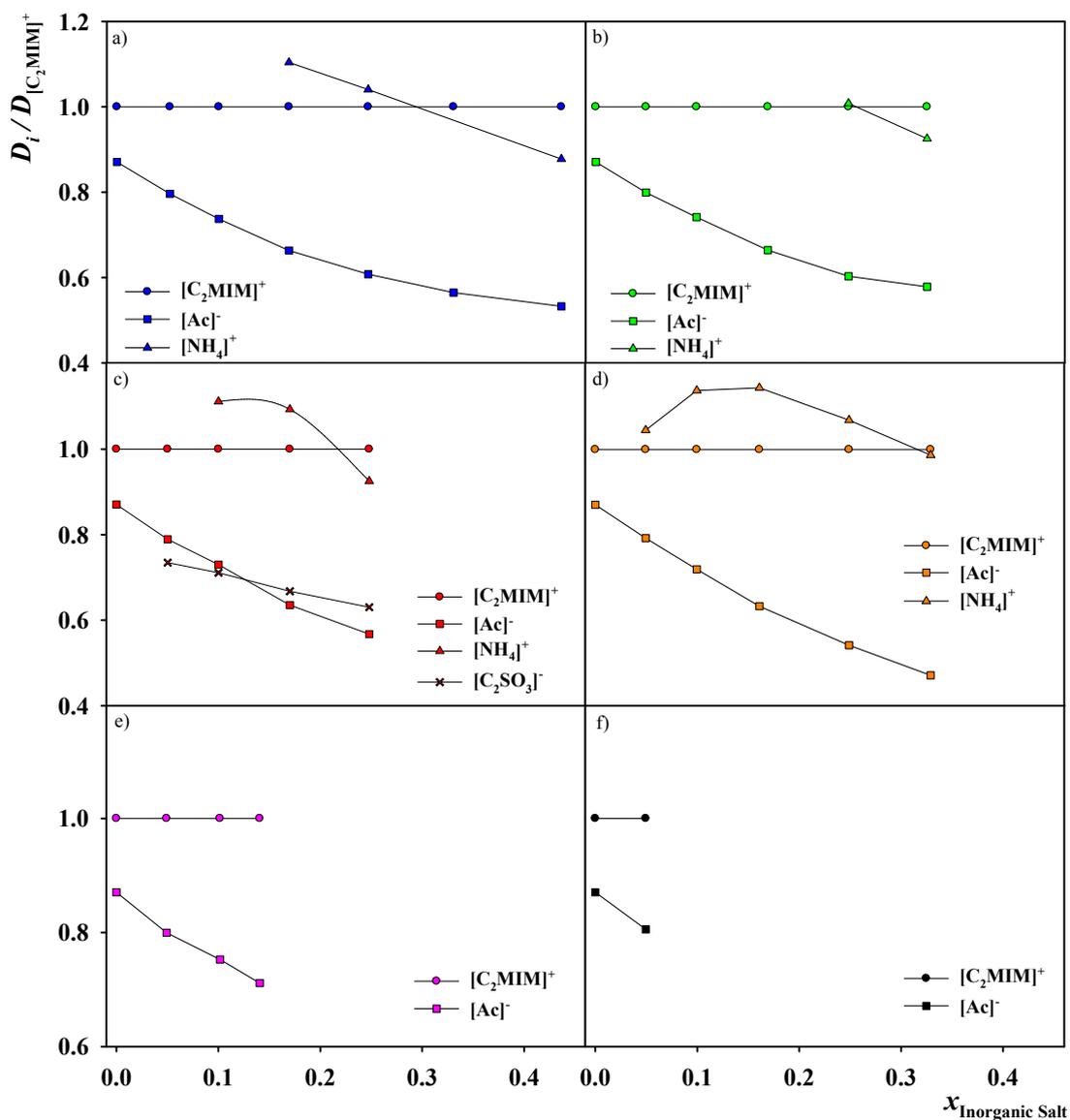


Figure S8. ^1H NMR relative self-diffusion coefficients for the different ions in the $[\text{C}_2\text{MIM}][\text{Ac}] + \text{IS}$ systems at 323.15 K. Each panel represents a different IS: a) $[\text{NH}_4][\text{Ac}]$; b) $[\text{NH}_4]\text{Cl}$; c) $[\text{NH}_4][\text{EtSO}_3]$; d) $[\text{NH}_4][\text{SCN}]$; e) $\text{Na}[\text{Ac}]$ and f) $\text{Na}[\text{SCN}]$;

Table S3. Electronic energies, SP and ZPVE, as well as the final energy (sum of SP and ZPVE), E , for the optimized structures of the pure IL and ISs.

Compound	SP / KJ·mol ⁻¹	ZPVE / KJ·mol ⁻¹	E / KJ·mol ⁻¹
[C ₂ MIM][Ac]	-1500984	577	-1500407
[NH ₄][Ac]	-748152	259	-747893
[NH ₄]Cl	-1356605	130	-1356475
[NH ₄][SCN]	-1436975	154	-1436821
[NH ₄][EtSO ₃]	-1992313	339	-1991974
Na[Ac]	-1023702	131	-1023571
Na[SCN]	-1712557	25	-1712532

Table S4. Electronic energies, SP and ZPVE, as well as the final energy of the cluster (sum of SP and ZPVE), E_{cluster} , for the optimized structures of the IL + IS systems.

System	Conformation	SP / KJ·mol ⁻¹	ZPVE / KJ·mol ⁻¹	E_{cluster} / KJ·mol ⁻¹
[C ₂ MIM][Ac] +	1	-2249198	839	-2248359
	2	-2249183	840	-2248343
	3	-2249204	840	-2248364
	4	-2249196	843	-2248353
	5	-2249174	841	-2248333
	6	-2249174	839	-2248335
[C ₂ MIM][Ac] +	1	-2857664	710	-2856954
	2	-2857648	708	-2856940
	3	-2857662	710	-2856952
	4	-2857659	712	-2856947
[C ₂ MIM][Ac] +	1	-2938041	734	-2937307
	2	-2938048	737	-2937311
	3	-2938043	734	-2937309
[C ₂ MIM][Ac] +	1	-3493379	918	-3492461
	2	-3493370	919	-3492451
	3	-3493381	921	-3492460
[C ₂ MIM][Ac] +	1	-2524703	711	-2523992
	2	-2524719	712	-2524007
	3	-2524736	716	-2524020
[C ₂ MIM][Ac] +	1	-3213595	608	-3212987
	2	-3213597	609	-3212988
	3	-3213587	606	-3212981

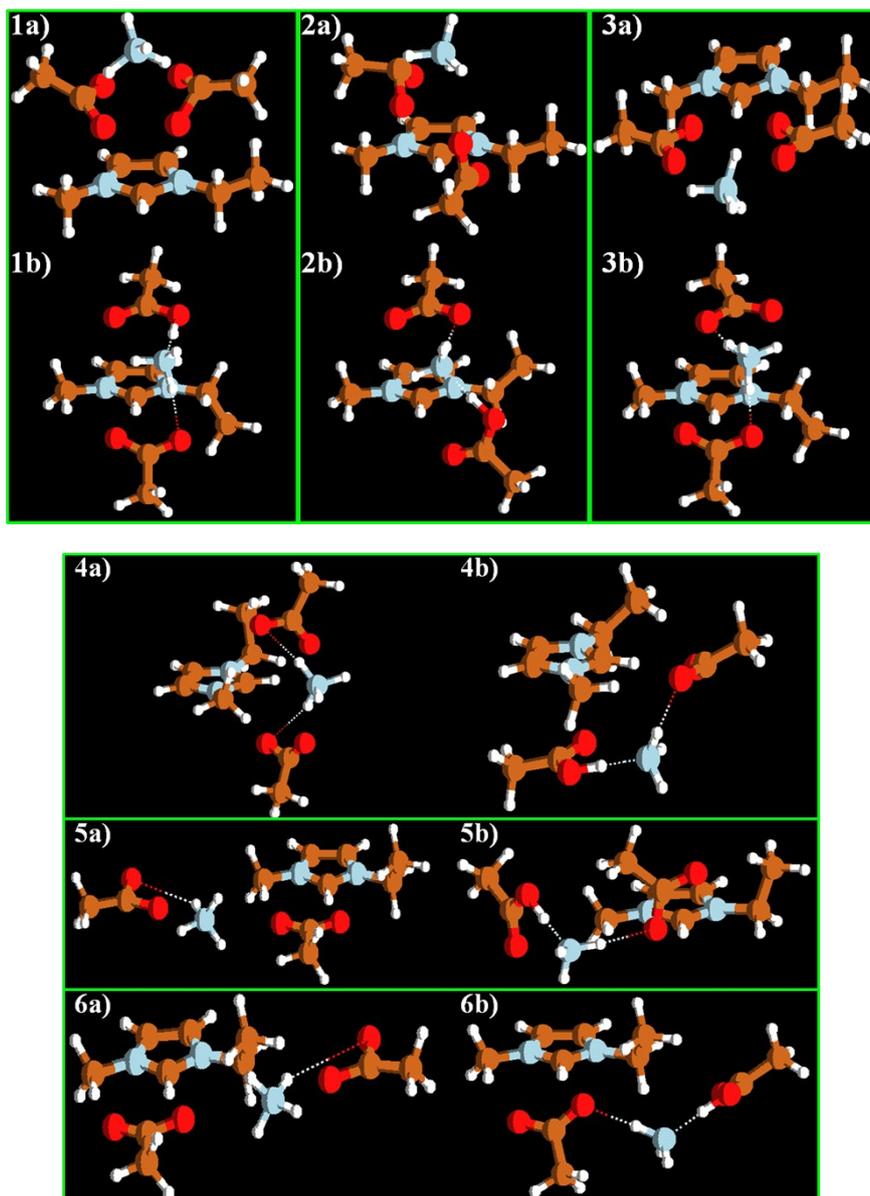


Figure S9. Conformations drawn for the system $[\text{C}_2\text{MIM}][\text{Ac}] + [\text{NH}_4][\text{Ac}]$. a) Initial conformation. b) Final conformation in ethanol.

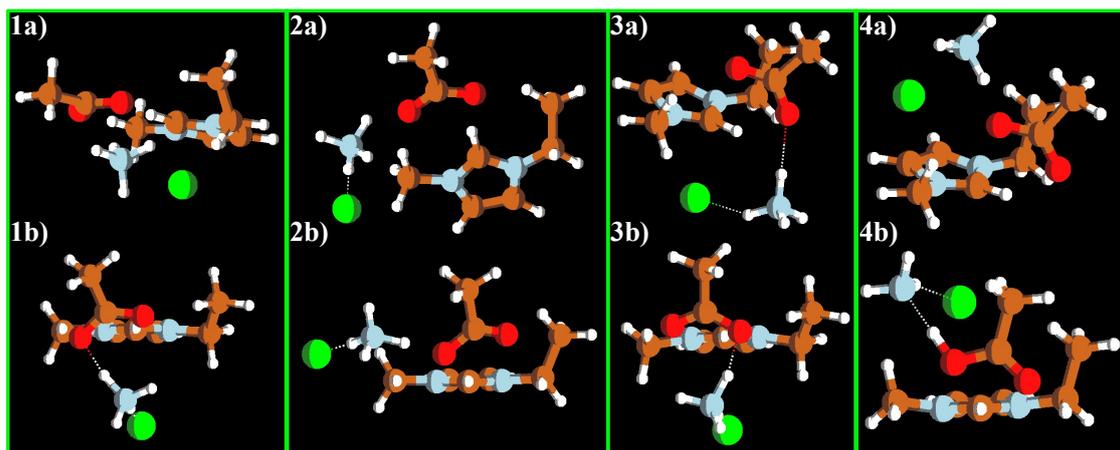


Figure S10. Conformations drawn for the system $[\text{C}_2\text{MIM}][\text{Ac}] + [\text{NH}_4][\text{Cl}]$. a) Initial conformation. b) Final conformation in ethanol.

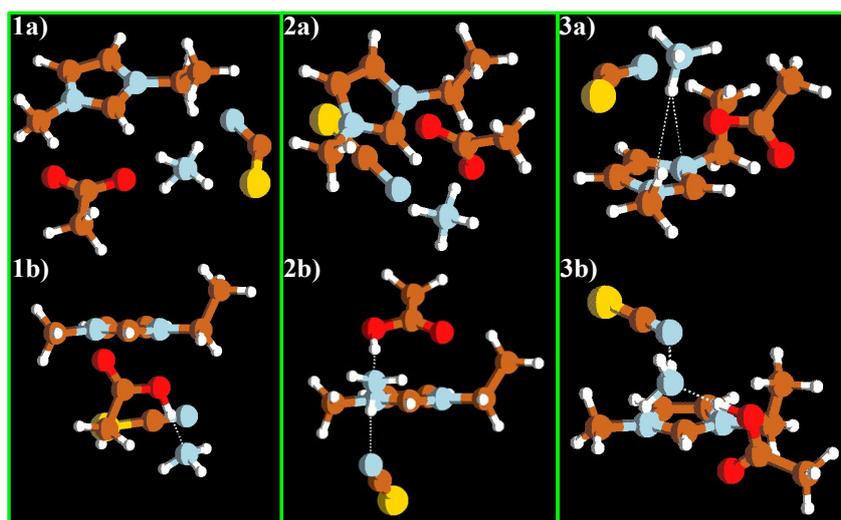


Figure S11. Conformations drawn for the system $[\text{C}_2\text{MIM}][\text{Ac}] + [\text{NH}_4][\text{SCN}]$. a) Initial conformation. b) Final conformation in ethanol.

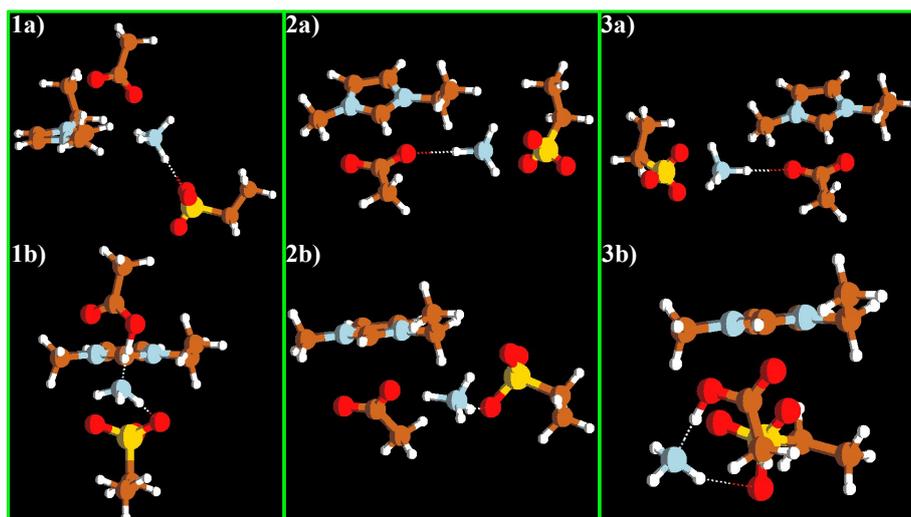


Figure S12. Conformations drawn for the system $[\text{C}_2\text{MIM}][\text{Ac}] + [\text{NH}_4][\text{EtSO}_3]$. a) Initial conformation. b) Final conformation in ethanol.

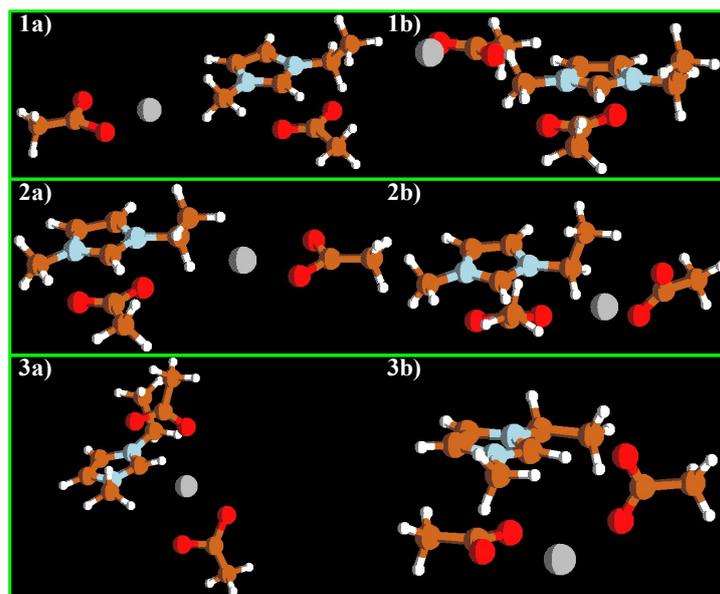


Figure S13. Conformations drawn for the system $[\text{C}_2\text{MIM}][\text{Ac}] + [\text{Na}][\text{Ac}]$. a) Initial conformation. b) Final conformation in ethanol.

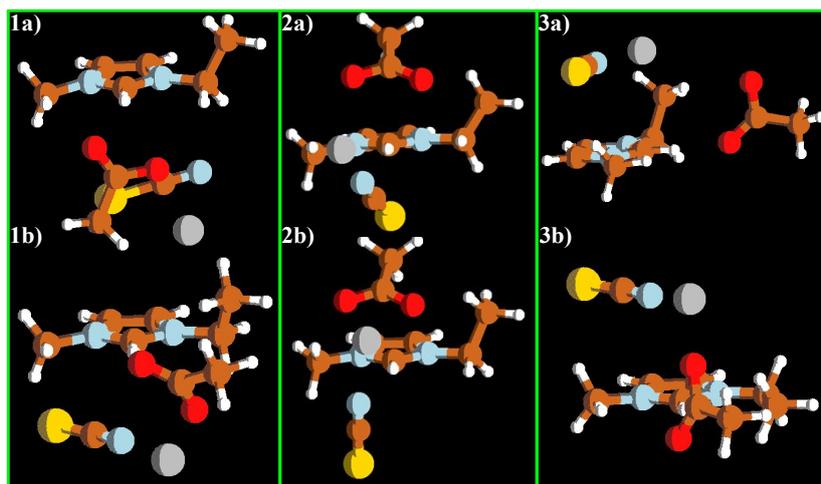


Figure S14. Conformations drawn for the system $[C_2MIM][Ac] + [Na][SCN]$. a) Initial conformation. b) Final conformation in ethanol.

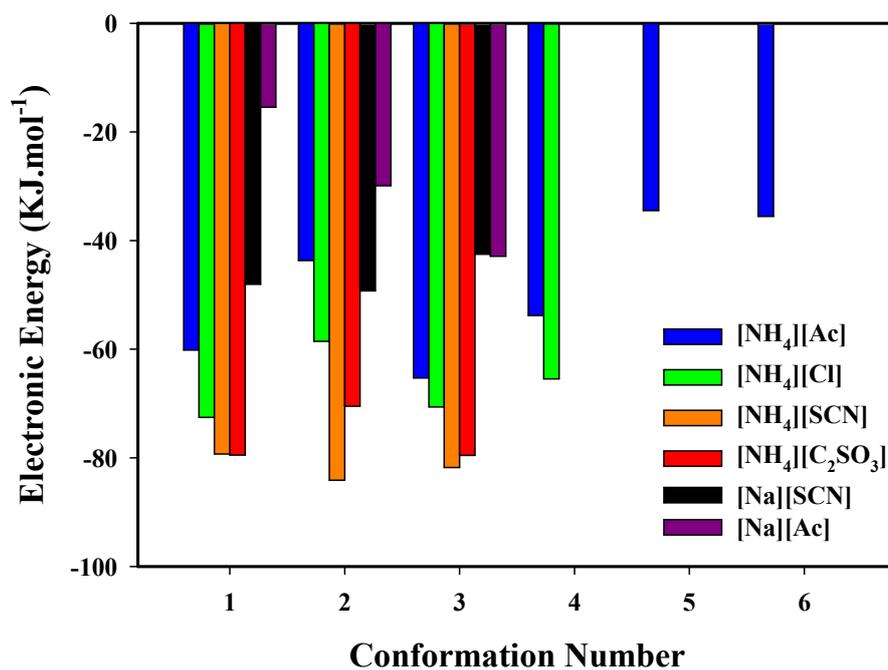


Figure S15. Binding energies for the different conformations of all IL + IS systems studied.