

Electronic Supplementary Information

*“Iso-Solvation Effects in Mixtures of Ionic Liquids on
the Kinetics of a model S_NAr Reaction”*

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Table S1. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMPF₆/BMIMFAP of different composition solution at 25°C ± 0.1°C.

[BMIM][PF ₆] ₀ [FAP] ₁		[BMIM][PF ₆] _{0.1} [FAP] _{0.9}		[BMIM][PF ₆] _{0.25} [FAP] _{0.75}	
10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
5.72	1.08	5.72	1.33	3.43	0.93
9.15	1.62	9.15	1.91	5.72	1.49
13.7	2.55	11.4	2.34	8.00	2.03
17.1	3.28	14.9	3.52	10.3	2.52
20.6	4.12	19.4	5.30	12.6	3.37
28.6	6.04	22.9	5.47	14.9	4.28
				17.1	4.45

Table S2. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMPF₆/BMIMFAP of different composition solution at 25°C ± 0.1°C.

[BMIM][PF ₆] _{0.5} [FAP] _{0.5}		[BMIM][PF ₆] _{0.75} [FAP] _{0.25}		[BMIM][PF ₆] ₁ [FAP] ₀	
10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ³ [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
3.43	1.30	3.43	1.97	5.70	0.40
5.72	2.12	5.72	3.48	8.55	0.75
8.00	3.04	8.00	3.84	17.1	1.25
10.3	3.83	10.3	6.62	34.3	3.18
12.6	4.31	12.6	6.81	57.2	5.07
14.9	5.66	14.9	7.75		
17.1	6.99	17.1	8.84		

Table S3. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMDCN / BMIMPF₆ of different composition solution at 25°C ± 0.1°C.

[BMIM][DCN] ₀ [PF ₆] ₁		[BMIM][DCN] _{0.1} [PF ₆] _{0.9}		[BMIM][DCN] _{0.25} [PF ₆] _{0.75}	
10 ³ [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
5.70	0.40	3.43	3.99	3.43	6.45
8.55	0.75	5.72	6.23	5.72	9.13
17.1	1.25	9.15	10.5	8.00	11.3
34.3	3.18	13.7	16.0	10.3	12.4
57.2	5.07	17.1	20.7	12.6	16.1
		19.4	21.2	14.9	19.5

Table S4. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMDCN / BMIMPF₆ of different composition solution at 25°C ± 0.1°C.

[BMIM][DCN] _{0.5} [PF ₆] _{0.5}		[BMIM][DCN] _{0.75} [PF ₆] _{0.25}		[BMIM][DCN] ₁ [PF ₆] ₀	
10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ³ [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
3.43	5.36	3.43	9.1	4.57	2.73
5.72	7.48	5.72	17.0	9.15	5.07
8.00	13.9	8.00	21.2	13.7	6.67
10.3	17.3	10.3	26.4	18.3	9.39
12.6	23.5	12.6	34.5	22.9	11.6
14.9	28.3	14.9	37.6	27.4	13.5
17.1	34.8	17.1	50.9	32.0	15.5

Table S5. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMDCN / BMIMFAP of different composition solution at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$.

[BMIM][DCN] ₀ [FAP] ₁		[BMIM][DCN] _{0.1} [FAP] _{0.9}		[BMIM][DCN] _{0.25} [FAP] _{0.75}	
$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
5.72	1.08	3.43	1.25	3.43	2.12
9.15	1.62	5.72	2.02	5.72	3.95
13.7	2.55	9.15	2.67	8.00	4.87
17.1	3.28	13.7	4.02	10.3	5.87
20.6	4.12	17.1	5.98	12.6	6.95
28.6	6.04	19.4	6.17	14.9	8.29
		22.9	6.93		

Table S6. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMDCN / BMIMFAP of different composition solution at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$.

[BMIM][DCN] _{0.5} [FAP] _{0.5}		[BMIM][DCN] _{0.75} [FAP] _{0.25}		[BMIM][DCN] ₁ [FAP] ₀	
$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^3 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
3.43	3.85	3.43	9.23	4.57	2.73
5.72	6.64	5.72	14.8	9.15	5.07
8.00	8.66	8.00	19.7	13.7	6.67
10.3	12.2	10.3	23.7	18.3	9.39
12.6	15.8	12.6	27.3	22.9	11.6
14.9	18.0	14.9	32.7	27.4	13.5
17.1	21.2			32.0	15.5

Table S7. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture EMIMSCN / EMIMDCN of different composition solution at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$.

[EMIM][SCN] ₀ [DCN] ₁		[EMIM][SCN] _{0.1} [DCN] _{0.9}		[EMIM][SCN] _{0.25} [DCN] _{0.75}	
$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^2 k_{\text{obs}}/\text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
3.43	1.01	3.43	9.53	3.43	7.89
4.57	1.29	5.72	13.6	5.72	12.0
5.72	1.75	9.15	20.6	8.00	17.8
8.00	2.47	13.7	33.4	10.3	24.8
9.15	2.76	17.1	38.4	12.6	30.9
11.4	3.32	19.4	49.4	14.9	33.8
13.7	3.96	22.9	53.4	17.1	37.0

Table S8. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture EMIMSCN / EMIMDCN of different composition solution at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$.

[EMIM][SCN] _{0.5} [DCN] _{0.5}		[EMIM][SCN] _{0.6} [DCN] _{0.4}		[EMIM][SCN] _{0.75} [DCN] _{0.25}	
$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}}/\text{M}$	$10^3 k_{\text{obs}}/\text{s}^{-1}$
3.43	6.51	3.43	9.86	3.43	4.33
5.72	11.8	5.72	12.8	5.72	7.66
8.00	15.6	8.00	18.1	8.00	8.94
10.3	19.8	10.3	23.7	10.3	12.5
12.6	22.7	12.6	25.0	12.6	17.4
14.9	28.4	14.9	32.5	14.9	19.7
17.1	34.3			17.1	22.7

Table S9. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture EMIMSCN / EMIMDCN of different composition solution at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$.

[EMIM][SCN] _{0.9} [DCN] _{0.1}		[EMIM][SCN] ₁ [DCN] ₀	
$10^2 [\text{N}]_{\text{total}} / \text{M}$	$10^3 k_{\text{obs}} / \text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}} / \text{M}$	$10^2 k_{\text{obs}} / \text{s}^{-1}$
3.43	14.0	1.14	0.03
5.72	24.4	3.43	1.27
8.00	31.4	5.72	2.58
10.3	36.3	8.00	3.45
12.6	50.5	11.4	4.80
14.9	57.7	17.1	7.23

Table S10. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMDCN / BMIMBF₄ of different composition solution at $25^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$.

[BMIM][DCN] ₀ [BF ₄] ₁		[BMIM][DCN] _{0.1} [BF ₄] _{0.9}		[BMIM][DCN] _{0.25} [BF ₄] _{0.75}	
$10^2 [\text{N}]_{\text{total}} / \text{M}$	$10^3 k_{\text{obs}} / \text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}} / \text{M}$	$10^3 k_{\text{obs}} / \text{s}^{-1}$	$10^2 [\text{N}]_{\text{total}} / \text{M}$	$10^3 k_{\text{obs}} / \text{s}^{-1}$
3.43	0.26	5.72	10.2	3.43	8.58
8.00	3.64	9.15	16.4	5.72	12.0
11.43	8.32	11.4	20.8	8.00	19.4
16.01	11.02	14.9	25.4	10.3	23.5
19.43	20.04	19.4	34.1	12.6	31.4
28.58	30.09	22.9	38.2	14.9	40.8

Table S11. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMDCN / BMIMBF₄ of different composition solution at 25°C ± 0.1°C.

[BMIM][DCN] _{0.5} [BF ₄] _{0.5}		[BMIM][DCN] _{0.75} [BF ₄] _{0.25}		[BMIM][DCN] ₁ [BF ₄] ₀	
10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ³ [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
3.43	12.4	3.43	13.0	4.57	2.73
5.72	19.2	5.72	19.9	9.15	5.07
8.00	24.7	8.00	23.5	13.7	6.67
10.3	30.8	10.3	29.7	18.3	9.39
12.6	34.9	12.6	40.2	22.9	11.6
14.9	49.0	14.9	44.2	27.4	13.5
				32.0	15.5

Table S12. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMBF₄ / BMIMPF₆ of different composition solution at 25°C ± 0.1°C.

[BMIM][BF ₄] ₀ [PF ₆] ₁		[BMIM][BF ₄] _{0.1} [PF ₆] _{0.9}		[BMIM][BF ₄] _{0.25} [PF ₆] _{0.75}	
10 ³ [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
5.70	0.40	3.43	3.20	3.43	5.12
8.55	0.75	5.72	5.08	5.72	6.86
17.1	1.25	6.86	6.08	8.00	9.13
34.3	3.18	8.00	6.30	10.3	12.4
57.2	5.07	10.3	7.92	12.6	15.7
		14.9	11.2	14.9	17.8

Table S13. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMBF₄ / BMIMPF₆ of different composition solution at 25°C $\pm$ 0.1°C.

[BMIM][BF ₄] _{0.5} [PF ₆] _{0.5}		[BMIM][BF ₄] _{0.75} [PF ₆] _{0.25}	
10 ³ [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
2.29	3.59	2.29	2.34
5.72	5.28	5.72	4.79
8.00	8.08	8.00	7.07
10.3	9.59	10.3	9.54
12.6	13.5	12.6	12.7
14.9	14.8	14.9	14.4

Table S14. Kinetic data for the reaction of 1-Chloro-2,4-dinitrobenzene with morpholine in mixture BMIMBF₄ / BMIMPF₆ of different composition solution at 25°C $\pm$ 0.1°C.

[BMIM][BF ₄] _{0.9} [PF ₆] _{0.1}		[BMIM][BF ₄] ₁ [PF ₆] ₀	
10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹	10 ² [N] _{total} /M	10 ³ k _{obs} /s ⁻¹
3.43	4.54	3.43	0.26
5.72	9.71	8.00	3.64
9.15	16.2	11.43	8.32
11.4	17.9	16.01	11.02
14.9	24.1	19.43	20.04
19.4	30.2	28.58	30.09

Figure S15. Comparison between the rate constants and molar fraction in [BMIM][PF₆]_a [FAP]_b.

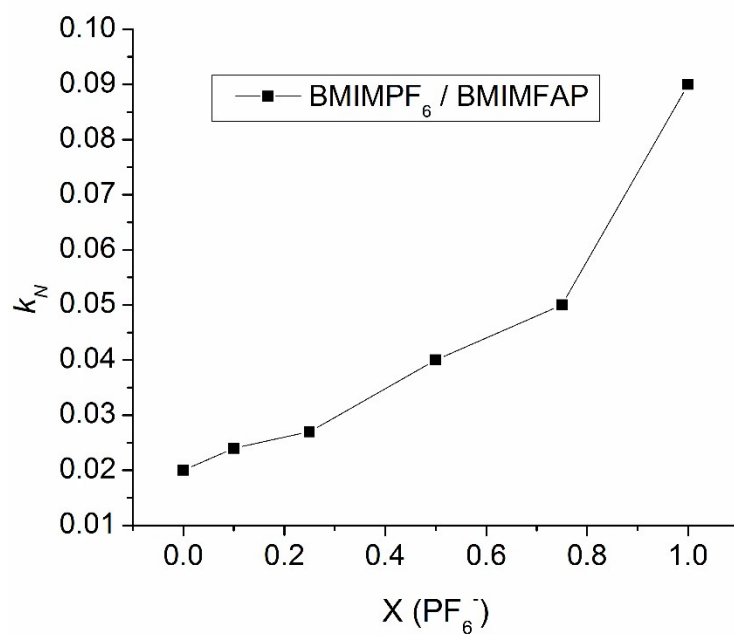


Figure S16. Comparison between the rate constants and molar fraction in [BMIM][DCN]_a [FAP]_b.

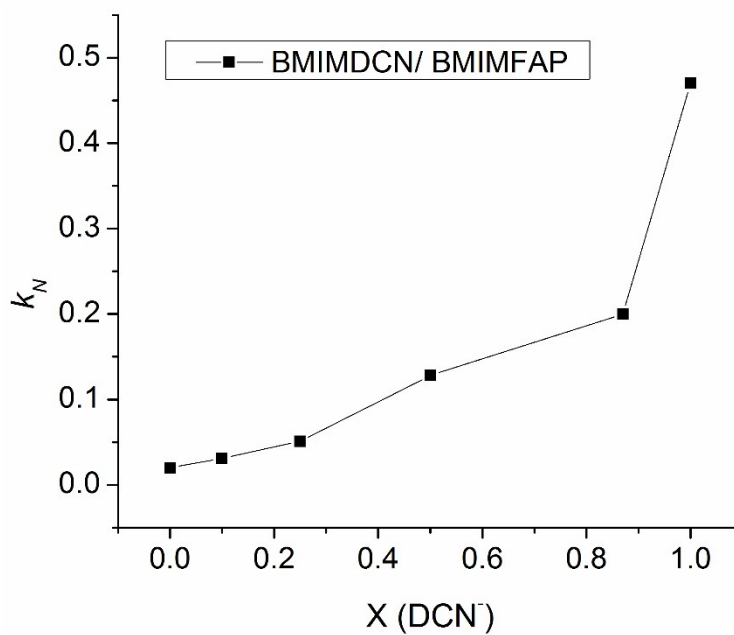


Figure S17. Comparison between β parameter and molar fraction in $[\text{EMIM}][\text{SCN}]_a$ $[\text{DCN}]_b$.

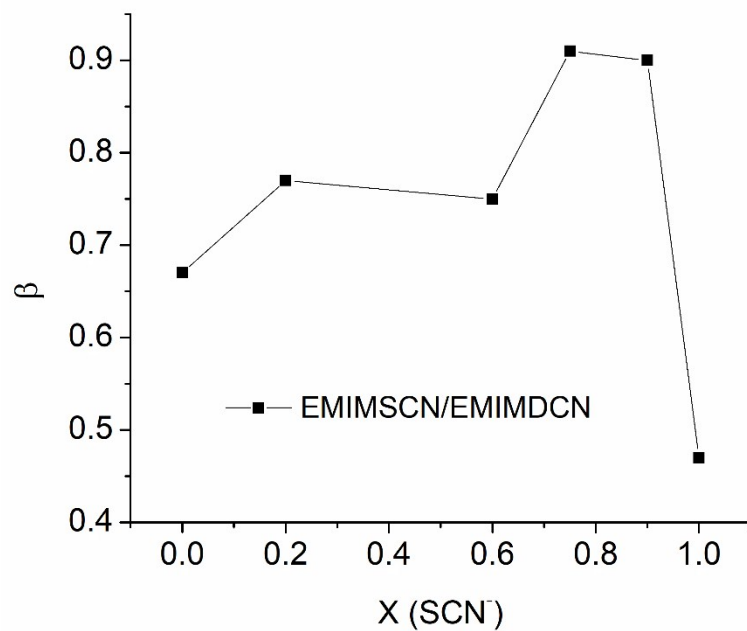


Figure S18. Comparison between π^* parameter and molar fraction in $[\text{EMIM}][\text{SCN}]_a$ $[\text{DCN}]_b$.

