Interaction of imidazolium-based ionic liquids with supported phospholipid bilayers as model biomembranes

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SUPPORTING INFORMATION

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Additional figures

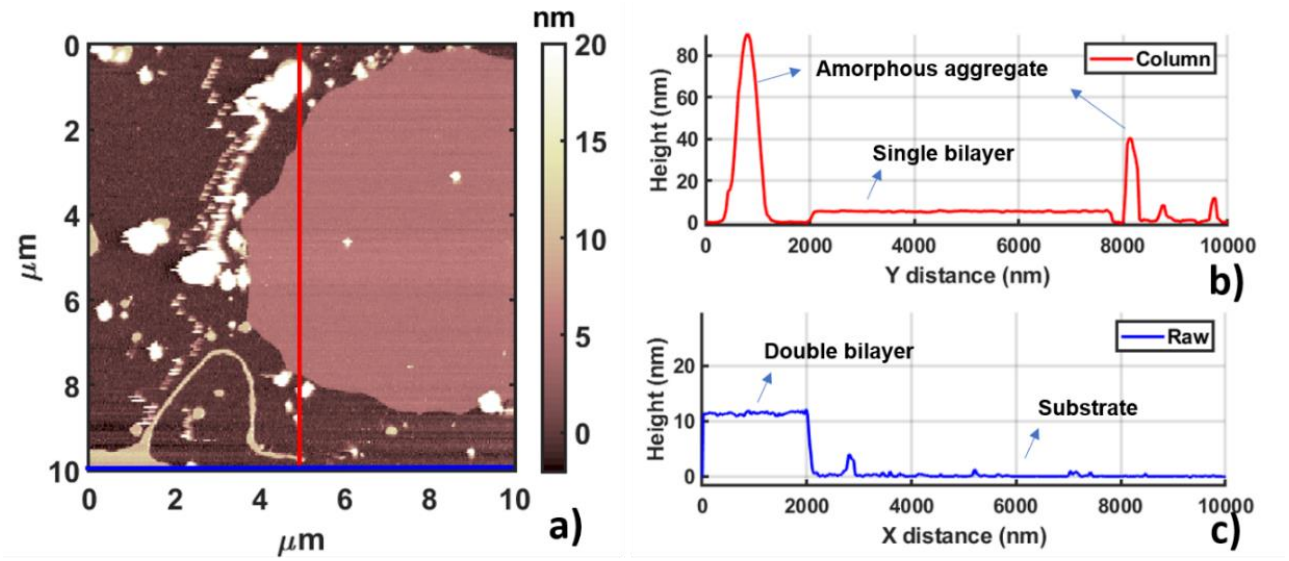

Figure SI1. Representative AFM imaging of a DOPC bilayer. a) Morphology (Figure 2a(i) of main text); b) height profile along the red line, showing amorphous aggregates and a single bilayer; c) height profile along the blue line, showing the substrate and a double bilayer.

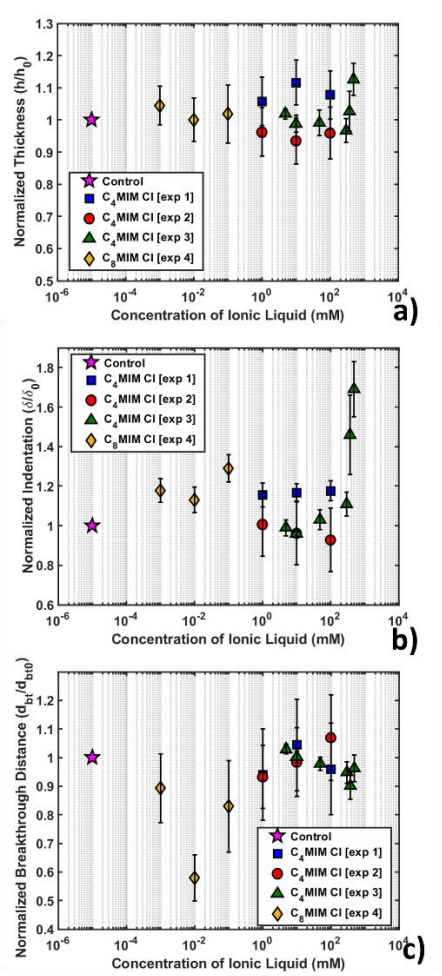

Figure SI2. Representation of morphological normalized quantities of DOPC bilayers after interaction with $[C_4MIM][Cl]$ and $[C_8MIM][Cl]$ at different concentrations. a) Thickness (h), b) maximum indentation (d_{MAX}), c) breakthrough distance (d_{bt}). For reference, the control data point is showed on the graphs at 10^{-5} mM.

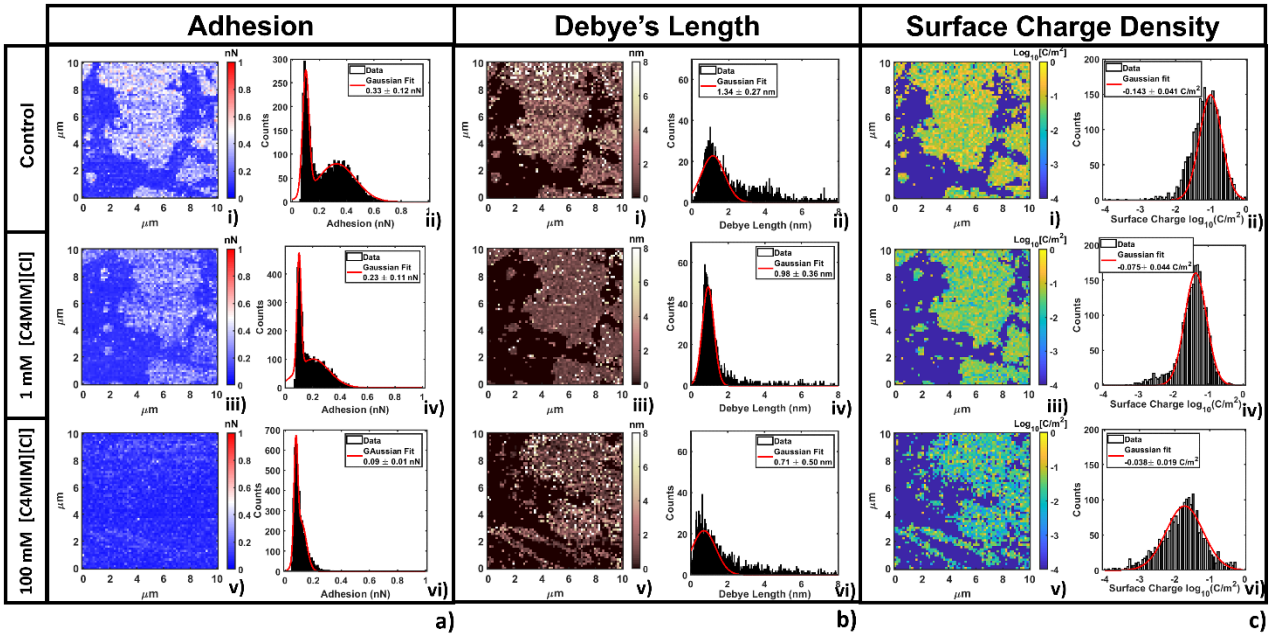

Figure SI3. Representative analysis of the evolution of a) adhesion force F_{ADH}, b) Debye's length l_D and c) surface charge density s_s for DOPC supported bilayer varying the concentration of $[C_4MIM][Cl]$. For each panel, image i) represents the map, image ii) the histogram with Gaussian fit focused on bilayer before interaction. In the same order iii-iv and v-vi, images represent the same location after 20 min interaction with 1 mM and 100 mM concentration, respectively.

Additional Tables

Impact of the water layer between the mica substrate and the lipid bilayer on the mechanical analysis

Table SI1. Mechanical analysis data after considering an error in the contact point determination (±0.5 nm). The values correspond to the force curve of Figure 1c. Symbol definition: R is tip radius (fixed at R = 20nm), C is the empirical multiplier of the number of Gaussian peak widths (standard deviations) away from the center (towards larger distances from the bilayer surface) in order to localize the contact point, h is thickness, Fb is breakthrough force, E is Young's modulus, k_A is compressibility modulus, l_D is Debye's length and s_s is density of surface charges. The equation used to extract mechanical parameter is shown above the respective columns.

			Eq. 1	**Eq. 2**	**Eq. 3**	**Eq. 4**	**Eq. 4**
C	**h (nm)**	**F_{bt} (nN)**	**E (MPa)**	**k_A (mN/m)**	**k_A (mN/m)**	**λ_D (nm)**	**σ_s (mC/m^2)**
2.5	5.94	8.36	24.0	198	190.1	1.97	-124
2.2	5.46	8.36	28.6	262	208.2	1.39	-532
2.8	6.42	8.36	20.8	148	178.0	1.91	-102

Mechanical Analysis Data

Each table represents an independent experiment using different probes or testing different conditions. Here, h represents the thickness of DOPC bilayer, F_{bt} is the breakthrough force, E is the corrected Young's modulus. For all the quantities, s[ ] represents the standard deviation of the mean, while var% is the percentage variation referenced with control (this quantity is averaged on the measurement group).

Table SI2a. Experiment 1. Mechanical data of DOPC phospholipid bilayer interacting with [C_4MIM][Cl] at different concentrations. k = 0.14 N/m, radius R = 10 nm, optical lever sensitivity Defl. Sens. = 22.4 nm/V. Data are shown in Figure 6 main text.

Condition	**h (nm)**	**σ[h] (nm)**	**var%**	**F_{bt} (nN)**	**σ[F_{bt}] (nN)**	**var%**	**E (MPa)**	**σ[E] (MPa)**	**var%**
Control	4.92	0.43		8.07	0.76		41	10.3	
	4.94	0.65		7.02	0.64		39.7	8.1	
1 mM	5.27	0.46		6.60	1.2		28.7	3.2	
	5.16	0.34	5%	5.55	0.43	-14%	30	3.2	-28%
10 mM	5.60	0.23		4.41	0.37		29.5	2.6	
	5.41	0.33	11%	4.06	0.49	-44%	21.9	2.9	-37%
100 mM	5.61	0.43		2.81	0.34		21.3	2.2	
	5.02	0.27	7%	2.93	0.28	-62%	20.1	2.3	-49%

Table SI2b. Experiment 2. Mechanical data of DOPC phospholipid bilayer interacting with [C4MIM][Cl] at different concentrations. k = 0.25 N/m, R = 10 nm, Defl. Sens = 49.1 nm/V.

Condition	h (nm)	σ[h] (nm)	var%	F_{bt} (nN)	σ[F_{bt}] (nN)	var%	E (MPa)	σ[E] (MPa)	var%
Control	5.96	0.59		9.83	2.2		196.5	14	
	6.39	0.47		12.38	3.12		142	11	
1 mM	5.86	0.34		9.7	1.4		119	33	
	5.06	0.48	-12%	10.3	0.72	-10%	195	21	-8%
10 mM	5.63	0.72		8.31	1.45		120	21	
	4.98	0.64	-14%	10.7	2.8	-15%	167	29	-16%
100 mM	5.4	0.52		6.08	1.5		91.4	17.3	
	5.49	0.73	-12%	5.54	1.41	-48%	111	18	-41%

Table SI2c. Experiment 3. Mechanical data of DOPC phospholipid bilayer interacting with [C4MIM][Cl] at different concentrations. k = 0.72 N/m, R = 10 nm, Defl. Sens = 13.6 nm/V.

Condition	h (nm)	σ[h] (nm)	var%	F_{bt} (nN)	σ[F_{bt}] (nN)	var%	E (MPa)	σ[E] (MPa)	var%
Control	5.32	0.09		1.54	0.13		66.3	5.75	
	5.43	0.1		1.54	0.11		68.3	4.9	
5 mM	5.5	0.11		1.46	0.13		66	5	
	5.5	0.11		1.41	0.13		67.6	5.2	
	5.44	0.1	2%	1.43	0.08	-7%	65	4	-2%
Control	4.59	0.12		2.52	0.2		53.6	3.2	
	4.61	0.13		2.51	0.21		53.7	3.3	
10 mM	4.59	0.13		2.21	0.22		46.7	3.1	
	4.61	0.15		2.02	0.19		45.8	3.5	
	4.44	0.16	-1%	2.05	0.17	-17%	45.1	3.1	-15%
Control	5.73	0.14		1.66	0.28		75	7.8	
	5.67	0.12		1.59	0.49		80.9	11.8	
	5.97	0.18		1.43	0.43		64.1	9.6	
50 mM	5.74	0.17		1.48	0.32		47.9	9.2	
	5.76	0.19		1.27	0.39		60	10	
	5.73	0.17	-1%	1.74	0.43	-5%	69.8	9.4	-20%
Control	5.32	0.1		2.91	0.15		145.5	5.4	
	5.31	0.09		2.67	0.13		92.1	7.2	
	5.24	0.1		2.89	0.15		63	4.8	
300 mM	4.93	0.15		1.85	0.12		71.3	8.1	
	5.2	0.12		1.86	0.12		85	9	
	5.22	0.17	-4%	2.13	0.16	-32%	56.9	5.4	-30%
Control	5.18	0.28		7.37	0.36		478.8	69	
383 mM	5.07	0.27		4.5	0.45		358	122	
	4.82	0.28		5.17	0.5		221	68	
	6.07	0.45	2%	4.05	0.41	-38%	83	13	-54%
500 mM	6.03	0.18		3.06	0.32		101	16	
	5.73	0.43		2.7	0.26		87	25	
	5.74	0.26	12%	3.17	0.32	-60%	89	27	-81%

Table SI2d. Experiment 4. Mechanical data of DOPC phospholipid bilayer interacting with [C_8MIM][Cl] at different concentrations. k = 1.65 N/m, R = 10 nm, Zsens = 14.6 nm/V.

Condition	h (nm)	σ[h] (nm)	var%	F_{bt} (nN)	σ[F_{bt}] (nN)	var%	E (MPa)	σ[E] (MPa)	var%
Control	4.93	0.44		14.47	1.31		85.6	2.1	
	4.97	0.33		14.6	1.56		88.2	6.0	
	5.27	0.26		14.97	0.62		80.1	5.9	
1 μM	5.09	0.18		13.17	1.07		89	4.1	
	5.55	0.47		13.32	0.72		81.3	3.9	
	5.17	0.28	4%	12.92	1.07	-11%	78.6	9.7	-4%
10 μM	4.97	0.07		11.95	1.1		79.5	6.2	
	5.19	0.17		11.65	0.92		80	4.4	
	5.2	0.19	0%	12.68	1.03	-19%	77	13	-6%
100 μM	5.09	0.28		10.32	1.02		67	4.8	
	5.34	0.18	2%	11.11	0.61	-28%	72.9	6.1	-17%

Electrostatic Force Analysis Data

Each table represents an independent experiment using different probes or testing different conditions. Here, F_{ADH} represents the adhesion force during retraction curve, λ_D is the Debye's length and σ_s is the surface charge density of the bilayer. For all the quantities, σ[] represents the standard deviation of the mean, while var% is the percentage variation referenced with control (this quantity is averaged on the measurement group).

Table SI3a. Experiment 1. Electrostatic data of DOPC phospholipid bilayer interacting with [C_4MIM][Cl] at different concentrations. k = 0.14 N/m, R = 10 nm, optical lever sensitivity Zsens = 22.4 nm/V and probe surface charge density $\sigma_P = -9 \times 10^{-3}$ C/m^2. Data are shown in Figure SI2 in SI.

Condition	F_{ADH} (nN)	σ[F_{ADH}] (nN)	var%	λ_D (nm)	σ[λ_D] (nm)	var%	σ_s (C/m^2)	σ[σ_s] (C/m^2)	var%
Control	0.283	0.139		0.930	0.540		-0.198	0.070	
	0.348	0.121		1.344	0.273		-0.143	0.041	
1 mM	0.249	0.115		1.271	0.512		-0.076	0.041	
	0.210	0.112	-26%	0.989	0.367	-1%	-0.075	0.044	-56%
10 mM	0.212	0.123		0.910	0.310		-0.069	0.031	
	0.148	0.109	-42%	0.891	0.578	-21%	-0.060	0.029	-62%
100 mM	0.075	0.012		0.719	0.464		-0.036	0.023	
	0.079	0.013	-76%	0.713	0.506	-38%	-0.038	0.019	-78%

Table SI3b. Experiment 2. Electrostatic data of DOPC phospholipid bilayer interacting with [C_4MIM][Cl] at different concentrations. k = 0.25 N/m, radius R = 10 nm, Zsens = 49.1 nm/V and σ_P= -9 x 10^{-3} C/m^2.

Condition	F_{ADH} (nN)	$\sigma[F_{ADH}]$ (nN)	var%	λ_D (nm)	$\sigma[\lambda_D]$ (nm)	var%	σ_s (C/m^2)	$\sigma[\sigma_s]$ (C/m^2)	var%
Control	0.29	0.21		0.48	0.14		-0.127	0.043	
	0.35	0.14		0.46	0.17		-0.133	0.053	
1 mM	0.38	0.13		1.1	0.35		-0.293	0.023	
	0.41	0.17	22%	1.29	0.43	152%	-0.104	0.052	53%
10 mM	1.06	0.67		1.16	0.5		-0.099	0.054	
	0.62	0.17	164%	1.42	0.55	172%	-0.061	0.021	-38%
100 mM	0.41	0.17		1.37	0.47		-0.031	0.008	
	0.64	0.21	65%	1.74	0.36	228%	-0.025	0.006	-79%

Table SI3c. Experiment 3. Electrostatic data of DOPC phospholipid bilayer interacting with [C_4MIM][Cl] at different concentrations. k = 0.72 N/m, R = 10 nm, Zsens = 13.6 nm/V, σ_P= -9 x 10^{-3} C/m^2.

Condition	F_{ADH} (nN)	$\sigma[F_{ADH}]$ (nN)	var%	λ_D (nm)	$\sigma[\lambda_D]$ (nm)	var%	σ_s (C/m^2)	$\sigma[\sigma_s]$ (C/m^2)	var%
Control	0.549	0.065		0.211	0.075		-0.099	0.025	
	0.564	0.062		0.224	0.073		-0.092	0.029	
5mM	0.572	0.075		0.207	0.061		-0.087	0.024	
	0.469	0.067		0.21	0.054		-0.084	0.023	
	0.416	0.070	-12%	0.205	0.066	-5%	-0.084	0.021	-12%
Control	1.063	0.147		0.622	0.084		-0.115	0.006	
	1.096	0.171		0.609	0.076		-0.113	0.017	
10mM	0.969	0.137		0.648	0.064		-0.109	0.009	
	0.788	0.136		1.035	0.168		-0.067	0.009	
	0.82	0.162	-21%	0.973	0.208	+43%	-0.068	0.014	-29%
Control	0.568	0.104		0.714	0.164		-0.087	0.026	
	0.495	0.099		1.15	0.44		-0.043	0.019	
50 mM	0.479	0.108		2.13	0.81		-0.027	0.014	
	0.478	0.14		0.819	0.659		-0.058	0.047	
	0.358	0.096	-18%	0.427	0.132	+20%	-0.076	0.026	-18%
Control	1.398	0.103		0.829	0.132		-0.205	0.018	
	1.057	0.112		0.838	0.156		-0.186	0.034	
	0.783	0.136		0.573	0.078		-0.198	0.024	
300 mM	0.289	0.095		0.882	0.131		-0.157	0.024	
	0.207	0.06		0.649	0.092		-0.111	0.018	
	0.209	0.073	-79%	0.622	0.103	-4%	-0.129	0.022	-33%
Control	1.44	0.42		4.06	0.57		-0.066	0.005	
383mM	1.98	0.3		2.4	0.9		-0.804	0.247	
	2.24	0.33		3.5	2.5		-0.007	0.003	
	1.48	0.35	+32%	3.4	4	-24%	-0.008	0.002	-52%
500 mM	2.31	0.34		1.13	0.79		-0.025	0.007	
	1.79	0.185		1.95	1.05		-0.016	0.004	
	1.79	0.19	+36%	1.92	0.85	-59%	-0.015	0.004	-92%

Table SI3d. Experiment 4. Electrostatic data of DOPC phospholipid bilayer interacting with [C_8MIM][Cl] at different concentrations. k = 1.65 N/m, R = 10 nm, Zsens = 14.6 nm/V, σ_P= -9 x 10^{-3} C/m^2.

Condition	F_{ADH} (nN)	$\sigma[F_{ADH}]$ (nN)	var%	λ_D (nm)	$\sigma[\lambda_D]$ (nm)	var%	σ_s (C/m^2)	$\sigma(\sigma_s)$ (C/m^2)	var%
Control	0.156	0.08		0.95	0.38		-0.831	0.140	
	0.58	0.15		1.48	3.14		-0.091	0.030	
	0.51	0.23		2.59	0.41		-0.145	0.025	
1 μM	0.91	0.18		1.69	0.61		-0.364	0.037	
	0.8	0.21		3.32	1.17		-0.128	0.061	
	0.74	0.16	+96%	3.25	1.2	+64%	-0.127	0.039	-42%
10 μM	0.78	0.15		1.24	2.23		-0.096	0.017	
	0.71	0.13		3.33	1.22		-0.091	0.033	
	0.78	0.16	-8%	2.29	1.32	-17%	-0.059	0.010	-77%
100 μM	0.99	0.14		1.95	1.12		-0.068	0.028	
	0.85	0.16	+21%	3.73	2.45	+18%	-0.045	0.016	-85%