ELECTRONIC SUPPORTING INFORMATION

Can the Scaling Behavior of Electric Conductivity be Used to Probe the Self-Organizational Changes in Solution with the Respect to the Ionic Liquid Structure? The case of $[C_8MIM][NTf_2]$

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1. Experimental Section

1.1. Sample preparation and purification

N-methylimidazole (99 %) and 1-bromooctane (98 %) were purchased from Sigma-Aldrich. All solvents used were HPLC grade purchased from Riedel de Haën. Lithium bis[(trifluoromethyl)sulfonyl]imide was purchased from 3M (> 98%). Microanalysis and Lithium content were performed by Analytical Services (ASEP and QUB). ^{1}H and ^{13}C NMR spectra were recorded at 293.15 K on a Bruker Avance DPX spectrometer at 300 MHz and 75 MHz, respectively and are reported herein in Figs. S1 and S2 of the supporting information. Chemical shifts are given in ppm downfield from TMS.

Synthesis of 1-methyl-3-octylimidazolium bromide

A mixture of 1-methylimidazole 99 % Sigma-Aldrich (4.10 g, 0.05 mol) and 1-bromooctane 98 % Sigma-Aldrich (5.99 g, 0.075 mol) was placed in a Parr autoclave sealed reaction vessel along with 30 cm^3 of HPLC grade acetonitrile. The reaction mixture was heated up to 343 K and then held at this temperature for 24h with stirring at 500 rpm. After cooling of the reaction mixture the acetonitrile was removed under vacuum. The highly viscous yellow product was recrystallized from acetonitrile/ethyl acetate mixture to afford an off-white solid, 78 % yield. The pure product was then characterized by ^{1}H NMR spectroscopy using a Bruker Avance machine.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.99 (t, 3H, CH_3, J= 7.45 Hz), 1.97 (m, 2H, CH_2), 4.14 (s, 3H, N-CH_3), 4.32 (t, 2H, CH_2, J= 7.31 Hz), 7.51 (s, 1H, Ar-H), 7.62 (d, 1H, Ar-H), 10.22 (s, 1H, Ar-H).

Synthesis of 1-methyl-3-octylimidazolium bis[(trifluoromethyl)sulfonyl]imide

A solution of lithium bis[(trifluoromethyl)sulfonyl]imide (143.55 g, 0.5 mol) in distilled water (300 cm^3) was added drop-wise to a rapidly stirred solution of 1-methyl-

3-propylimidazolium bromide (78.4 g, 0.49 mol) in dichloromethane (200 cm^3) and allowed to stir under ambient conditions overnight. The organic layer was then extracted and washed with distilled water (100 cm^3) repeatedly five times.

The organic layer was then dried *in vacuo* to give the product as an off-white liquid in < 98% yield which was found to contain < 22 ppm of lithium. Halide content was below the detectable limit by $AgNO_3$ testing.

CHNS calc. C: 35.58 %, H: 4.88 %, N: 8.84 %, S: 13.45 %; found C: 36.01 %, H: 4.99 %, N: 8.65 %, S: 13.14 %.

^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) = 9.12 (1 H, s), 7.77 (1 H, s), 7.71 (1 H, s), 4.17 (2 H, t, J = 7.1 Hz, N-CH_2), 3.87 (3 H, s, N-CH_3), 1.82 (2 H, m, CH_2), 1.24 (10 H, m, CH_2), , 0.87 (3 H, t, J = 7.4 Hz, CH_3)

^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) = 136.86, 123.95, 122.61, 122.00, 117.73, 49.17, 36.06, 31.51, 29.74, 28.82, 28.68, 25.85, 22.39, 14.20.

Figure S1. ^{1}H-NMR of 1-methyl-3-octylmethylimidazolium bis[(trifluoromethyl)sulfonyl]imide [C_8MIM][NTf_2]

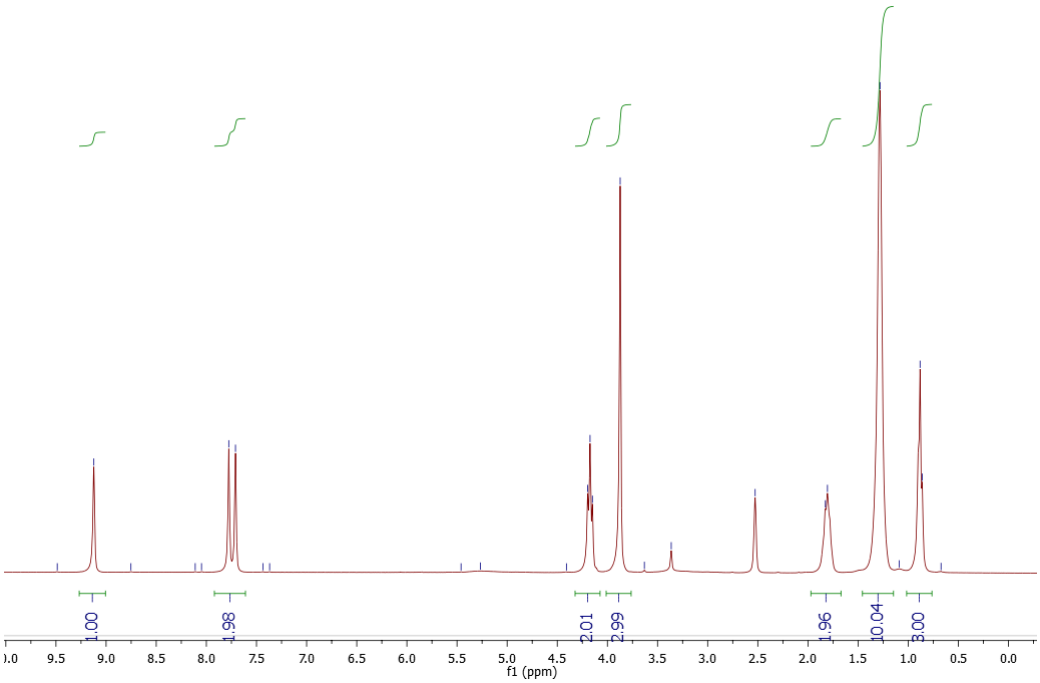
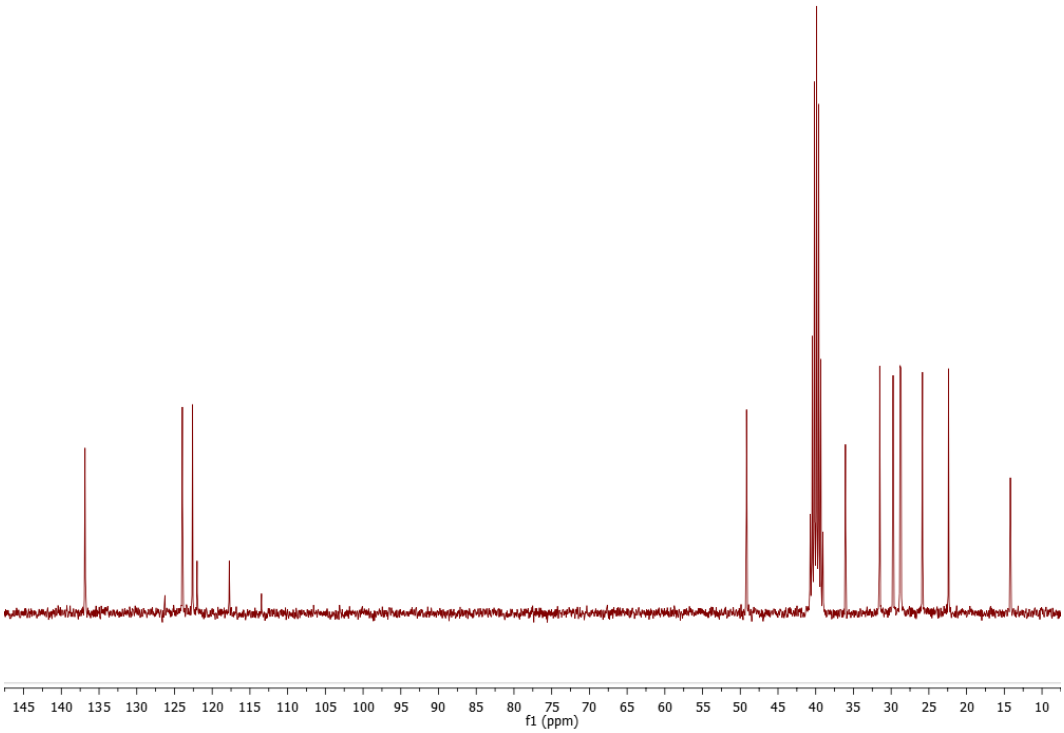


Figure S2. ^{13}C-NMR of 1-methyl-3-octylmethylimidazolium bis[(trifluoromethyl)sulfonyl]imide [C_8MIM][NTf_2]



1.2. Sample treatment

Prior to use, IL was treated for 15 hours at 323.15 K under vacuum (lower than 1 Pa), the sample was then considered as dried and was then stored under nitrogen atmosphere to avoid water contamination from atmosphere. Water content of the selected IL determined by Karl Fischer titration was close to 50 ppm, *i.e.* 0.005 wt%.

2. Raw Data and Fitting Parameters of the pVFT Equation and Volume Activated Model

Table S1. The electric conductivity of [C_8MIM][NTf_2] recorded under isobaric and isothermal conditions.

-log σ_{dc}/S·cm^{-1}											
T/K	Isobar 0.1MPa	T/K	Isobar 0.1MPa	P/MPa	Isotherm 213 K	P /MPa	Isotherm 223 K	P /MPa	Isotherm 233 K	P /MPa	Isotherm 243 K
408.15	2.519	273.15	4.134	2.5	7.538	0.1	6.698	455	11.252	450	9.439
403.15	2.537	268.15	4.294	17.5	7.737	50	7.144	430	10.864	426	9.169
398.15	2.556	263.15	4.467	32.5	7.966	70	7.377	405	10.476	400	8.917
393.15	2.579	258.15	4.663	47.5	8.221	90	7.637	380	10.114	375	8.666
388.15	2.596	253.15	4.874	62.5	8.457	110	7.898	355	9.754	350	8.405
383.15	2.624	248.15	5.088	77.5	8.701	130	8.145	330	9.419	325	8.171
378.15	2.650	243.15	5.369	92.5	8.945	150	8.404	305	9.111	300	7.938

373.15	2.679	238.15	5.641	107.5	9.205	170	8.678	280	8.816	275	7.713
368.15	2.707	233.15	5.954	122.5	9.467	190	8.939	255	8.536	250	7.488
363.15	2.735	228.15	6.315	137.5	9.742	210	9.226	230	8.256	225	7.282
358.15	2.775	223.15	6.715	152.5	10.032	230	9.528	205	7.974	200	7.066
353.15	2.814	220.15	6.997	167.5	10.323	250	9.843	180	7.707	0.1	5.344
348.15	2.854	218.15	7.194	182.5	10.645	270	10.185	155	7.453		
343.15	2.899	216.15	7.388	197.5	10.966	290	10.527	130	7.198		
338.15	2.951	214.15	7.592	212.5	11.302	310	10.884	105	6.943		
333.15	3.005	212.15	7.819	227.5	11.653	330	11.268	80	6.719		
328.15	3.062	210.15	8.056	242.5	12.021	350	11.7331	0.1	5.937		
323.15	3.128	208.15	8.327	257.5	12.404						
318.15	3.196	206.15	8.607	272.5	12.802						
313.15	3.268	204.15	8.912								
308.15	3.342	202.15	9.233								
303.15	3.421	200.15	9.604								
298.15	3.527	198.15	9.987								
293.15	3.615	196.15	10.421								
288.15	3.742	194.15	10.910								
283.15	3.857	192.15	11.455								
278.15	3.999	190.15	12.084								
		188.15	12.784								

Table S1. *Continued …*

-log σ_{dc}/S·cm^{-1}									
P/MPa	Isotherm 273 K	P/MPa	Isotherm 283 K	P/MPa	Isotherm 293 K	P/MPa	Isotherm 303 K	P/MPa	Isotherm 313 K
30	4.314	40	4.072	480	5.553	30	3.527	30	3.363
60	4.437	70	4.195	450	5.436	60	3.637	60	3.449
90	4.629	100	4.323	420	5.319	90	3.741	90	3.543
120	4.775	130	4.457	390	5.198	120	3.859	120	3.633
150	4.930	160	4.598	360	5.081	150	3.966	150	3.727
180	5.078	190	4.726	330	4.959	180	4.069	180	3.826
210	5.230	220	4.864	300	4.843	210	4.169	240	4.009
240	5.391	250	4.999	270	4.721	240	4.277	300	4.212
270	5.536	280	5.135	240	4.600	270	4.359	420	4.598
300	5.712	310	5.273	210	4.478	300	4.495	480	4.768
330	5.831	340	5.409	180	4.361	330	4.601	360	4.399
360	5.997	370	5.543	150	4.259	360	4.708		
390	6.147	400	5.677	120	4.118	390	4.814		
420	6.297	430	5.799	90	4.006	420	4.921		
450	6.465	460	5.905	60	3.875	450	5.021		
				30	3.739	480	5.115		

Table S2. Volumetric properties of $[C_8MIM][NTf_2]$ recorded under isobaric conditions.

Vsp/cm^3g^{-1}											
Pressure/MPa											
T/K	0.1	20	40	60	80	100	120	140	160	180	200
297.9	0.7587	0.7511	0.7444	0.7384	0.7328	0.7277	0.7231	0.7186	0.7145	0.71051	0.7068
297.0	0.7582	0.7506	0.7438	0.7379	0.7324	0.7274	0.7227	0.7183	0.7144	0.71019	0.70649
300.8	0.7598	0.7523	0.7455	0.7394	0.7339	0.7288	0.7241	0.7197	0.7154	0.71142	0.70766
305.8	0.7622	0.7544	0.7476	0.7413	0.7357	0.7306	0.7258	0.7213	0.717	0.713	0.70913
310.4	0.7646	0.7567	0.7496	0.7434	0.7377	0.7324	0.7275	0.7229	0.7186	0.71456	0.71074
315.1	0.7670	0.7589	0.7517	0.7453	0.7395	0.7342	0.7293	0.7246	0.7203	0.71612	0.71219
319.9	0.7694	0.7612	0.7539	0.7474	0.7415	0.7359	0.7310	0.7263	0.7219	0.71772	0.71371
324.9	0.7719	0.7635	0.756	0.7494	0.7434	0.7378	0.7328	0.7280	0.7235	0.71931	0.71526
329.6	0.7744	0.7657	0.7581	0.7513	0.7452	0.7397	0.7344	0.7297	0.7251	0.72083	0.71677
334.5	0.7768	0.7681	0.7603	0.7534	0.7472	0.7415	0.7362	0.7314	0.7267	0.72237	0.71829
339.3	0.7793	0.7703	0.7625	0.7554	0.7491	0.7433	0.7381	0.7330	0.7284	0.72398	0.71978
344.03	0.7817	0.7726	0.7645	0.7574	0.7510	0.7451	0.7397	0.7347	0.7300	0.72554	0.7213
348.9	0.7844	0.7750	0.7667	0.7595	0.7529	0.7468	0.7415	0.7364	0.7316	0.72708	0.72281
353.9	0.7870	0.7773	0.7689	0.7616	0.7549	0.7488	0.7433	0.7381	0.7332	0.72868	0.72433
358.8	0.7896	0.7797	0.7711	0.7635	0.7568	0.7507	0.7449	0.7397	0.7348	0.7302	0.72579
363.9	0.7922	0.7821	0.7733	0.7655	0.7586	0.7524	0.7467	0.7414	0.7364	0.73176	0.72732
368.7	0.7947	0.7845	0.7755	0.7677	0.7606	0.7543	0.7485	0.7431	0.7381	0.73327	0.72883
373.9	0.7974	0.7868	0.7778	0.7697	0.7625	0.7561	0.7502	0.7448	0.7397	0.73488	0.73034
378.7	0.8000	0.7892	0.7798	0.7717	0.7644	0.7579	0.7519	0.7464	0.7412	0.73639	0.7318
383.6	0.8026	0.7916	0.7821	0.7738	0.7664	0.7598	0.7536	0.7480	0.7428	0.73796	0.73323
388.6	0.8053	0.7939	0.7843	0.7758	0.7683	0.7616	0.7554	0.7498	0.7444	0.73951	0.73481
393.7	0.8081	0.7964	0.7865	0.7779	0.7702	0.7634	0.7571	0.7514	0.7459	0.74103	0.73625

*Data are in good agreement with values reported in refs.
Almantariotis, D.; Fandiño, O.; Coxam, J. Y.; Costa Gomes, M. F., Direct measurement of the heat of solution and solubility of carbon dioxide in 1-hexyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide and 1-octyl-3-methylimidazolium bis[trifluoromethylsulfonyl]amide. *International Journal of Greenhouse Gas Control* **2012,** 10, 329-340. and Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P., PρT Measurements of Imidazolium-Based Ionic Liquids. *Journal of Chemical & Engineering Data* **2007,** 52, (5), 1881-1888.

Table S3. Parameters obtained from fitting of pVFT equation and volume activated model to the experimental data of $[C_8MIM][NTf_2]$ ionic liquid.

pVFT	**$\log\sigma_0$**	**D_P**	**P_0**
isotherm 213 K	7.51±0.01	31.4±0.6	975±14
isotherm 223K	6.67±0.01	25.8±1.2	1130±35
isotherm 233K	5.98±0.02	34.3±1.8	1745±67
isotherm 243K	5.35±0.02	72.2±8.4	3920±90
volume activated model	**$\log\sigma_0$**	**ΔV**	
isotherm 273K	4.15±0.01	$3.58\cdot10^{-4}\pm1.6\cdot10^{-6}$	
isotherm 283K	3.88±0.01	$3.00\cdot10^{-4}\pm1.4\cdot10^{-6}$	
isotherm 293K	3.63±0.01	$2.61\cdot10^{-4}\pm9.7\cdot10^{-7}$	
isotherm 303K	3.42±0.01	$2.23\cdot10^{-4}\pm9.9\cdot10^{-7}$	
isotherm 313K	3.26±0.01	$1.93\cdot10^{-4}\pm9.1\cdot10^{-7}$	