Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Ion chromatography for monitoring $[NTf_2]^-$ anion contaminants in pure and saline water

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1. NMR Data

NMR were recorded on a JEOL ECZ 400MHz spectrometer with Royal HFX probe. Samples were prepared in DMSO-d_6 and spectra are referenced to the residual ^{1}H NMR signal at 2.50 ppm and the ^{13}C NMR signal at 39.52 ppm.

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_4C_1Im][NTf_2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (s, 1H), 7.72 (t, J = 1.9 Hz, 1H), 7.65 (t, J = 1.7 Hz, 1H), 4.12 (t, J = 7.0 Hz, 2H), 3.80 (s, 3H), 1.80 – 1.61 (m, 2H), 1.27 – 1.14 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 136.51, 123.63, 122.27, 119.49 (q, J = 322.0 Hz), 48.51, 35.74, 31.37, 18.78, 13.25. ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.67.

Data consistent with previous reported.[1]

1-Octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C_8C_1Im][NTf_2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 7.76 (t, J = 1.8 Hz, 1H), 7.69 (t, J = 1.8 Hz, 1H), 4.14 (t, J = 7.2 Hz, 2H), 3.84 (s, 3H), 1.34 – 1.18 (m, 12H), 0.86 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.49, 123.63, 122.27, 119.49 (q, J = 322.0 Hz), 48.78, 35.75, 31.18, 29.39, 28.49, 28.35, 25.50, 22.07, 13.94. ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.66.

Data consistent with previous reported.[1]

1,6-bis(3-methylimidazolium)hexane di[bis(trifluoromethanesulfonyl)imide], [C_6(C_1Im)$_2$][NTf_2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.08 (s, 2H), 7.74 (s, 2H), 7.70 (s, 2H), 4.14 (t, J = 6.8 Hz, 4H), 3.84 (s, 6H), 1.90 – 1.68 (m, 4H), 1.38 – 1.17 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.49, 123.66, 122.25, 119.50 (d, J = 321.9 Hz), 48.68, 35.76, 29.15, 24.94. ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.66.

Data consistent with previous reported. [2]

1,12-Bis(3-methylimidazolium)dodecane di[bis(trifluoromethanesulfonyl)imide], [C_{12}(C_1Im)$_2$][NTf_2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 2H), 7.75 (d, J = 1.7 Hz, 2H), 7.69 (d, J = 1.9 Hz, 2H), 4.14 (t, J = 7.3 Hz, 2H), 3.84 (s, 6H), 1.89 – 1.62 (m, 2H), 1.45 – 1.12 (m, 8H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 136.49, 123.62, 122.26, 119.50 (q, J = 322.1 Hz), 48.80, 35.74, 29.42, 28.99, 28.88, 28.44, 25.54. ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.68.

Data consistent with previous reported. [2]

Tetraoctylphosphonium bis(trifluoromethylsulfonyl)imid, [P_{8888}][NTf_2]:

^{1}H NMR (400 MHz, DMSO-d_6) δ 2.26 – 2.06 (m, 8H), 1.52 – 1.42 (m, 8H), 1.42 – 1.33 (m, 8H), 1.33 – 1.21 (m, 32H), 1.02 – 0.75 (m, 12H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.67.

Data consistent with previous reported.[3]

Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide, [P_{66614}][NTf_2]:

^{1}H NMR (400 MHz, DMSO-*d6*) δ 2.27 – 2.05 (m, 8H), 1.52 – 1.42 (m, 8H), 1.42 – 1.34 (m, 8H), 1.33 – 1.20 (m, 32H), 0.98 – 0.72 (m, 12H). ^{13}C NMR (101 MHz, DMSO-d6) δ 31.24 , 30.33 , 29.97 , 29.82 , 29.75 , 29.60 , 28.97 , 28.89 , 28.65 , 28.57 , 28.02 , 22.03 , 21.74 , 20.49 , 20.45 , 20.39 , 17.71 , 17.62 , 17.24 , 17.15 , 13.86 , 13.77 . ^{19}F NMR (376 MHz, DMSO-d_6) δ -78.67. ^{31}P NMR (162 MHz, DMSO-d_6) δ 34.36.

Data consistent with previous reported.[3]

2. Equations

$$R = \frac{(t_{r2} - t_{r1})}{(0.5(w_1 + w_2))} \quad \text{(S1)}$$

Where t_{rn} is the retention time, and w_n is the baseline peak width.

$$k = \frac{(t_R - t_0)}{t_0} \quad \text{(S2)}$$

Where t_R is the retention time of the $[NTf_2]^-$ analyte and t_0 is the retention time of a non-retained analyte, here we used the retention time of water from the sample matrix.

3. Additional Information

Table S1 Retention times for 1 mM $[NTf_2]^-$ and 1 mM Cl^- as a function of NaOH total eluent strength for 30% MeCN at 1 mL/min.

	Retention Time / min			
NaOH (mM)	$[NTf_2]^-$	σ	Cl^-	σ
5	25.380	0.029	4.847	0.011
10	15.722	0.029	3.853	0.014
20	9.634	0.007	3.258	0.005
30	7.694	0.004	3.075	0.006
40	6.760	0.004	3.003	0.005

Table S2 Retention times for 1 mM $[NTf_2]^-$ and 1 mM Cl^- as a function of MeCN eluent composition for 30 mM NaOH at 1 mL/min.

	Retention Time / min			
MeCN (%)	$[NTf_2]^-$	σ	Cl^-	σ
30	7.711	0.025	3.084	0.006
25	11.132	0.005	3.097	0.001
20	16.268	0.045	3.125	0.003
15	23.007	0.004	3.165	0.002
10	30.243	0.004	3.197	0.002

Table S3 Resolution between Cl^- and $[NTf_2]^-$ as a function of NaOH total eluent strength for 30% MeCN at 1 mL/min.

NaOH (mM)	Resolution	σ
5	43.759	0.291
10	9.586	0.134
20	3.143	0.042
30	1.820	0.051
40	1.299	0.021

Table S4 Resolution between Cl^- and $[NTf_2]^-$ as a function of MeCN eluent composition for 30 mM NaOH at 1 mL/min.

MeCN (%)	Resolution	σ
30	1.820	0.051
25	4.817	0.100
20	11.922	0.223
15	23.215	2.945
10	29.385	3.796

Table S5 Asymmetry factor for $[NTf_2]^-$ as a function of NaOH total eluent strength for 30 % MeCN at 1 mL/min.

	As	
NaOH (mM)	$[NTf_2]^-$	σ
5	2.77	0.003
10	2.495	0.005
20	2.175	0.006
30	2.005	0.001
40	1.9	0.004

Table S6 Asymmetry factor for $[NTf_2]^-$ as a function of MeCN eluent composition for 30 mM NaOH at 1 mL/min.

	As	
MeCN (%)	$[NTf_2]^-$	σ
30	1.997	0.012
25	2.355	0.035
20	2.710	0.020
15	3.007	0.061
10	3.050	0.062

Table S7 Concentration dependant peak parameters for $[NTf_2]^-$ for 20 mM NaOH and 30% MeCN at 1 mL/min, showing the retention time, asymmetry factor, signal-to-noise, absolute error, and relative error.

Concentration / mM	Retention Time / min	As	S/N	σ / mM	σ / %
0.001	9.933	1.043	1.167	0.003	370.0
0.005	9.904	1.008	3.560	0.000	1.500
0.01	9.911	1.143	7.967	0.000	6.000
0.1	9.872	1.290	86.83	0.002	1.525
1	9.584	2.133	225.6	0.038	28.67
4	9.172	3.133	251.0	0.369	11.29
10	9.007	3.853	220.8	0.427	2.911
50	7.916	5.310	161.4	0.407	3.644
100	7.182	6.497	132.9	0.246	0.542

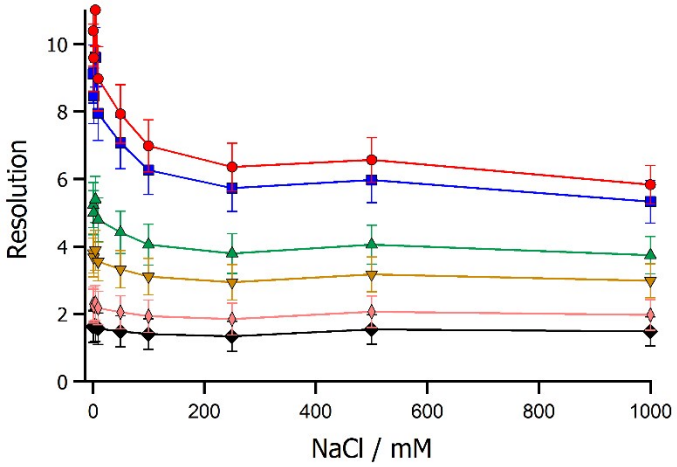

Figure S1 Resolution of $[NTf_2]^-$ and Cl^- for different concentration of NaCl: 0.1 mM (red circles), 1 mM (blue squares), 4 mM (green triangles), 10 mM (orange triangles), 50 mM (pink diamonds), and 100 mM (black diamonds) from 1 mL/min 20 mM NaOH and 30% MeCN.

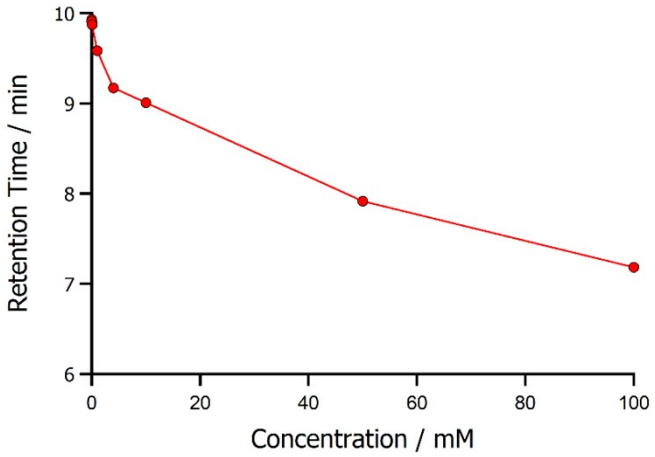

Figure S2 Retention time of $[NTf_2]^-$ for different analyte concentrations in 20 mM NaOH and 30% MeCN.

Note: All chromatograms are available upon request

(1) Clarke, C. J., Ionic Liquids as Designer Molecules for XPS Peak Fitting, *Thesis,* University of Nottingham, 2016.

(2) Mandai, T.; Imanari, M.; Nishikawa, K. Linker-Length Dependence of the Reorientational Dynamics and Viscosity of Bis(Imidazolium)-Based Ionic Liquids Incorporating Bis(Trifluoromethanesulfonyl) Amide Anions. *Chem. Phys. Lett.* **2012**, *543*, 72–75. https://doi.org/10.1016/j.cplett.2012.06.026.

(3) Blundell, R. K.; Licence, P. Quaternary Ammonium and Phosphonium Based Ionic Liquids: A Comparison of Common Anions. *Phys. Chem. Chem. Phys.* **2014**, *16*, 15278–15288. https://doi.org/10.1039/c4cp01901f.