10.1071/CH18481_AC

Australian Journal of Chemistry 2019, 72(1 & 2), 144-154

Supplementary Material

Using thermodynamics to assess the molecular interactions of tetrabutylphosphonium carboxylate-water mixtures

Darius J. Yeadon,[A,E] Johan Jacquemin,[A,B,E] Natalia V. Plechkova,[A] Margarida Costa Gomes,[C] and Kenneth R. Seddon[A,D]

[A]QUILL Research Centre, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG, Northern Ireland, UK.
[B]Université de Tours, Laboratoire PCM2E, Parc de Grandmont 37200, Tours, France.
[C]Laboratoire de Chimie, Ecole Normale Supérieure de Lyon and CNRS, 46 allée d'Italie, 69364 Lyon Cedex 07, France.
[D]Deceased.
[E]Corresponding authors. Email: dyeadon01@qub.ac.uk; jj@univ-tours.fr

General chemical characterisation of selected ionic liquids

Tetrabutylphosphonium ethanoate: ^{1}H NMR (d_6-dmso, 400 MHz, 353.15 K) δ/ppm = 0.53 (t, 12H, $(CH_2C\mathbf{H}_3)_4$); 1.05 (m, 8H, $(CH_2C\mathbf{H}_2CH_3)_4$); 1.19 (m, 8H, $(C\mathbf{H}_2CH_2CH_3)_4$, s, 3H, $C\mathbf{H}_3$-COO); 2.21 (m, 8H, $P(C\mathbf{H}_2)_4$). ^{13}C NMR (d_6-dmso, 101 MHz, 353.15 K) δ/ppm = 12.04 ($(CH_2CH_2\mathbf{C}H_3)_4$); 17.55 (d, P-$\mathbf{C}H_2$); 22.52 (d, $(CH_2\mathbf{C}H_2CH_3)_4$); 22.73 (d, $(\mathbf{C}H_2CH_2CH_3)_4$); 24.95 ($\mathbf{C}H_3COO$); 170.85 ($\mathbf{C}OO$). ^{31}P NMR ($PO_4(CH_3)_3$, 162 MHz, 353.15 K) δ/ppm = 33.45 (s, $\mathbf{P}(CH_2CH_2CH_2CH_3)_4$). MS ES+ *m/z* (% rel. Intensity): 259 M^+ (100). Calc. for $[P_{4\,4\,4\,4}]^+$ 259.2555, found 259.2531. MS ES- *m/z* (% rel. Intensity): 377 M^- (100). Calc. for $[\{P_{4\,4\,4\,4}\}\{C_1COO\}_2]^-$ 377.2821, found 377.2852.

Tetrabutylphosphonium propanoate: ^{1}H NMR (d_6-dmso, 400 MHz, 353.15 K) δ/ppm = 0.50 (t, 3H, $C\mathbf{H}_3CH_2COO$); 0.52 (t, 12H, $(CH_2CH_2C\mathbf{H}_3)_4$); 1.05 (m, 8H, $(CH_2C\mathbf{H}_2CH_3)_4$); 1.16 (m, 8H, $(C\mathbf{H}_2CH_2CH_3)_4$); 1.41 (q, 2H, $CH_3C\mathbf{H}_2COO$); 2.20 (m, 8H, $P(C\mathbf{H}_2)_4$). ^{13}C NMR (d_6-dmso, 101 MHz, 353.15 K) δ/ppm = 10.45 ($\mathbf{C}H_3CH_2COO$); 12.12 ($(CH_2CH_2\mathbf{C}H_3)_4$); 17.63 (d, $P(\mathbf{C}H_2)_4$); 22.58 (d, $(CH_2\mathbf{C}H_2CH_3)_4$); 22.72 (d, $(\mathbf{C}H_2CH_2CH_3)_4$); 31.13 ($CH_3\mathbf{C}H_2COO$); 174.09 ($\mathbf{C}OO$). ^{31}P NMR ($PO_4(CH_3)_3$, 162 MHz, 353.15 K) δ/ppm = 33.37 (s, $\mathbf{P}(CH_2CH_2CH_2CH_3)_4$). MS ES+ *m/z* (% rel. Intensity): 259 M^+ (100). Calc. for $[P_{4\,4\,4\,4}]^+$ 259.2555, found 259.2564. MS ES- *m/z* (% rel. Intensity): 405 M^- (100). Calc. for $[\{P_{4\,4\,4\,4}\}\{C_2COO\}_2]^-$ 405.3134, found 405.3124.

Tetrabutylphosphonium octanoate: ^{1}H NMR (d_6-dmso, 400 MHz, 353.15 K) δ/ppm = 0.46 (t, 3H, $C\mathbf{H}_3(CH_2)_6COO$); 0.54 (t, 12H, $(CH_2CH_2C\mathbf{H}_3)_4$); 0.86 (m, 10H, $(CH_3(C\mathbf{H}_2)_5CH_2COO$); 1.08 (m, 8H, $(CH_2C\mathbf{H}_2CH_3)_4$); 1.18 (m, 8H, $(C\mathbf{H}_2CH_2CH_3)_4$); 1.45 (t, 2H, $C\mathbf{H}_2COO$); 2.25 ($P(C\mathbf{H}_2)_4$). ^{13}C NMR (d_6-dmso, 101 MHz, 353.15 K) δ/ppm = 12.01 ($(CH_2CH_2\mathbf{C}H_3)_4$); 12.48 ($\mathbf{C}H_3(CH_2)_5CH_2COO$); 17.60 (d, $P(\mathbf{C}H_2)_4$); 21.27 ($CH_3\mathbf{C}H_2(CH_2)_5COO$); 22.60 (d, $(CH_2\mathbf{C}H_2CH_3)_4$); 22.75 (d, $(\mathbf{C}H_2CH_2CH_3)_4$); 26. 41 ($CH_3CH_2\mathbf{C}H_2(CH_2)_4COO$); 28.19 ($CH_3(CH_2)_2\mathbf{C}H_2(CH_2)_3COO$); 29.04 ($CH_3(CH_2)_3\mathbf{C}H_2(CH_2)_2COO$); 30.69 ($CH_3(CH_2)_4\mathbf{C}H_2CH_2COO$); 38.83 ($CH_3(CH_2)_5\mathbf{C}H_2COO$); 173.38 ($\mathbf{C}OO$). ^{31}P NMR ($PO_4(CH_3)_3$, 162 MHz, 353.15 K) δ/ppm = 33.36 (s, $\mathbf{P}(CH_2CH_2CH_2CH_3)_4$). MS ES+ *m/z* (% rel. Intensity): 259 M^+ (100). Calc. for $[P_{4\,4\,4\,4}]^+$ 259.2555, found 259.2499. MS ES- *m/z* (% rel. Intensity): 143 M^- (100). Calc. for $[C_7COO]^-$ 143.1072, found 143.1052.

Table S1. Elemental analysis and water content:

Ionic Liquid	%C		%H		Water content / ppm
	Calc.	Exp.	Calc.	Exp.	
$[P_{4\,4\,4\,4}][C_1COO]$	67.82	67.40	12.25	12.53	140
$[P_{4\,4\,4\,4}][C_2COO]$	68.57	67.72	12.33	11.84	180
$[P_{4\,4\,4\,4}][C_7COO]$	71.53	70.89	12.67	12.72	120

Table S2. Thermal gravimetric analysis:

Ionic Liquid	T_d (exp)/ ˚C	T_d (lit.)/ ˚C
$[P_{4\,4\,4\,4}][C_1COO]$	322.85	300.7 [1]
$[P_{4\,4\,4\,4}][C_2COO]$	300.82	305.0 [2]
$[P_{4\,4\,4\,4}][C_8COO]$	302.72	301.3 [1]

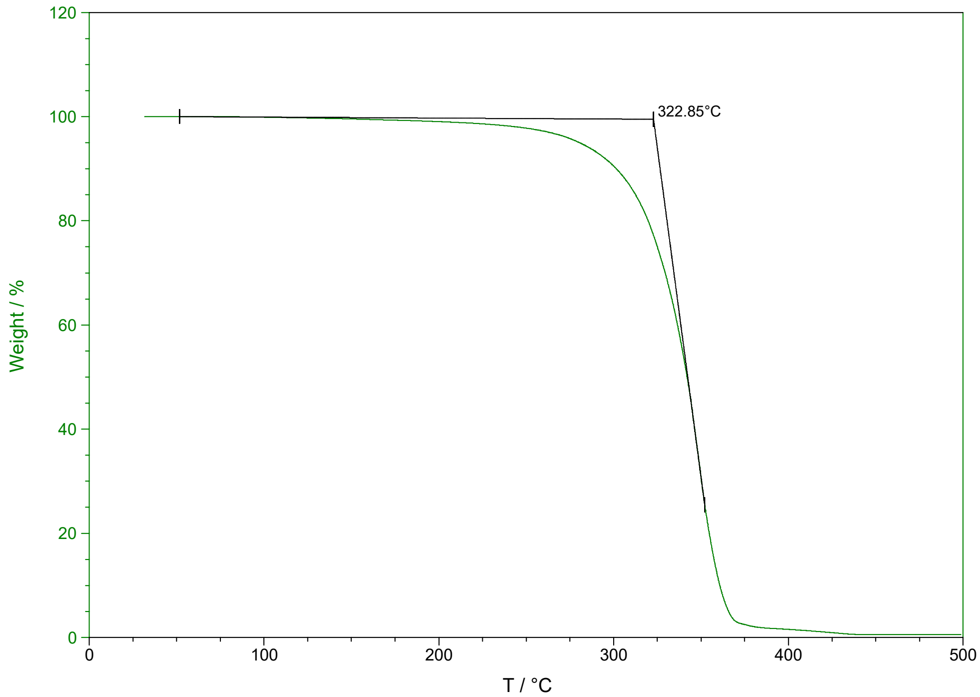

Figure S1. TGA trace for $[P_{4\,4\,4\,4}][C_1COO]$ at a heating rate of 10 ˚C min^{-1}.

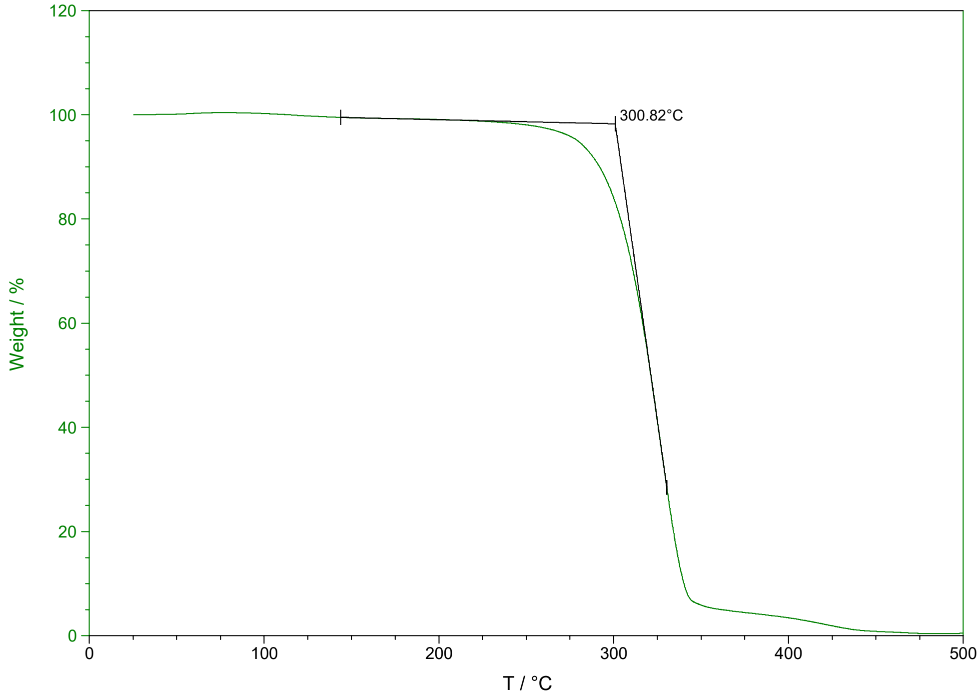

Figure S2. TGA trace for [$P_{4\,4\,4\,4}$][C_2COO] at a heating rate of 10 ˚C min^{-1}.

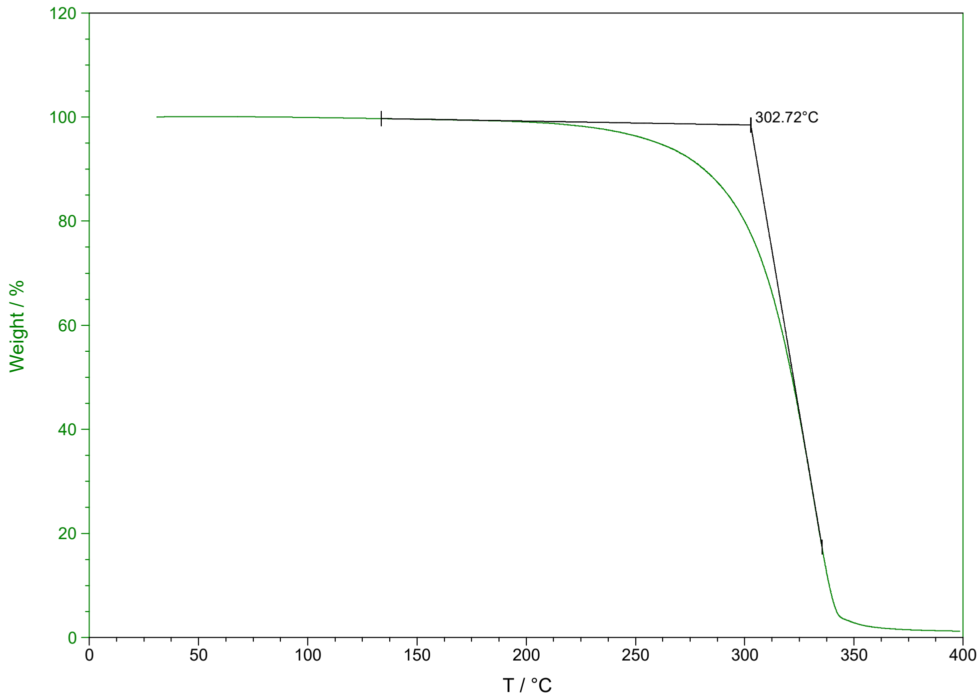

Figure S3. TGA trace for [$P_{4\,4\,4\,4}$][C_7COO] at a heating rate of 10 ˚C min^{-1}.

Table S3. Differential scanning calorimetry – heating:

Ionic Liquid	Glass transitions T_g / °C		Solid-solid transitions T_{sol} / °C ΔH_{sol} / kJ mol^{-1}		Melting T_m / °C ΔH_f / kJ mol^{-1}		
	T_g	T_g lit.	T_{sol}	ΔH	T_m	ΔH_f	T_m lit.
[$P_{4\,4\,4\,4}$][C_1COO]	–	–	-7.91	1.6	59.35	10.9	54.5 [1]
[$P_{4\,4\,4\,4}$][C_2COO]	-66.83	–	6.75	-0.2	50.89	13.2	–
[$P_{4\,4\,4\,4}$][C_7COO]	-60.88	-74.3 [1]	–	–	–	–	–

Table S4. Differential scanning calorimetry – cooling:

Ionic Liquid	Crystallisation T_c / °C ΔH / kJ mol^{-1}			
	T_c	ΔH_c	T_c	ΔH_c
[$P_{4\,4\,4\,4}$][C_1COO]	-55.21	-2.3	24.98	-10.8
[$P_{4\,4\,4\,4}$][C_2COO]	21.43	-16.0	24.40	–
[$P_{4\,4\,4\,4}$][C_7COO]	–	–	–	–

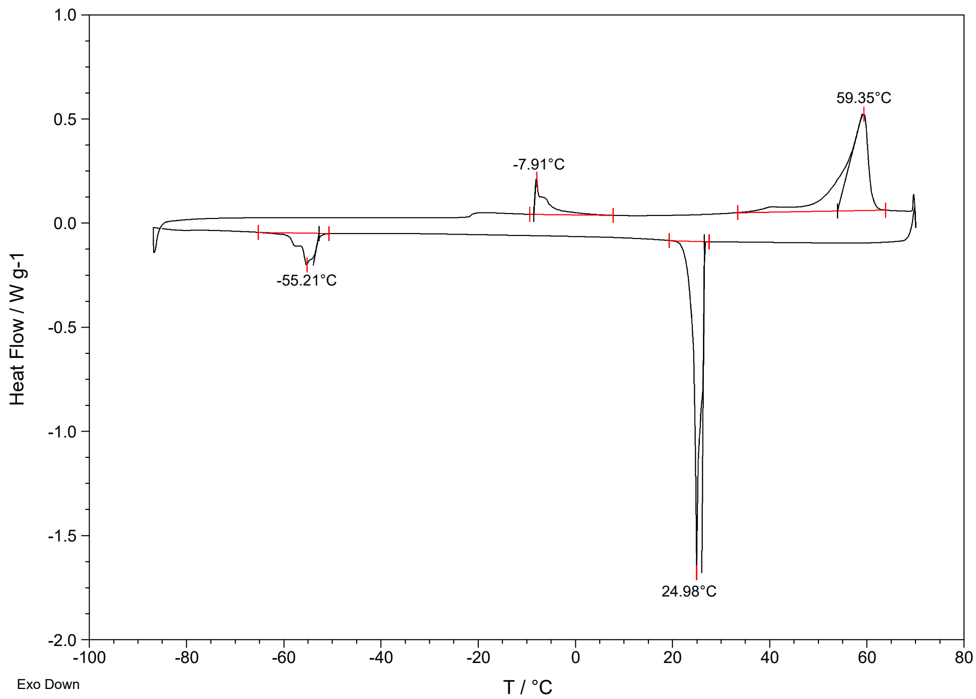

Figure S4. DSC trace of [$P_{4\,4\,4\,4}$][C_1COO] at a standard heating and cooling rate of 5 °C min^{-1}.

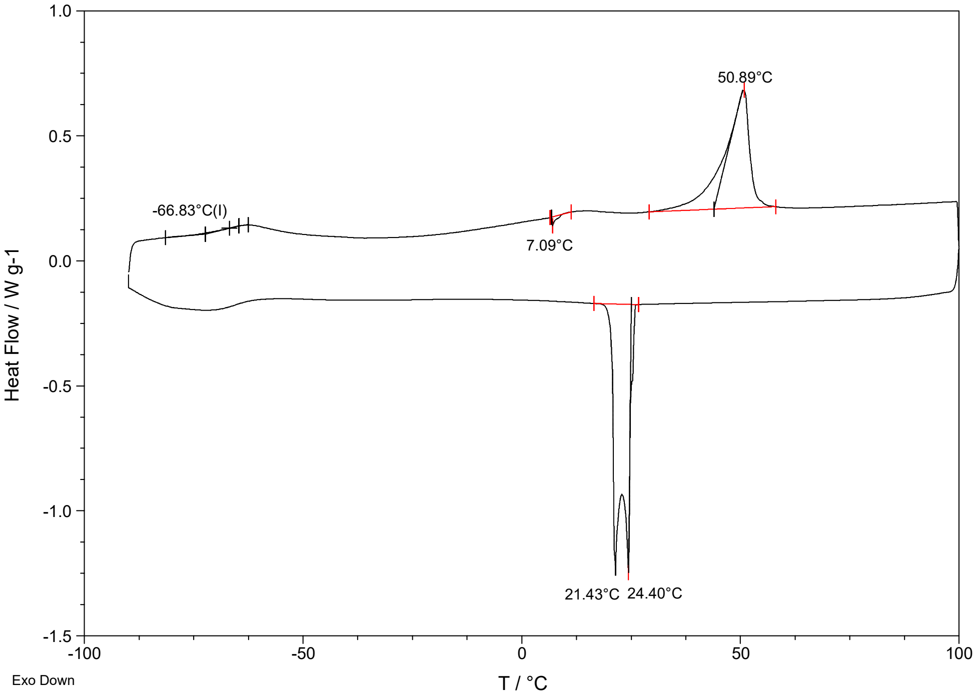

Figure S5. DSC trace of $[P_{4\,4\,4\,4}][C_2COO]$ at a standard heating and cooling rate of 5 ˚C min^{-1}.

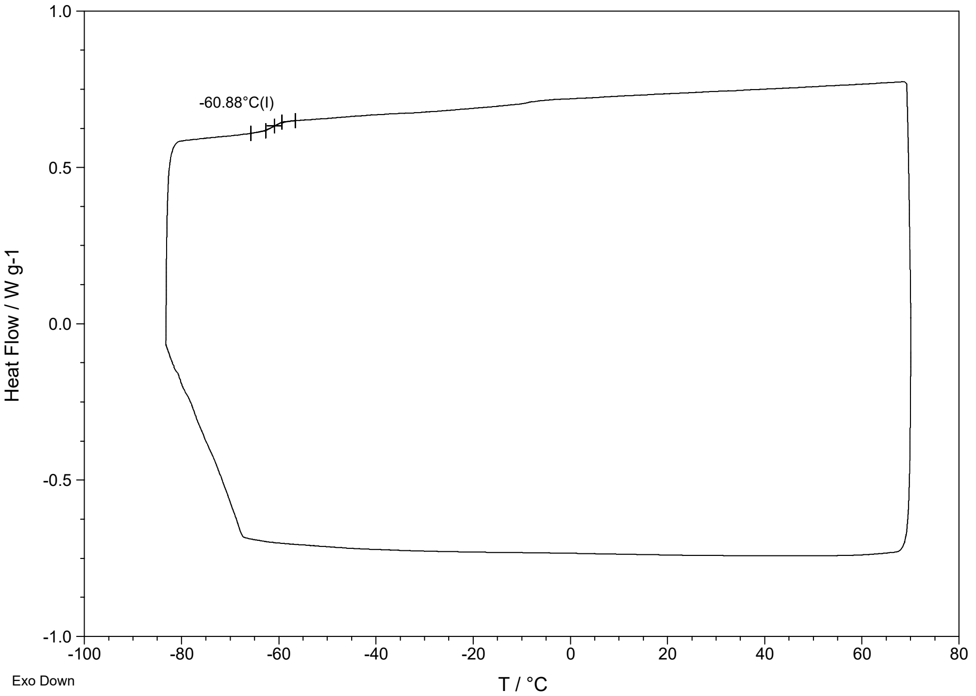

Figure S6. DSC trace of $[P_{4\,4\,4\,4}][C_7COO]$ at a standard heating and cooling rate of 5 ˚C min^{-1}.

Table S5. Densities, ρ, of the dry [$P_{4\,4\,4\,4}$][C_nCOO] ILs as a function of temperature, K.

T / K	[$P_{4\,4\,4\,4}$][C_1COO] H_2O: 140ppm	[$P_{4\,4\,4\,4}$][C_2COO] 180ppm	[$P_{4\,4\,4\,4}$][C_7COO] 120ppm
	ρ / g cm^{-3}		
293.15	–	–	0.913221
298.15	–	–	0.910147
303.15	–	–	0.907054
308.15	–	–	0.903956
313.15	–	–	0.900856
318.15	–	–	0.897749
323.15	–	0.917800	0.894643
328.15	–	0.914724	0.891542
333.15	0.916385	0.911657	0.888451
338.15	0.913410	0.908601	0.885369
343.15	0.910443	0.905554	0.882293
348.15	0.907476	0.902514	–
353.15	0.904519	0.899482	–
358.15	0.901563	0.896456	–
363.15	0.898612	0.893439	–

Experimental uncertainties: $u(\rho)$ = 0.000005 g cm^{-3}; $u(T)$ = 0.001 K; $u(x_w)$ = 0.00001

Table S6. Densities, ρ, of $[P_{4\,4\,4\,4}][C_nCOO]$ as a function of temperature, K, and mole fraction of water, x_w.

x_w	**293.15 K**	**298.15 K**	**303.15 K**	**308.15 K**	**313.15 K**	**318.15 K**	**323.15 K**	**328.15 K**	**333.15 K**	**338.15 K**	**343.15 K**
						ρ / g cm^{-3}					
						$[P_{4\,4\,4\,4}][C_1COO]$					
0									0.916385	0.913410	0.910443
0.2016					0.929175	0.926143	0.923111	0.920085	0.917065	0.914051	0.911046
0.3364	0.942662	0.939607	0.936540	0.933460	0.930370	0.927284	0.924203	0.921126	0.918057	0.914995	0.911936
0.4060	0.943780	0.940719	0.937627	0.934522	0.931415	0.928305	0.925200	0.922098	0.918998	0.915906	0.912816
0.4980	0.945795	0.942665	0.939516	0.936360	0.933203	0.930052	0.926902	0.923755	0.920612	0.917474	0.914338
0.6010	0.948772	0.945621	0.942424	0.939220	0.936014	0.932811	0.929607	0.926403	0.923199	0.919996	0.916792
0.6670	0.951497	0.948261	0.945020	0.941774	0.938528	0.935277	0.932025	0.928769	0.925513	0.922255	0.918996
0.7500	0.956437	0.953121	0.949800	0.946474	0.943140	0.939802	0.936454	0.933105	0.929748	0.926386	0.923017
0.8000	0.960651	0.957334	0.953955	0.950561	0.947155	0.943739	0.940313	0.936878	0.933434	0.929979	0.926519
0.8340	0.964390	0.960966	0.957527	0.954072	0.950609	0.947130	0.943639	0.940134	0.936620	0.933093	0.929554
0.8570	0.967726	0.964255	0.960769	0.957267	0.953749	0.950214	0.946665	0.943103	0.939524	0.935934	0.932328
1	0.998158	0.996999	0.995602	0.993987	0.992170	0.990168	0.987991	0.985650	0.983154	0.980511	0.977728
						$[P_{4\,4\,4\,4}][C_2COO]$					
0							0.917800	0.914724	0.911657	0.908601	0.905554
0.1103							0.918305	0.915213	0.912134	0.909063	0.906001
0.3371	0.939397	0.936355	0.933235	0.930083	0.926912	0.923746	0.920587	0.917435	0.914290	0.911150	0.908017
0.5015	0.942206	0.939031	0.935838	0.932639	0.929438	0.926242	0.923046	0.919855	0.916666	0.913480	0.910296
0.6006	0.945180	0.941966	0.938735	0.935501	0.932264	0.929027	0.925788	0.922548	0.919308	0.916067	0.912826
0.6679	0.948059	0.944812	0.941536	0.938253	0.934965	0.931667	0.928355	0.925027	0.921675	0.918277	0.915077
0.7483	0.952609	0.949289	0.945947	0.942597	0.939241	0.935878	0.932511	0.929134	0.925754	0.922368	0.918975
0.8004	0.957291	0.953892	0.950483	0.947063	0.943634	0.940195	0.936745	0.933285	0.929817	0.926340	0.922851
0.9000	0.971865	0.968069	0.964389	0.960750	0.957034	0.953911	0.950249	0.946565	0.942859	0.939134	0.935387
						$[P_{4\,4\,4\,4}][C_7COO]$					
0	0.913221	0.910147	0.907054	0.903956	0.900856	0.897749	0.894643	0.891542	0.888451	0.885369	0.882293
0.1218	0.913831	0.910731	0.907627	0.904516	0.901396	0.898271	0.895152	0.892041	0.888938	0.885840	0.882753
0.2168	0.914625	0.911520	0.908399	0.905268	0.902131	0.898990	0.895857	0.892729	0.889609	0.886498	0.883393
0.3448	0.916051	0.912957	0.909818	0.906658	0.903494	0.900330	0.897169	0.894017	0.890869	0.887730	0.884592
0.5142	0.919220	0.916046	0.912854	0.909650	0.906444	0.903238	0.900031	0.896831	0.893634	0.890436	0.887241
0.6046	0.921703	0.918484	0.915242	0.911987	0.908716	0.905427	0.902093	0.899026	0.895824	0.892578	0.889320
0.6697	0.924484	0.921233	0.917966	0.914695	0.911422	0.908144	0.904864	0.901581	0.898295	0.895006	0.891716
0.7517	0.928931	0.925605	0.922272	0.918937	0.915596	0.912251	0.908900	0.905542	0.902181	0.898809	0.895422
0.8343	0.936544	0.933131	0.929702	0.926264	0.922817	0.919357	0.915887	0.912409	0.908917	0.905415	0.901903
0.8578	0.939850	0.936410	0.932938	0.929431	0.925926	0.922411	0.918887	0.915410	0.911921	0.908398	0.904932
0.9006	0.948191	0.944684	0.941158	0.937612	0.934049	0.930469	0.926869	0.923248	0.919609	0.915952	0.912271

$u(\rho)$ = 0.000005 g cm^{-3}; $u(T)$ = 0.001 K; $u(x_w)$ = 0.00001

Table S7. Molar volume, V_m, excess molar volumes, V^E, apparent molar volumes, $V\phi_i$, and partial molar volumes, $\bar{V}_{m,i}$, for [$P_{4\,4\,4\,4}$][C_1COO]-water mixtures as a function of water mole fraction, x_w, and temperature, K.

333.15 K						
x_w	V_m / cm^3 mol^{-1}	V^E / cm^3 mol^{-1}	$V\phi_{IL}$ / cm^3 mol^{-1}	$V\phi_w$ / cm^3 mol^{-1}	$\bar{V}_{m,IL}$ / cm^3 mol^{-1}	$\bar{V}_{m,w}$ / cm^3 mol^{-1}
0	347.529	0	347.529		347.529	
0.2016	281.229	0.061	347.604	18.629	347.652	18.091
0.3364	236.791	0.017	347.555	18.380	347.815	17.880
0.4060	213.806	-0.067	347.415	18.163	347.851	17.685
0.4980	183.406	-0.181	347.168	17.965	347.934	17.526
0.6010	149.371	-0.308	346.756	17.816	348.018	17.476
0.6670	127.572	-0.380	346.388	17.759	347.998	17.534
0.7500	100.170	-0.459	345.692	17.717	347.669	17.688
0.8000	83.680	-0.488	345.086	17.718	347.168	17.818
0.8340	72.489	-0.487	344.596	17.745	346.661	17.922
0.8570	64.910	-0.495	344.071	17.752	346.071	17.971
1	18.329	0		18.329		18.329
338.15 K						
0	348.661	0	348.661		348.661	
0.2016	282.156	0.074	348.753	18.746	348.775	18.246
0.3364	237.583	0.042	348.724	18.503	348.948	17.999
0.4060	214.528	-0.038	348.596	18.284	348.993	17.792
0.4980	184.033	-0.146	348.369	18.084	349.082	17.630
0.6010	149.891	-0.269	347.985	17.930	349.163	17.583
0.6670	128.023	-0.339	347.642	17.870	349.136	17.641
0.7500	100.533	-0.416	346.998	17.824	348.815	17.789
0.8000	83.991	-0.443	346.443	17.824	348.345	17.911
0.8340	72.763	-0.442	345.998	17.848	347.878	18.008
0.8570	65.159	-0.450	345.516	17.853	347.332	18.053
1	18.378	0		18.378		18.378
343.15 K						
0	349.797	0	349.797		349.797	
0.2016	283.087	0.087	349.906	18.862	349.900	18.409
0.3364	238.380	0.067	349.898	18.631	350.084	18.125
0.4060	215.254	-0.008	349.783	18.411	350.138	17.904
0.4980	184.665	-0.112	349.574	18.206	350.236	17.735
0.6010	150.415	-0.230	349.220	18.047	350.314	17.692
0.6670	128.477	-0.298	348.900	17.983	350.281	17.750
0.7500	100.900	-0.372	348.309	17.935	349.967	17.893
0.8000	84.305	-0.399	347.802	17.932	349.524	18.007
0.8340	73.040	-0.397	347.404	17.954	349.097	18.098
0.8570	65.411	-0.405	346.964	17.958	348.594	18.138
1	18.430	0		18.430		18.430

Table S8. Molar volume, V_m, excess molar volumes, V^E, apparent molar volumes, $V\phi_i$, and partial molar volumes, $\bar{V}_{m,i}$, for [$P_{4\ 4\ 4\ 4}$][C_2COO]-water mixtures as a function of water mole fraction, x_w, and temperature, K.

x_w	V_m / cm^3 mol^{-1}	V^E / cm^3 mol^{-1}	$V\phi_{IL}$ / cm^3 mol^{-1}	$V\phi_w$ / cm^3 mol^{-1}	$\bar{V}_{m,IL}$ / cm^3 mol^{-1}	$\bar{V}_{m,w}$ / cm^3 mol^{-1}
323.15 K						
0	362.279	0	362.279		362.279	
0.1103	324.296	-0.025	362.252	18.017	362.362	17.338
0.3371	246.010	-0.277	361.862	17.418	362.296	17.379
0.5015	189.367	-0.383	361.511	17.476	362.317	17.475
0.6006	155.143	-0.513	360.996	17.386	362.366	17.295
0.6679	131.914	-0.585	360.517	17.362	362.413	17.268
0.7483	104.209	-0.627	359.790	17.402	362.332	17.415
0.8004	86.246	-0.664	358.954	17.410	361.789	17.548
0.9000	52.066	-0.585	356.426	17.589	359.000	17.932
1	18.239	0		18.239		18.239
328.15 K						
0	363.498	0	363.498		363.498	
0.1103	325.391	-0.018	363.478	18.123	363.577	17.476
0.3371	246.855	-0.254	363.115	17.530	363.524	17.470
0.5015	190.024	-0.355	362.785	17.574	363.548	17.561
0.6006	155.688	-0.480	362.295	17.483	363.582	17.393
0.6679	132.389	-0.544	361.858	17.467	363.633	17.379
0.7483	104.588	-0.587	361.166	17.498	363.535	17.513
0.8004	86.566	-0.622	360.382	17.505	363.021	17.637
0.9000	52.268	-0.544	358.062	17.678	360.452	18.000
1	18.282	0		18.282		18.282
333.15 K						
0	364.721	0	364.721		364.721	
0.1103	326.490	-0.012	364.707	18.218	364.796	17.609
0.3371	247.704	-0.231	364.372	17.644	364.753	17.571
0.5015	190.685	-0.327	364.065	17.677	364.780	17.653
0.6006	156.236	-0.448	363.599	17.583	364.801	17.494
0.6679	132.870	-0.500	363.215	17.580	364.868	17.495
0.7483	104.970	-0.548	362.545	17.597	364.746	17.611
0.8004	86.889	-0.580	361.813	17.604	364.262	17.727
0.9000	52.474	-0.502	359.699	17.771	361.912	18.070
1	18.329	0		18.329		18.329
338.15 K						
0	365.947	0	365.947		365.947	
0.1103	327.593	-0.006	365.940	18.323	366.019	17.738
0.3371	248.558	-0.207	365.635	17.764	365.986	17.681
0.5015	191.350	-0.298	365.349	17.784	366.009	17.753
0.6006	156.789	-0.415	364.909	17.688	366.020	17.599
0.6679	133.362	-0.449	364.596	17.706	366.125	17.622
0.7483	105.355	-0.508	363.929	17.699	365.969	17.707
0.8004	87.215	-0.539	363.249	17.705	365.520	17.816
0.9000	52.682	-0.461	361.335	17.866	363.390	18.141
1	18.378	0		18.378		18.378
343.15 K						
0	367.179	0	367.179		367.179	
0.1103	328.700	0.000	367.178	18.429	367.245	17.899
0.3371	249.415	-0.183	366.902	17.887	367.228	17.779
0.5015	192.019	-0.269	366.639	17.894	367.265	17.841
0.6006	157.346	-0.381	366.224	17.796	367.264	17.703
0.6679	133.896	-0.358	366.101	17.895	367.517	17.816
0.7483	105.744	-0.468	365.319	17.805	367.185	17.818
0.8004	87.544	-0.496	364.691	17.810	366.757	17.918
0.9000	52.893	-0.421	362.974	17.963	364.827	18.218
1	18.430	0		18.430		18.430

Table S9. Molar volume, V_m, excess molar volumes, V^E, apparent molar volumes, $V\phi_i$, and partial molar volumes, $\bar{V}_{m,i}$, for [P4 4 4 4][C7COO]-water mixtures as a function of water mole fraction, x_w, and temperature, K.

x_w	V_m / cm³ mol⁻¹	V^E / cm³ mol⁻¹	$V\phi_{IL}$ / cm³ mol⁻¹	$V\phi_w$ / cm³ mol⁻¹	$\bar{V}_{m,IL}$ / cm³ mol⁻¹	$\bar{V}_{m,w}$ / cm³ mol⁻¹
293.15 K						
0	440.901	0	429.150		440.901	
0.1218	389.331	-0.055	429.087	17.598	440.989	16.855
0.2168	349.075	-0.173	428.930	17.256	441.054	16.714
0.3448	294.773	-0.335	428.640	17.083	441.038	16.893
0.5142	222.873	-0.601	427.914	16.885	440.953	16.788
0.6046	184.552	-0.699	427.383	16.897	441.051	16.800
0.6697	156.914	-0.811	426.696	16.843	440.912	16.804
0.7517	122.200	-0.840	425.767	16.936	440.627	17.070
0.8343	87.284	-0.828	424.151	17.061	439.264	17.424
0.8578	77.353	-0.815	423.416	17.103	438.453	17.519
0.9006	59.341	-0.760	421.505	17.209	436.143	17.669
1	18.053	0		18.053		18.053
298.15 K						
0	442.390	0	430.600		442.390	
0.1218	390.656	-0.041	430.554	17.741	442.485	16.963
0.2168	350.264	-0.155	430.402	17.361	442.555	16.782
0.3448	295.772	-0.318	430.114	17.151	442.527	16.944
0.5142	223.645	-0.563	429.442	16.980	442.436	16.899
0.6046	185.199	-0.654	428.947	16.993	442.518	16.915
0.6697	157.468	-0.763	428.290	16.935	442.369	16.909
0.7517	122.639	-0.786	427.433	17.028	442.114	17.158
0.8343	87.603	-0.773	425.933	17.147	440.859	17.487
0.8578	77.637	-0.761	425.249	17.187	440.107	17.575
0.9006	59.561	-0.707	423.491	17.289	437.982	17.718
1	18.074	0		18.074		18.074
303.15 K						
0	443.899	0	432.068		443.899	
0.1218	391.992	-0.032	432.031	17.834	443.990	17.092
0.2168	351.467	-0.138	431.892	17.462	444.059	16.896
0.3448	296.793	-0.295	431.618	17.243	444.038	17.025
0.5142	224.427	-0.527	430.984	17.076	443.953	16.990
0.6046	185.855	-0.609	430.527	17.092	444.028	17.019
0.6697	158.028	-0.718	429.895	17.028	443.861	17.008
0.7517	123.083	-0.737	429.101	17.119	443.616	17.247
0.8343	87.926	-0.721	427.715	17.235	442.447	17.556
0.8578	77.926	-0.708	427.088	17.274	441.754	17.639
0.9006	59.784	-0.657	425.465	17.371	439.788	17.772
1	18.100	0		18.100		18.100
308.15 K						
0	445.420	0	433.549		445.420	
0.1218	393.340	-0.024	433.522	17.934	445.505	17.246
0.2168	352.683	-0.121	433.395	17.573	445.574	17.029
0.3448	297.827	-0.268	433.140	17.353	445.567	17.115
0.5142	225.218	-0.490	432.540	17.176	445.493	17.074
0.6046	186.519	-0.565	432.119	17.194	445.563	17.119
0.6697	158.593	-0.675	431.506	17.121	445.372	17.105
0.7517	123.529	-0.690	430.770	17.211	445.126	17.338
0.8343	88.252	-0.671	429.496	17.324	444.033	17.629
0.8578	78.220	-0.655	428.938	17.365	443.410	17.709
0.9006	60.010	-0.608	427.432	17.454	441.582	17.829
1	18.129	0		18.129		18.129
313.15 K						
0	446.953	0	435.041		446.953	
0.1218	394.702	-0.012	435.027	18.061	447.036	17.404
0.2168	353.909	-0.102	434.911	17.692	447.104	17.152
0.3448	298.870	-0.240	434.674	17.465	447.110	17.203
0.5142	226.015	-0.455	434.104	17.277	447.041	17.160
0.6046	187.190	-0.520	433.725	17.302	447.114	17.225
0.6697	159.163	-0.634	433.122	17.216	446.893	17.201
0.7517	123.980	-0.645	432.444	17.305	446.653	17.428
0.8343	88.582	-0.623	431.278	17.415	445.637	17.703
0.8578	78.516	-0.606	430.780	17.456	445.075	17.780
0.9006	60.239	-0.562	429.393	17.539	443.389	17.888
1	18.162	0		18.162		18.162
318.15 K						
0	448.500	0	436.546		448.500	
0.1218	396.075	-0.002	436.544	18.182	448.581	17.550

0.2168	355.146	-0.085	436.438	17.807	448.649	17.271
0.3448	299.920	-0.216	436.216	17.572	448.663	17.291
0.5142	226.817	-0.423	435.675	17.375	448.595	17.250
0.6046	187.870	-0.474	435.347	17.415	448.681	17.339
0.6697	159.737	-0.595	434.745	17.311	448.424	17.299
0.7517	124.435	-0.602	434.123	17.398	448.192	17.518
0.8343	88.915	-0.577	433.064	17.507	447.259	17.778
0.8578	78.816	-0.558	432.621	17.548	446.755	17.851
0.9006	60.471	-0.517	431.350	17.625	445.205	17.950
1	18.199	0		18.199		18.199
323.15 K						
0	450.057	0	438.062		450.057	
0.1218	397.455	0.006	438.069	18.286	450.136	17.687
0.2168	356.388	-0.071	437.971	17.911	450.200	17.393
0.3448	300.977	-0.194	437.766	17.677	450.219	17.394
0.5142	227.625	-0.392	437.254	17.476	450.150	17.346
0.6046	188.564	-0.420	437.001	17.545	450.276	17.468
0.6697	160.316	-0.557	436.375	17.407	449.965	17.394
0.7517	124.893	-0.560	435.808	17.494	449.750	17.606
0.8343	89.252	-0.532	434.854	17.602	448.906	17.853
0.8578	79.118	-0.511	434.464	17.643	448.459	17.923
0.9006	60.706	-0.473	433.307	17.714	447.045	18.013
1	18.239	0		18.239		18.239
328.15 K						
0	451.622	0	439.586		451.622	
0.1218	398.841	0.012	439.599	18.380	451.694	17.840
0.2168	357.637	-0.058	439.512	18.015	451.759	17.510
0.3448	302.038	-0.173	439.321	17.780	451.804	17.460
0.5142	228.437	-0.363	438.839	17.577	451.756	17.429
0.6046	189.208	-0.422	438.520	17.585	451.768	17.518
0.6697	160.900	-0.519	438.013	17.507	451.520	17.516
0.7517	125.357	-0.518	437.500	17.594	451.276	17.725
0.8343	89.592	-0.487	436.647	17.699	450.474	17.949
0.8578	79.418	-0.471	436.275	17.734	450.040	18.005
0.9006	60.944	-0.429	435.267	17.805	448.794	18.085
1	18.282	0		18.282		18.282
333.15 K						
0	453.193	0	441.115		453.193	
0.1218	400.233	0.019	441.136	18.482	453.261	17.984
0.2168	358.891	-0.044	441.058	18.124	453.325	17.634
0.3448	303.106	-0.151	440.884	17.890	453.383	17.551
0.5142	229.254	-0.333	440.430	17.682	453.344	17.524
0.6046	189.884	-0.395	440.117	17.676	453.323	17.612
0.6697	161.489	-0.481	439.659	17.611	453.082	17.628
0.7517	125.824	-0.476	439.199	17.696	452.836	17.831
0.8343	89.937	-0.442	438.449	17.799	452.102	18.038
0.8578	79.722	-0.430	438.090	17.827	451.683	18.083
0.9006	61.185	-0.386	437.230	17.900	450.604	18.158
1	18.329	0		18.329		18.329
338.15 K						
0	454.771	0	442.651		454.771	
0.1218	401.633	0.027	442.681	18.599	454.837	18.128
0.2168	360.150	-0.031	442.611	18.234	454.899	17.752
0.3448	304.177	-0.130	442.452	18.001	454.965	17.651
0.5142	230.078	-0.301	442.030	17.792	454.929	17.631
0.6046	190.574	-0.358	441.746	17.787	454.899	17.727
0.6697	162.082	-0.442	441.314	17.719	454.649	17.740
0.7517	126.296	-0.433	440.908	17.803	454.414	17.935
0.8343	90.284	-0.396	440.258	17.903	453.758	18.125
0.8578	80.031	-0.388	439.925	17.926	453.367	18.162
0.9006	61.429	-0.343	439.197	17.997	452.441	18.231
1	18.378	0		18.378		18.378
343.15 K						
0	456.356	0	444.194		456.356	
0.1218	403.037	0.033	444.231	18.699	456.418	18.266
0.2168	361.416	-0.018	444.170	18.345	456.478	17.883
0.3448	305.256	-0.108	444.029	18.117	456.551	17.764
0.5142	230.906	-0.270	443.638	17.906	456.519	17.740
0.6046	191.273	-0.318	443.389	17.904	456.492	17.844
0.6697	162.680	-0.402	442.976	17.830	456.230	17.851
0.7517	126.773	-0.388	442.632	17.915	456.019	18.040
0.8343	90.636	-0.351	442.074	18.010	455.437	18.214
0.8578	80.338	-0.351	441.723	18.021	455.031	18.236
0.9006	61.677	-0.300	441.174	18.097	454.303	18.308
1	18.430	0		18.430		18.430

Table S10. Excess molar volume, V^E, and partial molar volume, $\bar{V}_{m,i}$, fitting parameters obtained from least squares test

T / K	A_0	A_1	A_2	A_3	AAD / %
			$[P_{4\,4\,4\,4}][C_1COO]$		
333.15	-0.672	-2.424	-1.822	-1.467	0.01
338.15	-0.537	-2.349	-1.687	-1.202	0.01
343.15	-0.400	-2.278	-1.566	-0.917	0.01
			$[P_{4\,4\,4\,4}][C_2COO]$		
323.15	-1.601	-1.598	-2.539	-3.502	0.01
328.15	-1.488	-1.538	-2.332	-3.237	0.01
333.15	-1.372	-1.466	-2.148	-2.984	0.01
338.15	-1.249	-1.369	-1.972	-2.792	0.01
343.15	-1.137	-1.349	-1.775	-2.444	0.01
			$[P_{4\,4\,4\,4}][C_7COO]$		
293.15	-2.229	-2.608	-2.783	-3.368	0.02
298.15	-2.104	-2.425	-2.472	-3.270	0.02
303.15	-1.969	-2.315	-2.243	-2.996	0.02
308.15	-1.829	-2.247	-2.033	-2.663	0.02
313.15	-1.692	-2.177	-1.816	-2.388	0.02
318.15	-1.563	-2.091	-1.609	-2.152	0.02
323.15	-1.428	-1.976	-1.449	-1.955	0.01
328.15	-1.354	-1.989	-1.170	-1.503	0.02
333.15	-1.247	-1.931	-0.963	-1.205	0.02
338.15	-1.130	-1.834	-0.769	-0.988	0.01
343.15	-1.006	-1.733	-0.615	-0.781	0.01

Table S11. Viscosities, η, of dry $[P_{4\,4\,4\,4}][C_nCOO]$ ILs, as a function of temperature, K.

T / K	η / mPa·s
$[P_{4\,4\,4\,4}][C_1COO]$	
333.15	65.642
338.15	52.487
343.15	42.360
348.15	34.637
353.15	28.617
358.15	23.928
363.15	20.241
$[P_{4\,4\,4\,4}][C_2COO]$	
328.15	63.376
333.15	50.261
338.15	40.485
343.15	33.039
348.15	27.326
353.15	22.830
358.15	19.308
363.15	16.397
$[P_{4\,4\,4\,4}][C_7COO]$	
293.15	541.380
298.15	373.280
303.15	264.260
308.15	191.940
313.15	142.390
318.15	107.830
323.15	83.138
328.15	65.246
333.15	52.365
338.15	42.344
343.15	34.666

$[P_{4\,4\,4\,4}][C_1COO]$ and $[P_{4\,4\,4\,4}][C_2COO]$: $u_r(\eta)$ = 0.35 %; $u(T)$ = 0.005 K

$[P_{4\,4\,4\,4}][C_7COO]$: $u_r(\eta)$ = 0.1 %; $u(T)$ = 0.005 K

Table S12. Viscosities, η, of binary [$P_{4\,4\,4\,4}$][C_nCOO]-water mixtures as a function of temperature, K.

x_w	**293.15 K**	**298.15 K**	**303.15 K**	**308.15 K**	**313.15 K**	**318.15 K**	**323.15 K**	**328.15 K**	**333.15 K**	**338.15 K**	**343.15 K**
						η / mPa·s					
					[$P_{4\,4\,4\,4}$][C_1COO]						
0.3364	358.800	251.280	180.220	132.460	99.351	76.019	59.084	47.047	37.861	30.893	25.529
0.4060	296.890	209.770	151.480	111.830	84.453	65.018	51.167	40.768	32.951	26.989	22.413
0.4980	230.270	163.700	119.270	88.925	67.612	52.467	41.450	33.075	27.038	22.337	18.828
0.6010	166.100	119.200	87.698	66.028	50.915	39.963	31.854	25.784	21.190	17.722	14.953
0.6670	125.760	91.440	68.059	51.946	40.378	31.972	25.735	21.038	17.544	14.691	12.377
0.7500	79.301	59.156	44.920	34.957	27.702	22.348	18.335	15.240	12.751	10.741	9.118
0.8000	55.995	42.491	32.961	26.095	21.037	17.273	14.202	11.771	9.870	8.361	7.180
0.8340	43.481	33.463	26.226	20.944	17.033	13.944	11.509	9.584	8.107	7.030	5.920
0.8570	35.584	27.733	21.927	17.661	14.295	11.670	9.646	8.065	6.784	5.838	5.070
1	1.002	0.890	0.797	0.719	0.653	0.596	0.547	0.504	0.466	0.433	0.404
					[$P_{4\,4\,4\,4}$][C_2COO]						
0.3371	295.940	208.420	150.470	111.160	83.812	64.515	50.968	40.535	32.801	26.919	22.381
0.5015	215.720	152.970	111.280	82.916	62.968	49.604	39.002	31.290	25.503	21.107	17.760
0.6006	161.670	116.050	85.324	64.291	49.487	38.761	30.881	25.023	20.592	17.222	14.397
0.6679	123.800	90.045	67.092	51.141	39.712	31.429	25.305	20.699	17.212	14.292	11.975
0.7483	78.827	58.752	44.909	34.971	27.728	22.361	18.411	15.214	12.634	10.578	8.967
0.8004	53.737	40.958	31.892	25.314	20.457	16.792	13.767	11.393	9.538	8.092	6.935
0.9000	22.931	18.202	14.497	11.660	9.513	7.890	6.624	5.651	4.855	4.219	3.697
					[$P_{4\,4\,4\,4}$][C_7COO]						
0.1218	469.440	327.080	233.380	170.540	127.710	96.964	75.271	59.291	48.195	39.171	32.220
0.2168	389.250	273.390	197.240	145.410	109.440	83.876	65.492	52.594	42.296	34.528	28.534
0.3448	314.470	223.050	162.150	120.460	91.277	70.330	55.880	44.510	35.969	29.490	24.510
0.5142	236.170	168.510	123.060	91.778	69.870	54.492	42.989	34.463	28.052	23.161	19.351
0.6046	193.780	139.400	102.520	76.949	58.924	45.998	36.530	29.435	24.074	19.962	16.819
0.6697	152.360	110.770	82.294	62.367	48.524	38.145	30.500	24.763	20.413	17.127	14.330
0.7517	97.941	73.017	55.705	43.195	34.061	27.353	22.308	18.526	15.353	12.803	10.794
0.8343	56.149	42.950	33.536	26.674	21.584	17.749	14.564	12.041	10.104	8.526	7.290
0.8578	46.565	35.959	28.322	22.736	18.567	15.126	12.414	10.341	8.705	7.398	6.371
0.9006	31.774	24.878	19.866	16.082	12.984	10.649	8.842	7.435	6.327	5.454	4.737

$u_r(\eta)$ = 0.1 %; $u(T)$ = 0.005 K; $u(x_w)$ = 0.0001

Table S13. Fitting parameters from the Vogel-Fulcher-Tammann equation for viscosities, η, of binary $[P_{4\,4\,4\,4}][C_nCOO]$-water mixtures as a function of temperature, K.

x_w	η_0 / mPa·s	B / K	T_0 / K	10^4 AAD / %
	$[P_{4\,4\,4\,4}][C_1COO]$			
0	0.035	496.507	169.267	0.02
0.3364	0.037	481.728	169.802	0.08
0.4060	0.043	448.865	172.811	0.09
0.4980	0.061	390.134	179.494	0.08
0.6010	0.065	372.663	179.815	0.03
0.6670	0.063	359.702	177.192	0.03
0.7500	0.037	409.854	164.043	0.02
0.8000	0.037	409.854	164.043	0.10
0.8340	0.024	454.392	153.746	0.05
0.8570	0.008	601.106	128.843	0.03
1	0.027	231.407	145.042	0.01
	$[P_{4\,4\,4\,4}][C_2COO]$			
0	0.062	434.551	183.627	0.00
0.3371	0.045	457.303	173.410	0.07
0.5015	0.059	405.149	179.384	0.04
0.6006	0.055	398.404	178.261	0.05
0.6679	0.053	391.836	176.709	0.01
0.7483	0.047	394.868	170.782	0.09
0.8004	0.025	461.718	154.641	0.10
0.9000	0.019	438.372	150.980	0.13
	$[P_{4\,4\,4\,4}][C_7COO]$			
0	0.040	506.473	170.575	0.08
0.1218	0.041	500.697	169.709	0.12
0.2168	0.045	483.365	170.248	0.08
0.3448	0.043	480.455	168.931	0.05
0.5142	0.040	462.864	170.319	0.07
0.6046	0.037	461.791	169.003	0.08
0.6697	0.044	432.359	170.984	0.04
0.7517	0.039	436.917	164.612	0.04
0.8343	0.021	495.244	148.554	0.12
0.8578	0.012	571.748	134.421	0.09
0.9006	0.008	592.623	128.051	0.07

Table S14. Excess Gibbs free energy of viscous flow ΔG^E, for binary $[P_{4\,4\,4\,4}][C_1COO]$-water mixtures as a function of temperature, K.

	333.15 K	338.15 K	343.15 K
x_w	ΔG^E / kJ mol^{-1}		
0	0	0	0
0.3364	4.77	4.68	4.62
0.4060	5.62	5.52	5.44
0.4980	6.66	6.54	6.46
0.6010	7.66	7.54	7.43
0.6670	8.15	8.00	7.85
0.7500	8.41	8.24	8.08
0.8000	8.29	8.12	7.98
0.8340	8.09	7.97	7.76
0.8570	7.80	7.65	7.51
1	0	0	0

Table S15. Excess Gibbs free energy of viscous flow ΔG^E, for binary $[P_{4\,4\,4\,4}][C_2COO]$-water mixtures as a function of temperature, K.

	328.15 K	333.15 K	338.15 K	343.15 K
x_w	ΔG^E / kJ mol^{-1}			
0	0	0	0	0
0.3371	4.92	4.84	4.76	4.69
0.5015	7.01	6.88	6.76	6.66
0.6006	7.97	7.82	7.69	7.54
0.6679	8.45	8.30	8.13	7.96
0.7483	8.68	8.50	8.31	8.15
0.8004	8.49	8.30	8.14	7.98
0.9000	7.33	7.17	7.03	6.90
1	0	0	0	0

Table S16. Excess Gibbs free energy of viscous flow ΔG^E, for binary [$P_{4\,4\,4\,4}$][C_7COO]-water mixtures as a function of temperature, K.

x_w	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K	338.15 K	343.15 K
	ΔG^E / kJ mol^{-1}										
0	0	0	0	0	0	0	0	0	0	0	0
0.1218	2.17	2.15	2.14	2.12	2.12	2.10	2.09	2.08	2.10	2.10	2.10
0.2168	3.64	3.61	3.59	3.57	3.55	3.54	3.53	3.55	3.52	3.52	3.52
0.3448	5.67	5.62	5.58	5.54	5.50	5.47	5.48	5.45	5.42	5.41	5.40
0.5142	8.21	8.11	8.02	7.94	7.87	7.82	7.77	7.72	7.68	7.65	7.64
0.6046	9.35	9.24	9.14	9.04	8.96	8.88	8.82	8.77	8.72	8.69	8.67
0.6697	9.88	9.76	9.65	9.55	9.48	9.41	9.34	9.29	9.24	9.23	9.18
0.7517	10.09	9.99	9.90	9.82	9.75	9.69	9.65	9.62	9.56	9.50	9.45
0.8343	9.82	9.73	9.65	9.58	9.53	9.49	9.42	9.35	9.29	9.23	9.18
0.8578	9.62	9.53	9.45	9.39	9.35	9.27	9.19	9.12	9.06	9.00	8.97
0.9006	9.03	8.94	8.86	8.79	8.69	8.59	8.51	8.44	8.38	8.34	8.30
1	0	0	0	0	0	0	0	0	0	0	0

Table S17. Stoichiometric data and heat effects of the calorimetry experiments with [$P_{4\,4\,4\,4}$][C_1COO] + water at 313.15 K. The subscript c and d mean cell (or container) and dispenser (or syringe) respectively.

$n_{w,c}$ / mol	$n_{IL,c}$ / mol	$n_{w,d}$ / mol	x_w	Q_w / J
9.32E-04	2.43E-03	2.20E-04	0.2772	-1.92
1.15E-03	2.43E-03	2.20E-04	0.3212	-1.90
1.37E-03	2.43E-03	2.20E-04	0.3605	-1.86
1.59E-03	2.43E-03	2.20E-04	0.3955	-1.82
1.81E-03	2.43E-03	2.20E-04	0.4269	-1.78
2.03E-03	2.43E-03	2.20E-04	0.4552	-1.73
2.25E-03	2.43E-03	2.20E-04	0.4808	-1.68
2.47E-03	2.43E-03	2.20E-04	0.5041	-1.61
2.69E-03	2.43E-03	2.20E-04	0.5254	-1.54
2.91E-03	2.43E-03	2.20E-04	0.5449	-1.48
3.13E-03	2.43E-03	2.20E-04	0.5629	-1.41
3.35E-03	2.43E-03	2.20E-04	0.5796	-1.35
3.57E-03	2.43E-03	2.20E-04	0.5950	-1.28
3.79E-03	2.43E-03	2.20E-04	0.6093	-1.21
2.11E-03	2.28E-03	2.75E-04	0.4806	-2.24
2.38E-03	2.28E-03	2.75E-04	0.5107	-2.15
2.66E-03	2.28E-03	2.75E-04	0.5385	-2.05
2.93E-03	2.28E-03	2.75E-04	0.5624	-1.94
3.21E-03	2.28E-03	2.75E-04	0.5847	-1.83
3.48E-03	2.28E-03	2.75E-04	0.6042	-1.72
3.76E-03	2.28E-03	2.75E-04	0.6225	-1.61
4.03E-03	2.28E-03	2.75E-04	0.6387	-1.50
4.31E-03	2.28E-03	2.75E-04	0.6540	-1.40
4.58E-03	2.28E-03	2.75E-04	0.6676	-1.31
4.86E-03	2.28E-03	2.75E-04	0.6807	-1.22
5.13E-03	2.28E-03	2.75E-04	0.6923	-1.14
5.41E-03	2.28E-03	2.75E-04	0.7035	-1.06
5.68E-03	2.28E-03	2.75E-04	0.7136	-1.00
5.96E-03	2.28E-03	2.75E-04	0.7233	-0.94
6.23E-03	2.28E-03	2.75E-04	0.7321	-0.89
6.51E-03	2.28E-03	2.75E-04	0.7406	-0.84
7.54E-03	2.05E-03	2.75E-04	0.7862	-0.64
7.81E-03	2.05E-03	2.75E-04	0.7921	-0.61
8.08E-03	2.05E-03	2.75E-04	0.7976	-0.59
8.36E-03	2.05E-03	2.75E-04	0.8031	-0.57
8.63E-03	2.05E-03	2.75E-04	0.8081	-0.55
8.91E-03	2.05E-03	2.75E-04	0.8130	-0.53
9.18E-03	2.05E-03	2.75E-04	0.8175	-0.51
9.46E-03	2.05E-03	2.75E-04	0.8219	-0.51
9.73E-03	2.05E-03	2.75E-04	0.8260	-0.50
1.00E-02	2.05E-03	2.75E-04	0.8299	-0.49
1.03E-02	2.05E-03	2.75E-04	0.8340	-0.48
1.06E-02	2.05E-03	2.75E-04	0.8379	-0.47
1.08E-02	2.05E-03	2.75E-04	0.8405	-0.46
1.11E-02	2.05E-03	2.75E-04	0.8441	-0.45
1.14E-02	2.05E-03	2.75E-04	0.8476	-0.44
1.17E-02	2.05E-03	2.75E-04	0.8509	-0.44
1.19E-02	2.05E-03	2.75E-04	0.8530	-0.43
1.22E-02	2.05E-03	2.75E-04	0.8561	-0.42
1.25E-02	2.05E-03	2.75E-04	0.8591	-0.42
1.28E-02	2.05E-03	2.75E-04	0.8620	-0.42
1.30E-02	2.05E-03	2.75E-04	0.8638	-0.41
1.33E-02	2.05E-03	2.75E-04	0.8664	-0.40
1.36E-02	2.05E-03	2.75E-04	0.8690	-0.41
1.39E-02	2.05E-03	2.75E-04	0.8715	-0.40
1.41E-02	2.05E-03	2.75E-04	0.8731	-0.40
1.44E-02	2.05E-03	2.75E-04	0.8754	-0.39
1.47E-02	2.05E-03	2.75E-04	0.8776	-0.39
1.50E-02	2.05E-03	2.75E-04	0.8798	-0.39
1.52E-02	2.05E-03	2.75E-04	0.8812	-0.38
1.55E-02	2.05E-03	2.75E-04	0.8832	-0.38
1.58E-02	2.05E-03	2.75E-04	0.8852	-0.38
1.61E-02	2.05E-03	2.75E-04	0.8871	-0.38
1.63E-02	2.05E-03	2.75E-04	0.8883	-0.37

$u(Q_w)$ = 10 mJ; $u(T)$ = 50 μK

Table S18. Stoichiometric data and heat effects of the calorimetry experiments with [$P_{4\,4\,4\,4}$][C_2COO] + water at 313.15 K. The subscript c and d mean cell (or container) and dispenser (or syringe) respectively.

$n_{w,c}$ / mol	$n_{IL,c}$ / mol	$n_{w,d}$ / mol	x_w	Q_w / J
8.25E-04	2.17E-03	2.75E-04	0.4706	-2.46
1.10E-03	2.17E-03	2.75E-04	0.5039	-2.27
1.65E-03	2.17E-03	2.75E-04	0.5593	-2.10
1.93E-03	2.17E-03	2.75E-04	0.5826	-1.96
2.20E-03	2.17E-03	2.75E-04	0.6036	-1.81
2.48E-03	2.17E-03	2.75E-04	0.6226	-1.67
2.75E-03	2.17E-03	2.75E-04	0.6398	-1.53
3.03E-03	2.17E-03	2.75E-04	0.6555	-1.40
3.30E-03	2.17E-03	2.75E-04	0.6699	-1.29
3.58E-03	2.17E-03	2.75E-04	0.6832	-1.18
3.85E-03	2.17E-03	2.75E-04	0.6954	-1.09
4.13E-03	2.17E-03	2.75E-04	0.7067	-1.01
4.40E-03	2.17E-03	2.75E-04	0.7172	-0.93
4.68E-03	2.17E-03	2.75E-04	0.7270	-0.87
4.95E-03	2.17E-03	2.75E-04	0.7362	-0.82
1.10E-03	1.35E-03	5.49E-04	0.9075	-0.59
1.65E-03	1.35E-03	5.49E-04	0.9108	-0.58
2.20E-03	1.35E-03	5.49E-04	0.9139	-0.58
2.75E-03	1.35E-03	5.49E-04	0.9168	-0.57
3.30E-03	1.35E-03	5.49E-04	0.9196	-0.57
3.84E-03	1.35E-03	5.49E-04	0.9221	-0.56
4.39E-03	1.35E-03	5.49E-04	0.9245	-0.56
4.94E-03	1.35E-03	5.49E-04	0.9267	-0.56
5.49E-03	1.35E-03	5.49E-04	0.9288	-0.55
6.04E-03	1.35E-03	5.49E-04	0.9308	-0.55
6.59E-03	1.35E-03	5.49E-04	0.9327	-0.54
7.14E-03	1.35E-03	5.49E-04	0.9345	-0.54
7.69E-03	1.35E-03	5.49E-04	0.9362	-0.53
8.24E-03	1.35E-03	5.49E-04	0.9378	-0.53
8.79E-03	1.35E-03	5.49E-04	0.9393	-0.52
9.34E-03	1.35E-03	5.49E-04	0.9408	-0.52
9.89E-03	1.35E-03	5.49E-04	0.9422	-0.51
1.04E-02	1.35E-03	5.49E-04	0.9435	-0.51
1.10E-02	1.35E-03	5.49E-04	0.9448	-0.50
1.15E-02	1.35E-03	5.49E-04	0.9460	-0.50
1.21E-02	1.35E-03	5.49E-04	0.9471	-0.49
1.26E-02	1.35E-03	5.49E-04	0.9483	-0.49
1.32E-02	1.35E-03	5.49E-04	0.9493	-0.48

$u(Q_w)$ = 10 mJ; $u(T)$ = 50 μK

Table S19. Stoichiometric data and heat effects of the calorimetry experiments with [$P_{4\,4\,4\,4}$][C_7COO] + water at 313.15 K. The subscript c and d mean cell (or container) and dispenser (or syringe) respectively.

$n_{w,c}$ / mol	$n_{IL,c}$ / mol	$n_{w,d}$ / mol	x_w	Q_w / J
1.10E-03	1.82E-03	2.75E-04	0.3882	-2.42
1.38E-03	1.82E-03	2.75E-04	0.4401	-2.39
1.65E-03	1.82E-03	2.75E-04	0.4839	-2.31
1.93E-03	1.82E-03	2.75E-04	0.5213	-2.18
2.20E-03	1.82E-03	2.75E-04	0.5537	-2.03
2.48E-03	1.82E-03	2.75E-04	0.5819	-1.85
2.75E-03	1.82E-03	2.75E-04	0.6068	-1.66
3.03E-03	1.82E-03	2.75E-04	0.6289	-1.48
3.30E-03	1.82E-03	2.75E-04	0.6487	-1.32
3.58E-03	1.82E-03	2.75E-04	0.6664	-1.16
3.85E-03	1.82E-03	2.75E-04	0.6825	-1.04
4.13E-03	1.82E-03	2.75E-04	0.6970	-0.93
4.40E-03	1.82E-03	2.75E-04	0.7103	-0.84
4.68E-03	1.82E-03	2.75E-04	0.7225	-0.76
4.95E-03	1.82E-03	2.75E-04	0.7337	-0.70
2.75E-03	1.15E-03	5.49E-04	0.9201	-0.43
3.30E-03	1.15E-03	5.49E-04	0.9230	-0.42
3.84E-03	1.15E-03	5.49E-04	0.9258	-0.41
4.39E-03	1.15E-03	5.49E-04	0.9283	-0.40
4.94E-03	1.15E-03	5.49E-04	0.9306	-0.40
5.49E-03	1.15E-03	5.49E-04	0.9329	-0.39
6.04E-03	1.15E-03	5.49E-04	0.9349	-0.38
6.59E-03	1.15E-03	5.49E-04	0.9369	-0.37
7.14E-03	1.15E-03	5.49E-04	0.9387	-0.36
7.69E-03	1.15E-03	5.49E-04	0.9405	-0.35
8.24E-03	1.15E-03	5.49E-04	0.9421	-0.34
8.79E-03	1.15E-03	5.49E-04	0.9437	-0.33
9.34E-03	1.15E-03	5.49E-04	0.9451	-0.32
9.89E-03	1.15E-03	5.49E-04	0.9465	-0.32
1.04E-02	1.15E-03	5.49E-04	0.9478	-0.31
1.10E-02	1.15E-03	5.49E-04	0.9491	-0.30
1.15E-02	1.15E-03	5.49E-04	0.9503	-0.29
1.21E-02	1.15E-03	5.49E-04	0.9515	-0.29
1.26E-02	1.15E-03	5.49E-04	0.9526	-0.28
1.32E-02	1.15E-03	5.49E-04	0.9536	-0.27

$u(Q_w)$ = 10 mJ; $u(T)$ = 50 µK

Table S20. Fitting parameters obtained for the partial excess enthalpies of water, $\overline{H}_w^E$, with the Redlich-Kister equation

IL water mixture	A_0 / kJ mol^{-1}	A_1 / kJ mol^{-1}	A_2 / kJ mol^{-1}	AAD / %
[$P_{4\,4\,4\,4}$][C_1COO]	-16.923	12.914	-5.412	0.02
[$P_{4\,4\,4\,4}$][C_2COO]	-17.682	16.098		0.36
[$P_{4\,4\,4\,4}$][C_7COO]	-17.082	14.164		0.21

References

[1] Q. Yang, D. Xu, J. Zhang, Y. Zhu, Z. Zhang, C. Qian, et al. Long-Chain Fatty Acid-Based Phosphonium Ionic Liquids with Strong Hydrogen-Bond Basicity and Good Lipophilicity: Synthesis, Characterization, and Application in Extraction. ACS Sustainable Chem. Eng. **2015**, *3*, 309.

[2] Y. Cao, T. Mu. Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis. Ind. Eng. Chem. Res. **2014**, *53*, 8651.