Supporting Information

Tetraalkylammonium chlorides as melting point depressants of ionic liquids

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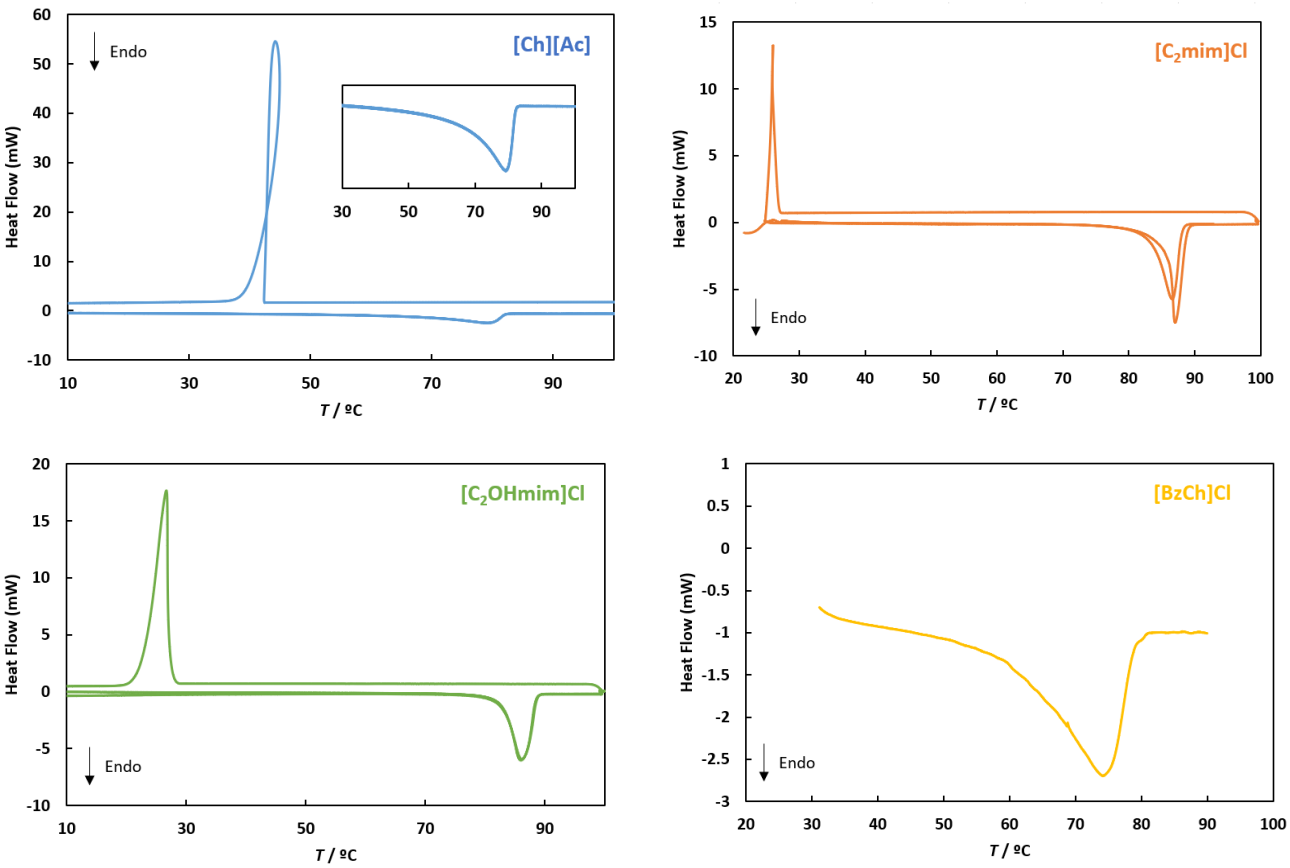

Figure S1. DSC thermograms of [Ch][Ac], [C_2mim]Cl, [C_2OHmim]Cl, and [BzCh]Cl.

Table S1. Experimental SLE data for ammonium salts (1) + ionic liquids (2) eutectic systems, including molar fraction, *x*, melting temperature, *T*, and activity coefficient, γ.[a,b]

x_1	T / K	γ_2	x_1	T / K
$[N_{1,1,1,1}]Cl$ (1) + [Ch][Ac] (2)				
0	355.8	1	0.432	369.7
0.101	351.6	1.047	0.512	401.8
0.201	339.3	0.978	0.600	438.0
0.284	326.4	0.882	0.701	490.2
			0.799	531.5
			0.899	585.0
			1	612.9
$[N_{2,2,2,2}]Cl$ (1) + [Ch][Ac] (2)				
0	355.8	1	0.398	339.8
0.100	350.7	1.033	0.500	381.9
0.202	331.0	0.856	0.598	420.1
0.299	318.6	0.787	0.703	445.0
			0.788	478.1
			0.899	504.9
			1	535.4
$[N_{3,3,3,3}]Cl$ (1) + [Ch][Ac] (2)				
0	355.8	1	0.406	347.8
0.101	353.8	1.081	0.500	375.9
0.201	337.6	0.950	0.599	402.2
0.303	318.9	0.795	0.689	428.5
			0.798	459.8
			0.895	478.2
			1	503.1
$[N_{1,1,1,1}]Cl$ (1) + $[C_2mim]Cl$ (2)				
0	359.9	1	0.503	377.7
0.102	348.6	0.958	0.601	419.8
0.200	344.6	1.018	0.699	484.6
0.302	343.4	1.147	0.799	529.6
0.399	339.7	1.264	0.898	584.4
			0.949	599.5
			1	612.9
$[N_{2,2,2,2}]Cl$ (1) + $[C_2mim]Cl$ (2)				
0	359.9	1	0.496	360.0
0.101	348.2	0.952	0.592	391.0
0.203	344.2	1.015	0.701	427.7

0.303	338.4	1.069	0.800	466.7
0.400	328.4	1.068	0.897	495.7
			0.948	520.9
			1	535.4
$[N_{3,3,3,3}]Cl$ (1) + $[C_2mim]Cl$ (2)				
0	359.9	1	0.398	334.8
0.101	340.1	0.849	0.498	363.5
0.200	324.7	0.756	0.600	390.5
0.300	312.4	0.707	0.702	426.4
			0.798	448.2
			0.896	473.6
			0.946	487.7
			1	503.1
$[N_{1,1,1,1}]Cl$ (1) + $[C_2OHmim]Cl$ (2)				
0	359.5	1	0.499	378.8
0.101	355.8	1.028	0.599	428.9
0.201	353.4	1.099	0.700	481.6
0.300	352.4	1.227	0.800	531.2
0.401	350.8	1.382	0.900	574.5
			1	612.9
$[N_{2,2,2,2}]Cl$ (1) + $[C_2OHmim]Cl$ (2)				
0	359.5	1	0.500	374.6
0.103	356.4	1.043	0.600	407.8
0.201	353.3	1.095	0.700	438.4
0.299	350.7	1.180	0.798	470.7
0.400	341.6	1.119	0.899	495.5
			1	535.4
$[N_{3,3,3,3}]Cl$ (1) + $[C_2OHmim]Cl$ (2)				
0	359.5	1	0.499	361.6
0.101	357.2	1.060	0.599	386.8
0.200	354.4	1.120	0.699	410.6
0.299	341.6	0.957	0.793	447.3
0.407	332.8	0.917	0.900	474.9
			1	503.1
$[N_{1,1,1,1}]Cl$ (1) + [MeCh]Cl (2)				
0	442.0	1	0.392	396.8
0.101	415.8	0.991	0.500	428.9
0.203	378.7	0.925	0.599	472.6
0.302	354.9	0.915	0.701	501.6
			0.799	551.8

			0.899	589.7
			0.9	598.1
			1	612.9
$[N_{2,2,2,2}]Cl$ (1) + [MeCh]Cl (2)				
0	442.0	1	0.399	383.1
0.101	413.0	0.978	0.499	407.5
0.197	380.8	0.928	0.600	440.2
0.300	351.8	0.894	0.702	460.5
			0.801	492.2
			0.899	516.6
			0.949	529.9
			1	535.4
$[N_{3,3,3,3}]Cl$ (1) + [MeCh]Cl (2)				
0	442.0	1	0.402	368.8
0.101	411.8	0.973	0.497	393.6
0.201	374.3	0.900	0.599	416.0
0.300	345.6	0.858	0.700	441.0
			0.803	463.2
			0.894	484.2
			0.9	494.5
			1	503.1
$[N_{1,1,1,1}]Cl$ (1) + [BzCh]Cl (2)				
0	346.7	1	0.400	373.5
0.101	348.6	1.142	0.496	416.6
0.201	345.4	1.228	0.600	458.2
0.301	342.2	1.343	0.701	491.7
			0.800	528.1
			0.899	569.6
			1	612.9
$[N_{2,2,2,2}]Cl$ (1) + [BzCh]Cl (2)				
0	346.7	1	0.397	360.6
0.100	348.0	1.131	0.501	390.8
0.196	344.3	1.201	0.601	423.9
0.300	340.6	1.310	0.699	452.0
			0.799	482.0
			0.900	505.4
			1	535.4
$[N_{3,3,3,3}]Cl$ (1) + [BzCh]Cl (2)				
0	346.7	1	0.402	349.5
0.101	343.4	1.062	0.501	366.0

0.200	338.0	1.103	0.599	388.6
0.300	335.4	1.214	0.699	420.7
			0.800	445.9
			0.898	475.3
			1	503.1

[a]Standard uncertainties, u: $u(T)$ < 1 K, $u_r(p)$ = 0.05 and $u_r(x)$ = 0.002. [b]Measured at atmospheric pressure.

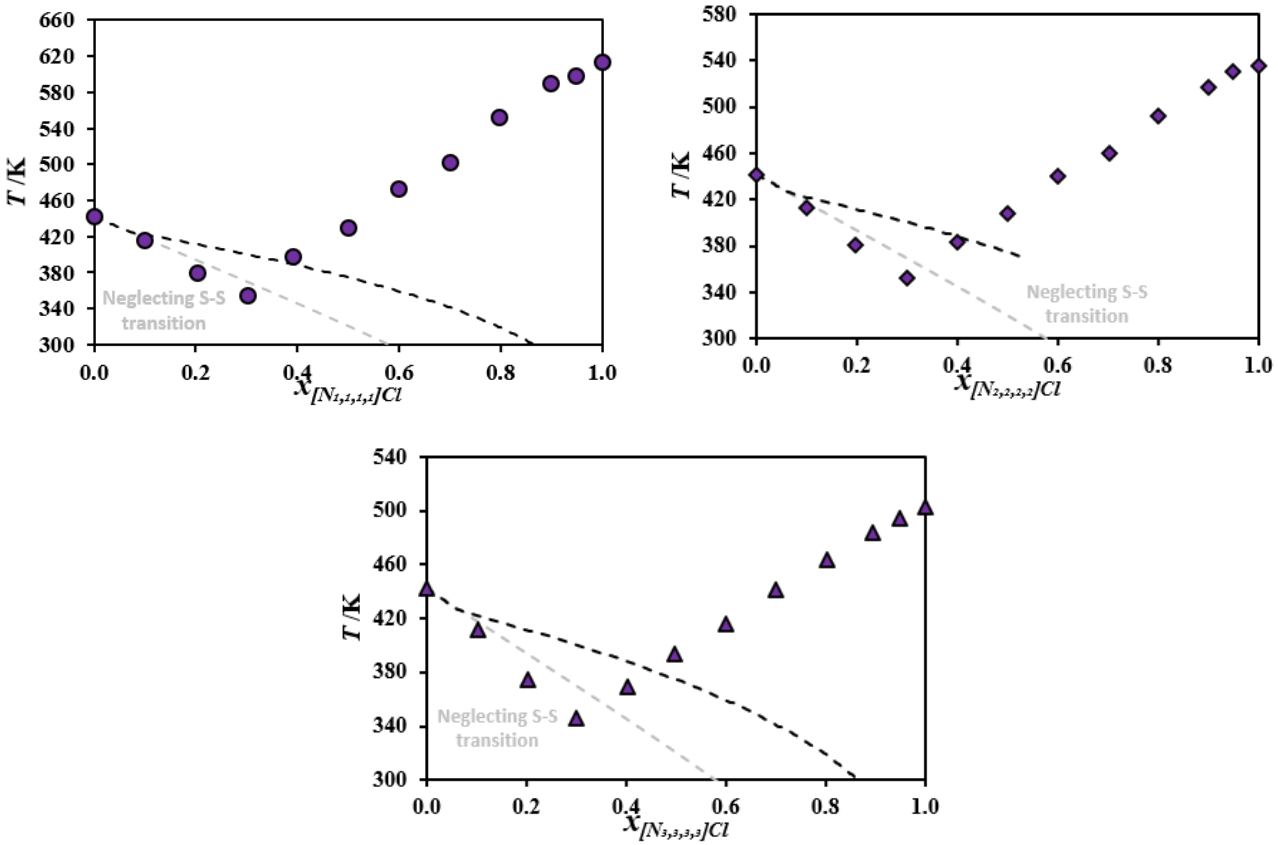

Figure S2. SLE phase diagrams of [MeCh]Cl and $[N_{1,1,1,1}]Cl$, $[N_{2,2,2,2}]Cl$, or $[N_{3,3,3,3}]Cl$. Symbols represent the data measured in this work while the dashed lines represent the ideal solubility curves calculated with and without the [MeCh]Cl solid-solid transition.

Table S2. Melting enthalpies available for the ammonium salts investigated.

Salt	$\Delta_m h$ **/kJ·mol^{-1}**
Tetramethylammonium chloride, $[N_{1,1,1,1}]Cl$	20.49 [1][a], 12.03 [2][c], 8.47 [2][d]
Tetraethylammonium chloride, $[N_{2,2,2,2}]Cl$	51.24 [1][b], 14.83 [2][c], 28.19 [2][d]
Tetrapropylammonium chloride, $[N_{3,3,3,3}]Cl$	66.58 [1][b], 12.41 [2][c], 39.03 [2][d]

[a]Fitted to the experimental data using the activity coefficients estimated by the COSMO-RS model [1]. [b]Experimentally measured using DSC [1]. [c]Obtained using PC-SAFT equation of state [2]. [d]Obtained using COSMO-RS [2].

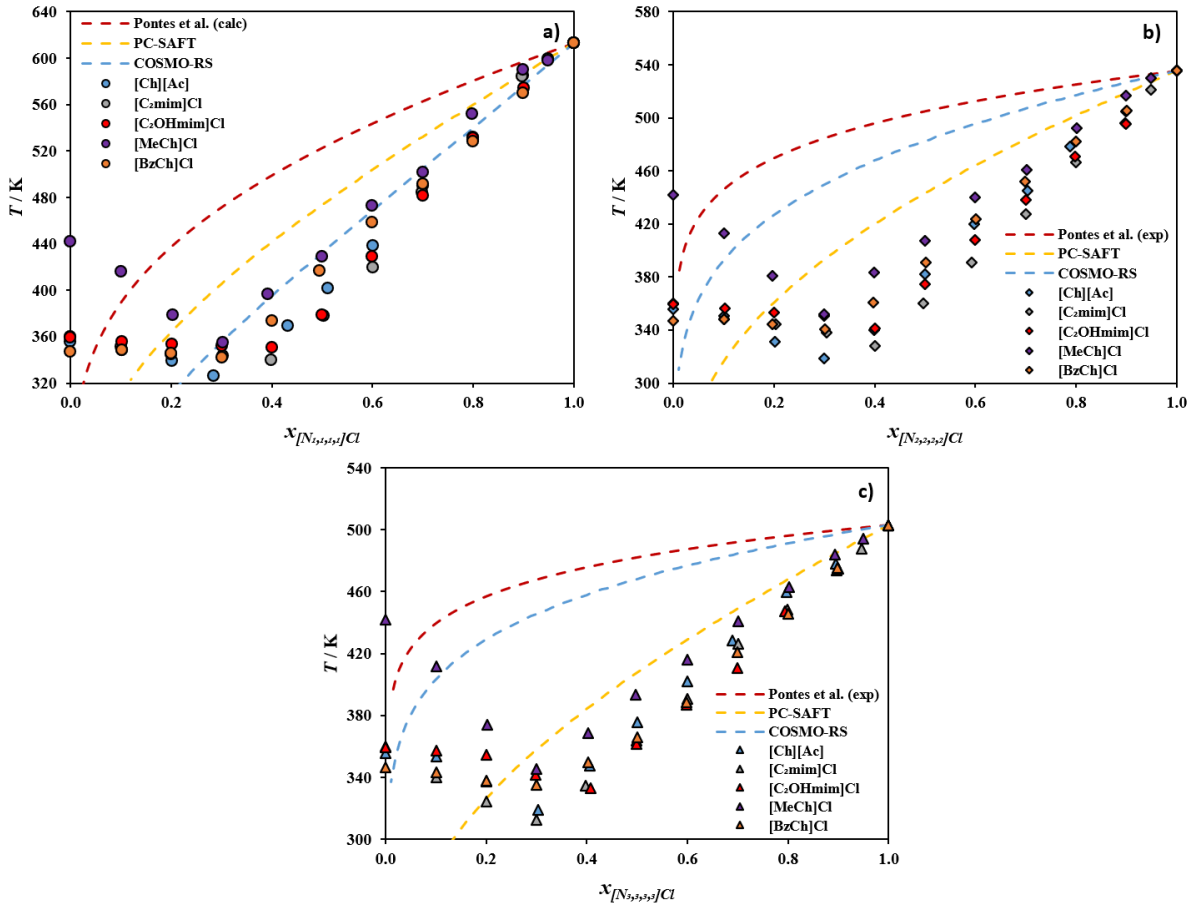

Figure S3. SLE phase diagrams of ILs and: a) $[N_{1,1,1,1}]Cl$, b) $[N_{2,2,2,2}]Cl$, or c) $[N_{3,3,3,3}]Cl$. Symbols represent the data measured in this work while the dashed lines represent the ideal solubility curves calculated using different melting enthalpies: ---, Pontes et al. [1]; ---, PC-SAFT [2]; ---, COSMO-RS [2].

References

1. Pontes, P.V.A., Crespo, E.A., Martins, M.A.R., Silva, L.P., Neves, C.M.S.S., Maximo, G.J., Hubinger, M.D., Batista, E.A.C., Pinho, S.P., Coutinho, J.A.P., Sadowski, G., Held, C.: Measurement and PC-SAFT modeling of solid-liquid equilibrium of deep eutectic solvents of quaternary ammonium chlorides and carboxylic acids. Fluid Phase Equilib. 448, 69–80 (2017). https://doi.org/10.1016/j.fluid.2017.04.007
2. Vilas-Boas, S.M., Abranches, D.O., Crespo, E.A., Ferreira, O., Coutinho, J.A.P., Pinho, S.P.: Experimental solubility and density studies on aqueous solutions of quaternary ammonium halides, and thermodynamic modelling for melting enthalpy estimations. J. Mol. Liq. 300, 112281 (2020). https://doi.org/10.1016/j.molliq.2019.112281