Supporting Information

The Role of Polyfunctionality in the Formation of [Ch]Cl-carboxylic acid-based DES

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Table S1. Experimental (x_2, T) and calculated (γ_i) data of the SLE of systems involving choline chloride and carboxylic acids at atmospheric pressure.[1]

x_2	T / K	γ_1	x_2	T / K	γ_2
Solid Phase: [Ch]Cl (1)			Solid Phase: Polycarboxylic acid (2)		
Glycolic acid					
0	597[a]	1	0.549	287.45[c]	0.424
0.054	563.15[b]	1.004	0.600	297.38[c]	0.508
0.101	532.58[b]	1.002	0.649	300.78[c]	0.512
0.152	504.58[b]	1.006	0.700	306.72[c]	0.551
0.204	477.55[b]	1.011	0.753	313.95[c]	0.610
0.250	450.18[b]	1.006	0.799	321.95[c]	0.691
0.301	420.15[b]	0.993	0.850	330.28[b]	0.779
0.351	387.98[b]	0.966	0.900	337.62[b]	0.857
0.402	364.15[b]	0.961	0.950	345.42[b]	0.948
0.452	335.38[c]	0.928	1	350.85[b]	1
0.501	301.95[c]	0.859			
Lactic acid					
0	597[a]	1	0.901	287.75[c]	1.073
0.050	565.55[b]	1.003	0.950	288.35[c]	1.027
0.104	537.15[b]	1.014	1	289.82[c]	1
0.153	501.55[b]	1.001			
0.201	466.85[b]	0.983			
0.251	434.82[c]	0.966			
0.303	406.45[c]	0.955			
0.347	386.65[c]	0.956			
0.401	351.42[c]	0.912			
0.450	316.88[c]	0.845			
0.498	296.95[c]	0.831			
Oxalic acid					
0	597[a]	1	0.547	320.78[c]	0.216
0.050	567.25[b]	1.006	0.587	333.82[c]	0.265
0.106	527.48[b]	0.998	0.600	337.48[c]	0.279
0.152	497.42[b]	0.991	0.650	354.08[c]	0.351
0.200	471.78[b]	0.994	0.700	369.68[c]	0.425
0.251	436.25[b]	0.970	0.756	387.65[c]	0.521
0.301	411.48[b]	0.968	0.800	400.72[b,c]	0.594
0.352	385.48[b]	0.959	0.850	416.62[b,c]	0.692
0.402	364.62[b]	0.962	0.900	432.65[b,c]	0.797
0.450	332.38[c]	0.913	0.950	444.38[b,c]	0.865
0.503	308.18[c]	0.893	1	462.45[b]	1
Malonic acid					
0	597[a]	1	0.500	291.48[c]	0.124
0.053	553.58[b]	0.986	0.550	298.52[c]	0.141
0.100	534.42[b]	1.004	0.601	304.58[c]	0.156
0.152	502.28[b]	1.001	0.650	317.52[c]	0.208
0.202	469.68[b]	0.990	0.688	328.68[b,c]	0.265
0.300	404.12[b]	0.945	0.750	343.98[b,c]	0.354
0.350	360.45[b]	0.872	0.800	363.22[b,c]	0.509

0.400	335.55[b]	0.849	0.850	379.85[b,c]	0.670
0.450	301.48[b]	0.778	0.899	387.95[b,c]	0.738
			0.950	396.45[b,c]	0.814
			1	411.55[b]	1
Succinic acid					
0	597[a]	1	0.500	340.38[b,c]	0.096
0.051	564.75[b]	1.003	0.551	354.48[b,c]	0.138
0.101	535.55[b]	1.007	0.597	368.85[b,c]	0.197
0.153	513.72[b]	1.026	0.651	382.58[b,c]	0.265
0.202	488.15[b]	1.033	0.699	393.12[b,c]	0.326
0.250	464.82[b]	1.043	0.750	402.05[b]	0.380
0.302	432.35[b]	1.031	0.799	415.65[b]	0.493
0.350	401.95[b]	1.011	0.850	424.98[b]	0.571
0.400	368.22[b]	0.974	0.899	439.58[b]	0.736
0.450	335.58[b]	0.926	0.949	448.12[b]	0.828
			1	460.70[b]	1
Glutaric acid					
0	597[a]	1	0.505	304.55[b]	0.461
0.051	571.62[b]	1.014	0.550	311.15[b]	0.504
0.102	539.75[b]	1.015	0.601	320.45[b]	0.582
0.150	504.28[b]	1.004	0.648	326.58[b]	0.624
0.201	475.42[b]	1.003	0.701	333.48[b]	0.676
0.301	418.72[b]	0.989	0.750	341.02[b]	0.745
0.250	444.45[b]	0.991	0.799	345.38[b]	0.767
0.351	396.78[b]	0.995	0.849	352.58[b]	0.836
0.402	372.65[b]	0.993	0.899	358.68[b]	0.890
0.448	342.85[b]	0.954	0.950	364.25[b]	0.937
			1	370.60[b]	1
Malic acid					
0	597[a]	1	0.450	334.55[b]	0.295
0.050	570.35[b]	1.011	0.500	338.42[b]	0.304
0.100	538.38[b]	1.012	0.549	345.92[b,c]	0.357
0.151	505.68[b]	1.007	0.601	358.68[b,c]	0.488
0.201	474.48[b]	1.001	0.649	364.75[b]	0.543
0.251	441.62[b]	0.984	0.699	371.42[b]	0.612
0.300	417.18[b]	0.984	0.751	376.42[b]	0.656
0.400	358.52[b]	0.937	0.800	383.62[b]	0.749
			0.850	387.88[b]	0.789
			0.899	391.75[b]	0.825
			0.944	395.18[b]	0.857
			1	404.30[b]	1
Tartaric acid					
0	597[a]	1	0.400	330.62[b]	0.087
0.053	557.95[b]	0.994	0.450	341.62[b,c]	0.118
0.100	514.45[b]	0.967	0.502	352.35[b,c]	0.157
0.151	471.75[b]	0.936	0.552	364.32[b,c]	0.214
0.199	435.52[b]	0.906	0.593	374.55[b,c]	0.276
0.251	386.68[b]	0.834	0.652	385.82[b,c]	0.354
0.295	357.62[b]	0.795	0.700	393.65[b]	0.413
0.327	321.55[b]	0.708	0.799	411.58[b]	0.586

			0.900	428.02[b]	0.782
			0.949	437.95[b]	0.934
			1	443.28[b]	1.000
Citric acid					
0	597[a]	1	0.400	348.98[b]	0.195
0.052	557.85[b]	0.992	0.451	356.75[b]	0.234
0.101	512.35[b]	0.964	0.499	364.05[b]	0.277
0.151	478.98[b]	0.951	0.552	370.98[b]	0.322
0.200	431.68[b]	0.897	0.600	379.48[b]	0.397
0.250	387.12[b]	0.834	0.650	384.02[b]	0.426
0.314	343.55[b]	0.770	0.700	393.48[b]	0.536
			0.748	397.98[b]	0.577
			0.800	404.48[b]	0.656
			0.850	411.35[b]	0.754
			0.898	418.28[b]	0.868
			0.938	423.15[b]	0.950
			1	427.48[b]	1

[1]Standard uncertainties, u, are $u(T)$=1.5 K, $u_r(p)$=0.05, $u_r(x)$=0.002. [a]Fernandez et al., 2017, Fluid Phase Equilibria, **448**, 9-14; [b]Data obtained using the melting points device method; [c]Data obtained using the oil bath method.

Table S2. Water content of the eutectic points of the investigated mixtures after melting.

System	H_2O/ppm
[Ch]Cl + glycolic acid	2089
[Ch]Cl + lactic acid	13321
[Ch]Cl + oxalic acid	2167
[Ch]Cl + malonic acid	2684
[Ch]Cl + succinic acid	5475
[Ch]Cl + glutaric acid	4012
[Ch]Cl + malic acid	3445
[Ch]Cl + tartaric acid	4828
[Ch]Cl + citric acid	2513

Table S3. Eutectic point coordinates assuming an ideal liquid phase and applying the PCSAFT EoS.

System	Ideal		PC-SAFT		Depressions	
	x^E	T^E	x^E	T^E	$\lvert \Delta x^E \rvert$	ΔT^E
[Ch]Cl + glycolic acid	0.5277	319.94	0.5213	278.22	0.0064	41.72
[Ch]Cl + lactic acid	0.6591	266.24	0.6009	265.43	0.0582	0.81
[Ch]Cl + oxalic acid	0.3791	385.14	0.5023	308.57	0.1232	76.57
[Ch]Cl + malonic acid	0.4233	365.06	0.4927	273.77	0.0694	91.29
[Ch]Cl + succinic acid	0.3303	408.14	0.4572	322.48	0.1269	85.66
[Ch]Cl + glutaric acid	0.4917	335.18	0.5008	304.88	0.0091	30.30
[Ch]Cl + malic acid	0.4112	370.12	0.4003	330.24	0.0109	39.88

[Ch]Cl + tartaric acid	0.3468	400.25	0.3253	306.39	0.0215	93.86
[Ch]Cl + citric acid	0.3633	392.45	0.3132	336.03	0.0501	56.42

Table S4. Experimental density results, ρ, at 0.1 MPa as a function of temperature, for the mixtures involving choline chloride and (poly)carboxylic acids. The mole fraction of the acid (x_{acid}) is provided.[a]

	ρ / g·cm^{-3}								
[Ch]Cl +	Glutaric Acid	Glycolic Acid	Oxalic Acid	Malic Acid	Malonic Acid	Lactic Acid	Succinic Acid	Tartaric Acid	Citric Acid
x_{acid} / ***T* / K**	0.501	0.547	0.502	0.453	0.500	0.598	0.450	0.350	0.300
283.15						1.1675			
288.15						1.1642			
293.15		1.2190				1.1611			
298.15		1.2157			1.2302	1.1581			
303.15		1.2125	1.2014		1.2271	1.1551			
308.15	1.1796	1.2094	1.1981		1.2239	1.1521			
313.15	1.1765	1.2064	1.1948		1.2208	1.1492			
318.15	1.1735	1.2034	1.1916		1.2175	1.1462			
323.15	1.1704	1.2004	1.1883		1.2143	1.1433			
328.15	1.1675	1.1974	1.1850		1.2110	1.1403			
333.15	1.1646	1.1944	1.1819	1.2355	1.2077	1.1374			
338.15	1.1618	1.1914	1.1787	1.2327	1.2016	1.1344		1.2399	
343.15	1.1591	1.1884	1.1755	1.2300		1.1315	1.1765	1.2393	1.2276
348.15	1.1564	1.1853		1.2272		1.1285	1.1737	1.2374	1.2249
353.15	1.1537	1.1823		1.2244		1.1256	1.1710	1.2348	1.2223
358.15	1.1512	1.1794		1.2215		1.1226	1.1683	1.2321	1.2197
363.15		1.1766		1.2188			1.1654	1.2294	1.2169
368.15		1.1739							
373.15		1.1713							

[a]Uncertainties are $u(T)$ = 0.02 K, $u(\rho)$ = 0.0005 g·cm^{-3} and $u_r(p)$ = 0.05.

Table S5. Experimental viscosity results, η, at 0.1 MPa as a function of temperature, for the mixtures involving choline chloride and (poly)carboxylic acids. The mole fraction of the acid (x_{acid}) is provided.[a]

	η / mPa·s								
[Ch]Cl +	Glutaric Acid	Glycolic Acid	Oxalic Acid	Malic Acid	Malonic Acid	Lactic Acid	Succinic Acid	Tartaric Acid	Citric Acid
x_{acid} / ***T* / K**	0.501	0.547	0.502	0.453	0.500	0.598	0.450	0.350	0.300
283.15						655.81			

288.15						446.59			
293.15		524.28				313.10			
298.15		369.28			1873.80	225.37			
303.15		266.96	150.35		1324.20	166.05			
308.15	1199.30	197.41	113.05		957.38	124.94			
313.15	868.41	149.12	86.76		706.22	95.85			
318.15	640.99	114.78	67.83		527.20	74.86			
323.15	482.54	89.93	53.94		401.03	59.42			
328.15	369.78	71.60	43.50		310.40	47.88			
333.15	287.92	57.84	35.69	1809.30	244.32	39.11			
338.15	227.28	47.37	29.80	1276.20	198.73	32.30		10399.70	
343.15	181.70	39.27	25.11	935.58		27.00	313.18	7843.30	6708.80
348.15	146.57	32.93		697.45		22.80	242.84	5399.80	4710.00
353.15	119.25	27.90		522.06		19.40	189.03	3773.30	3391.30
358.15	88.67	23.88		400.77		17.00	151.27	2671.00	2440.50
363.15		20.62		312.40			122.62	1921.50	1786.50
368.15		17.95							
373.15		15.76							

[a]Uncertainties are $u(T)$ = 0.02 K, $u_r(\eta)$ = 0.35% and $u_r(p)$ = 0.05.

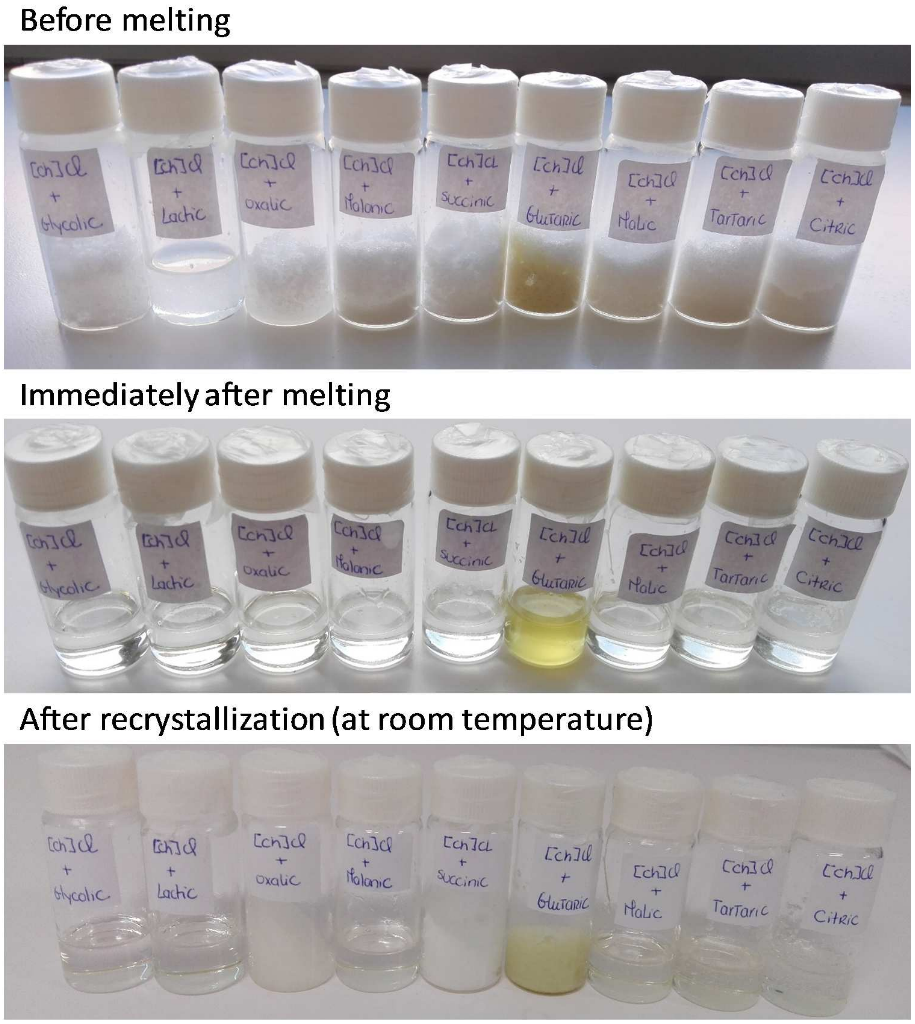
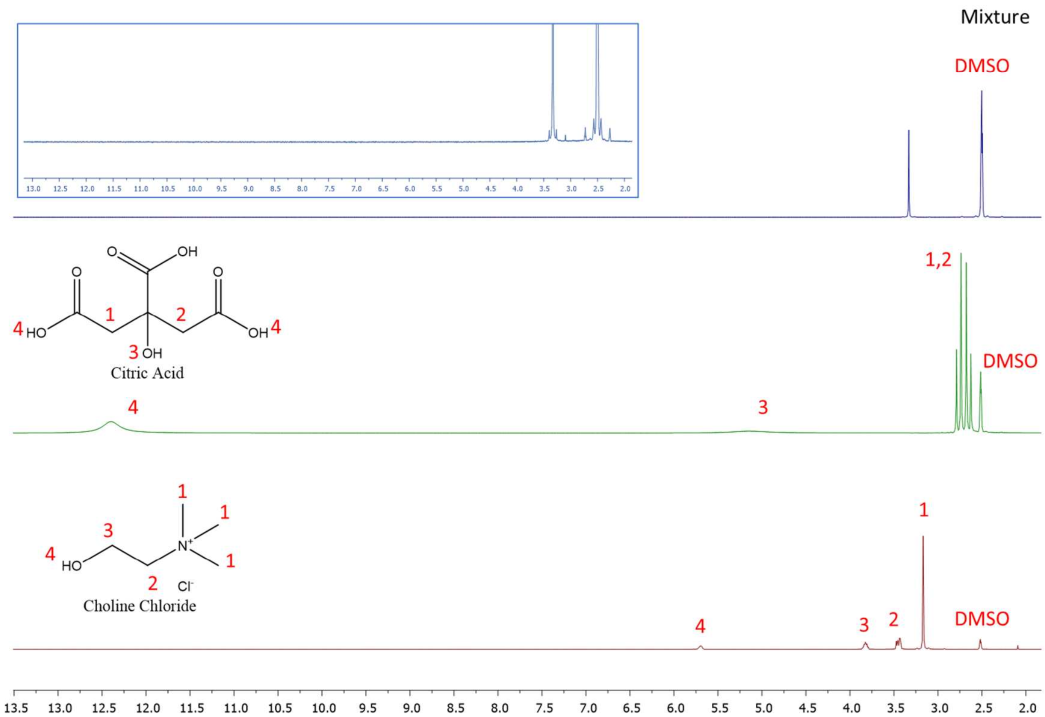


Figure S1. Investigated mixtures at the eutectic composition before melting, right after melting and after recrystallization (at room temperature).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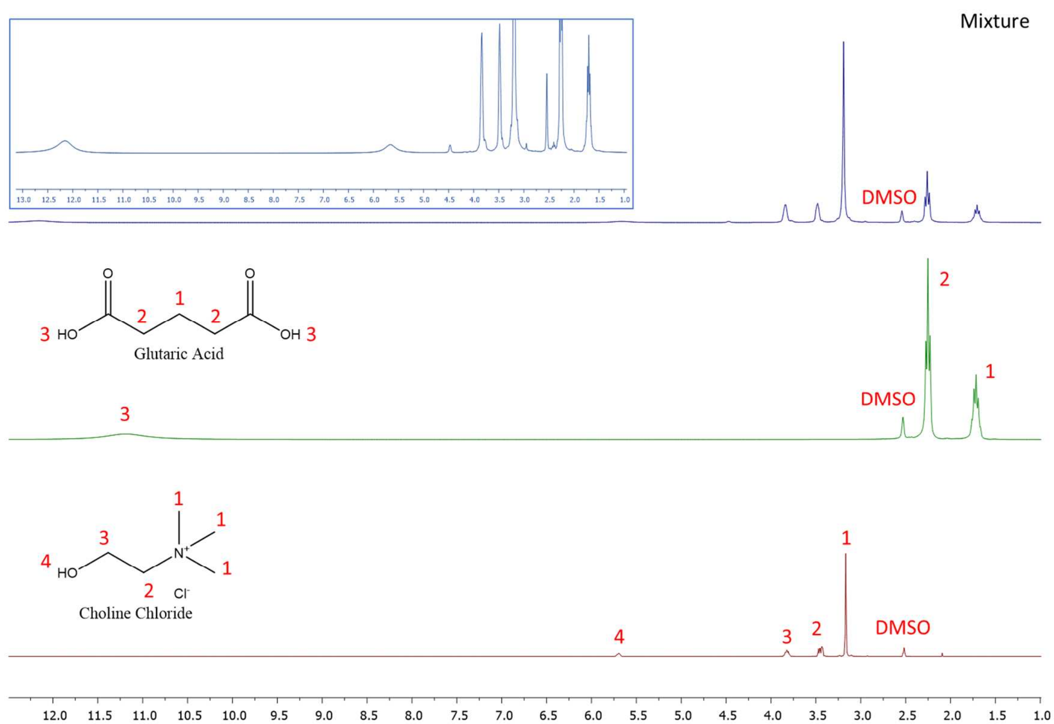
DMSO
Citric Acid
1,2
DMSO
4
3
Choline Chloride
1
4
3
2
DMSO
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0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Glutaric Acid
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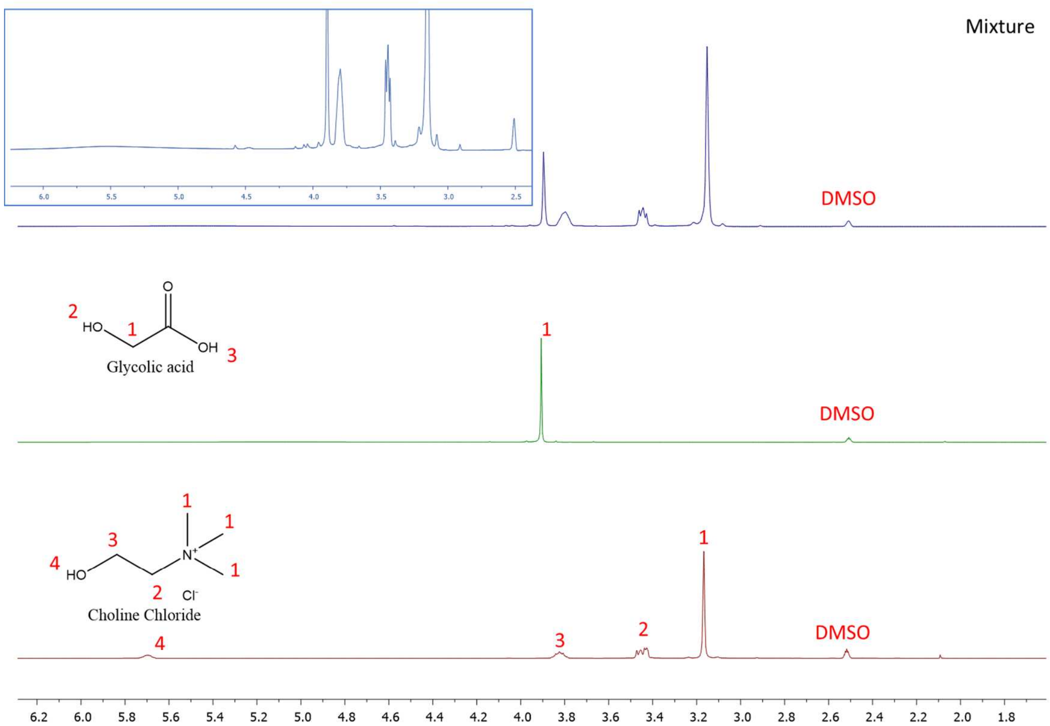
1
DMSO
3
Choline Chloride
1
4
3
2
DMSO
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0


Mixture
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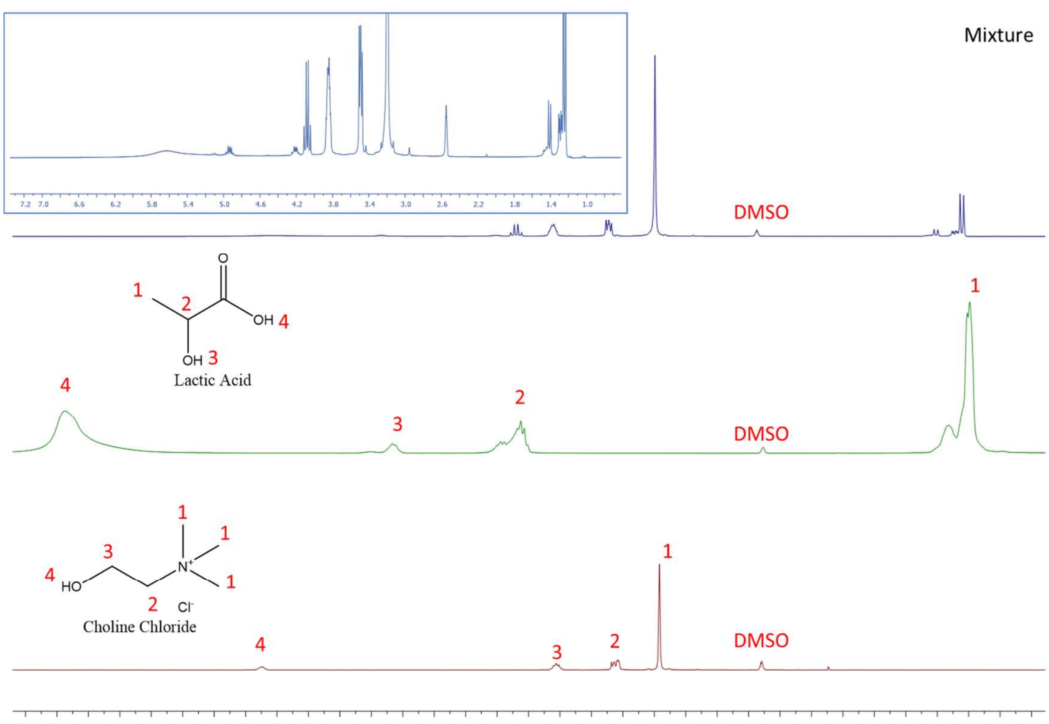
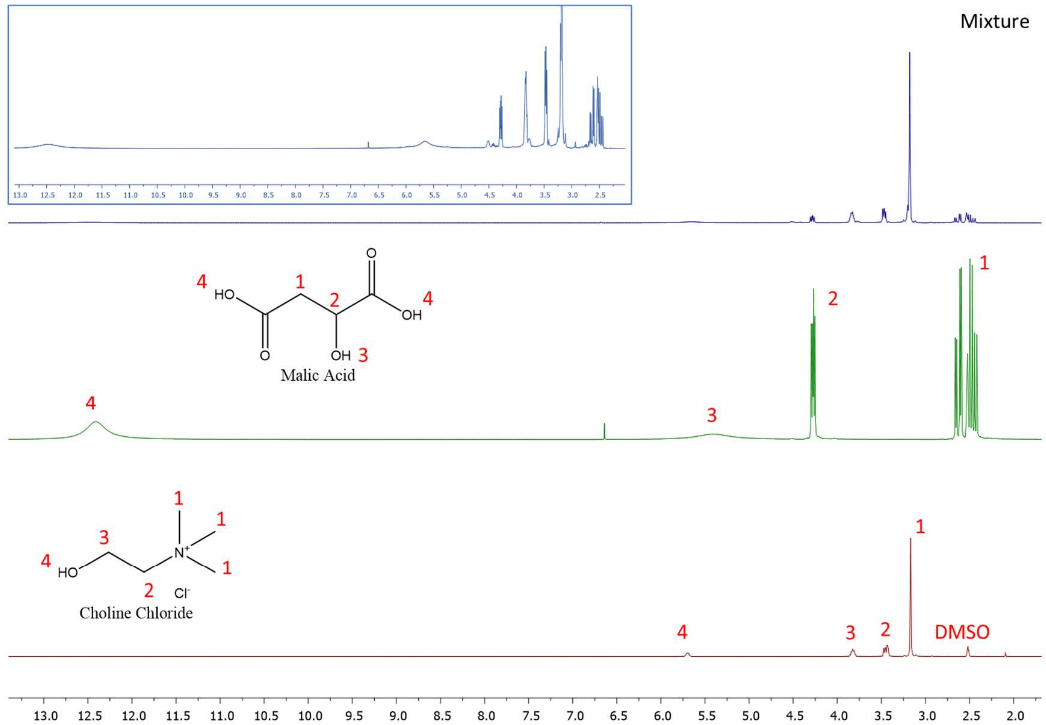
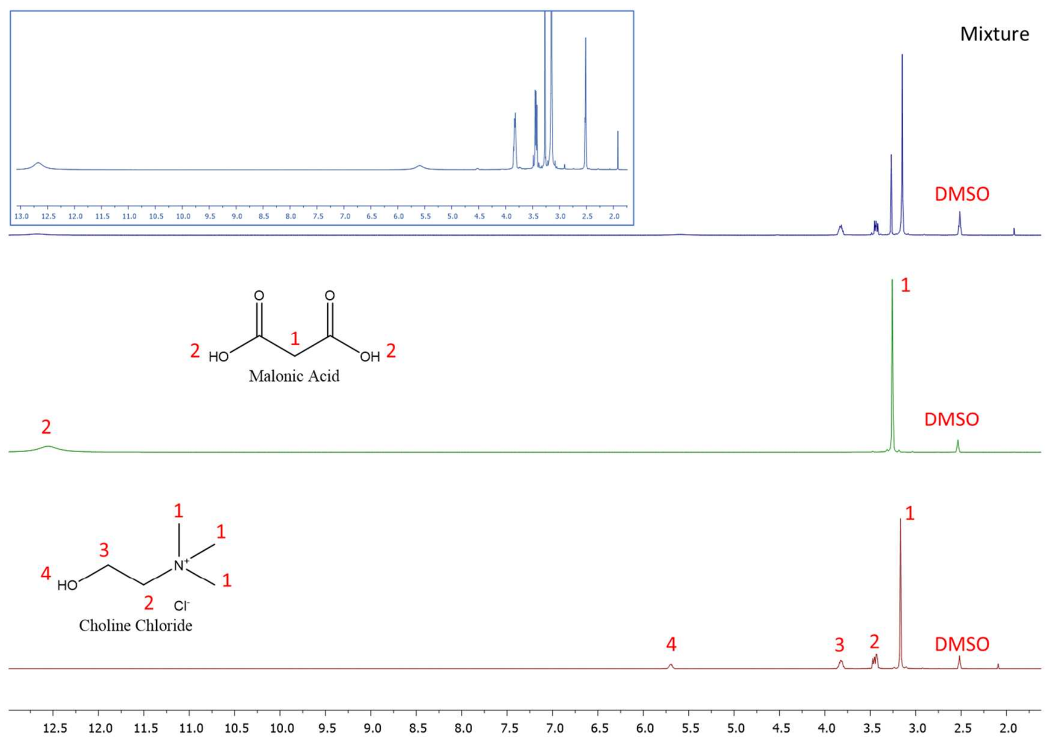
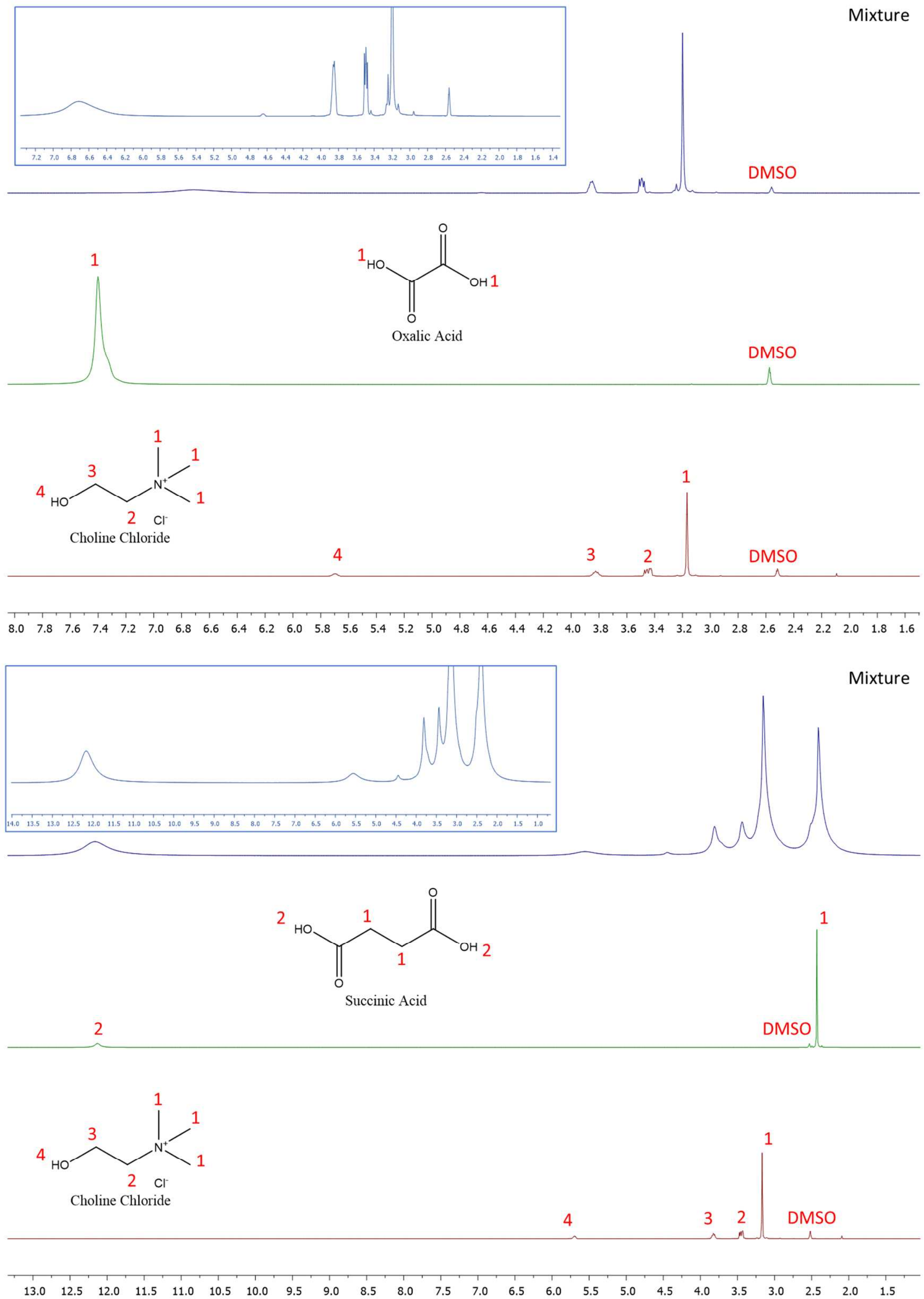
Glycolic acid
1
2
3
HO
OH
O
DMSO
Choline Chloride
N+
Cl-
4
3
2
1
DMSO
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8


Mixture
DMSO
Lactic Acid
1
2
3
4
OH
O
DMSO
Choline Chloride
N+
Cl-
HO
DMSO
7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8


Mixture
Malic Acid
Choline Chloride
DMSO


Mixture
DMSO
Malonic Acid
DMSO
Choline Chloride
DMSO



Mixture
DMSO
Oxalic Acid
1
DMSO
Choline Chloride
4
3
2
1
DMSO
Mixture
Succinic Acid
2
1
DMSO
Choline Chloride
4
3
2
1
DMSO

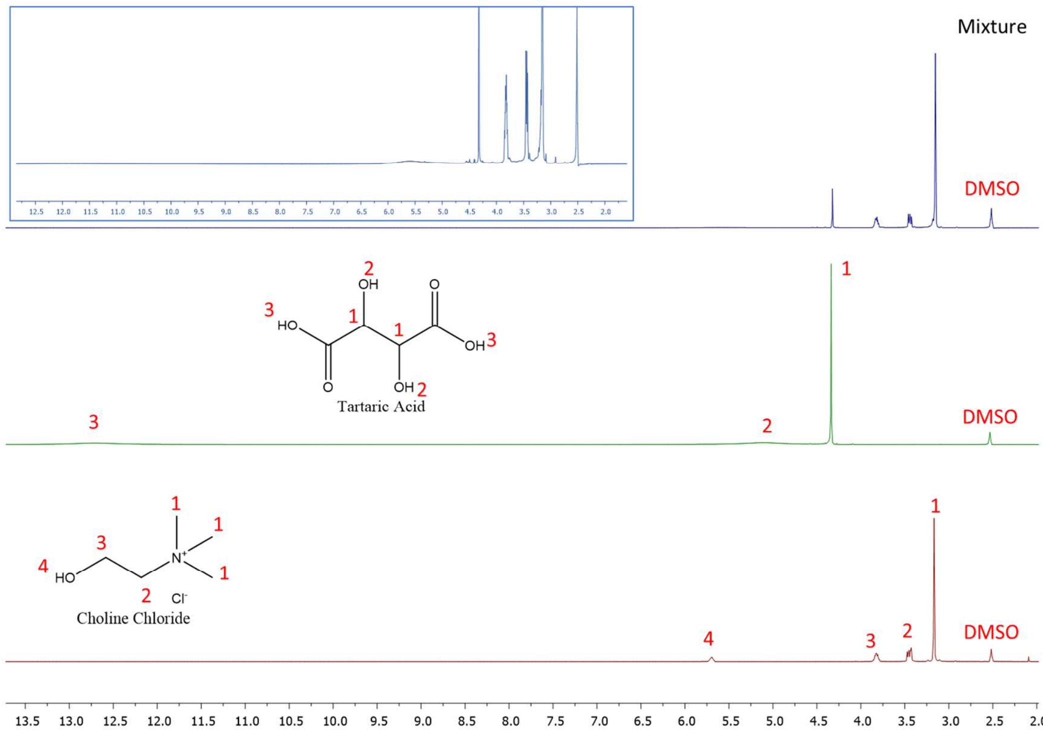


Figure S2. [1]H spectra of pure components and their mixtures at the eutectic point and at room temperature.

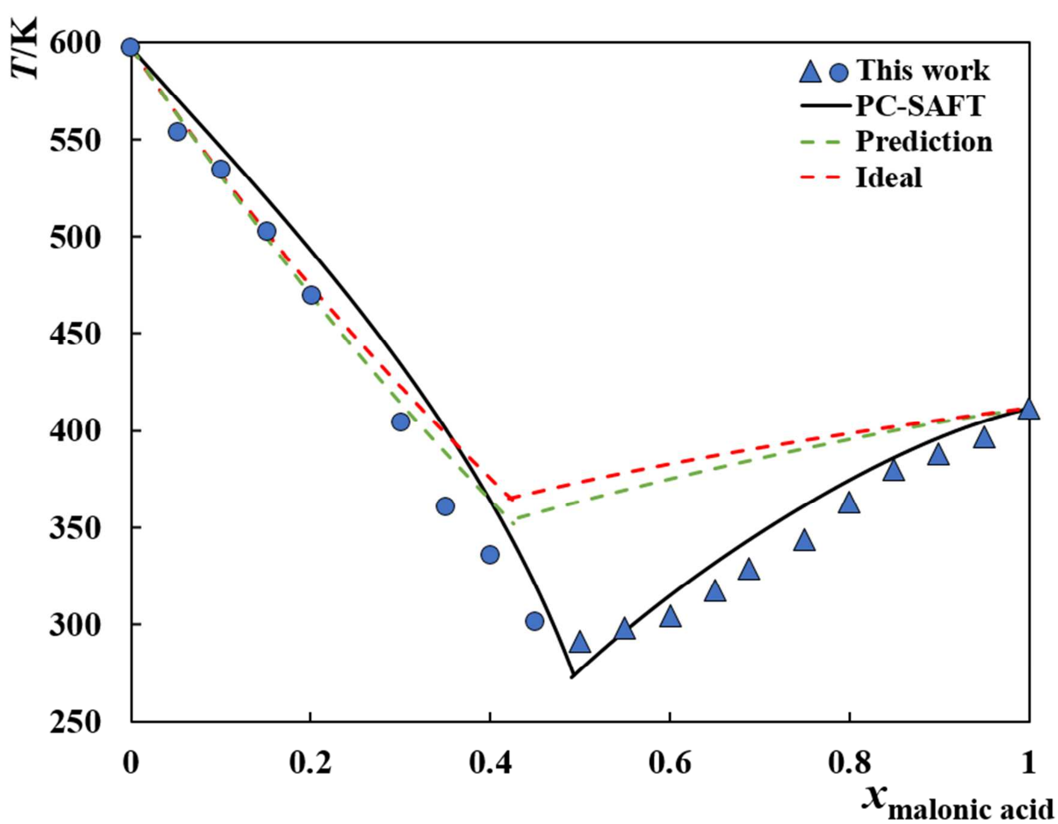


Figure S3. SLE phase diagram of [Ch]Cl + malonic acid. PC-SAFT prediction considers $k_{ij} = 0$ and $k_{ij\_eps} = 0$.