

Supplemental Material:

Differences on the Impact of Water on The Deep Eutectic Solvents Betaine/Urea and Choline/Urea

Dinis O. Abranches,¹ Liliana P. Silva,¹ Mónia A. R. Martins,¹ João A. P. Coutinho ^{1,*}

¹ CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

* Corresponding author e-mail: jcoutinho@ua.pt

S1. Experimental Data

Table S1. Experimental solid-liquid equilibrium data (water-free basis mole fraction of betaine, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system betaine (1) + urea (2) + water (3) with roughly 1% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.897	1.41	0.824	0.095	0.081	509.3	538.8	0.792	
0.799	1.25	0.743	0.187	0.069	477.2	525.4	0.660	
0.699	1.28	0.652	0.281	0.067	435.3	509.1	0.486	
0.592	1.57	0.547	0.377	0.077	414.2	488.8	0.450	
0.499	1.63	0.461	0.463	0.075	394.3	470.8	0.410	
0.400	1.68	0.371	0.557	0.073	379.3	449.4	0.411	
0.300	1.78	0.278	0.650	0.072	366.4	424.1	0.448	
0.201	1.10	0.192	0.766	0.042	353.2	395.4		0.675
0.100	1.23	0.096	0.861	0.043	379.7	397.9		0.850

Table S2. Experimental solid-liquid equilibrium data (water-free basis mole fraction of betaine, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system betaine (1) + urea (2) + water (3) with roughly 2% of water. Data taken from Abranches et al.¹ and recalculated as ternary in this work.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.898	2	0.798	0.090	0.112	502.6	534.5	0.773	
0.798	2	0.713	0.180	0.107	463.5	520.1	0.602	
0.697	2	0.626	0.272	0.102	426.5	504.4	0.457	
0.600	2	0.542	0.362	0.097	397.8	487.9	0.366	
0.501	2	0.455	0.454	0.091	353.9	469.4	0.222	
0.399	2	0.364	0.550	0.086	244.5 ^{a)}	447.8	0.018	
0.300	2	0.276	0.644	0.080	b)	423.5		
0.200	2	0.185	0.740	0.075	344.5	392.7		0.616
0.100	2	0.093	0.838	0.069	367.0	398.2		0.744

a) Data measured using DSC.

b) Mixture did not recrystallize.

Table S3. Experimental solid-liquid equilibrium data (water-free basis mole fraction of betaine, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system betaine (1) + urea (2) + water (3) with roughly 5% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.897	5.01	0.677	0.077	0.246	492.2	513.7	0.832	
0.799	5.06	0.608	0.154	0.238	448.4	501.0	0.603	
0.699	5.04	0.540	0.232	0.228	411.3	487.5	0.439	
0.599	5.04	0.469	0.314	0.217	384.2	472.5	0.349	
0.500	4.98	0.397	0.398	0.205	a)	456.0		
0.400	5.31	0.318	0.477	0.205	a)	435.5		
0.301	5.21	0.244	0.566	0.191	a)	413.4		
0.201	5.68	0.162	0.645	0.193	335.6	391.2		0.618
0.100	5.04	0.084	0.754	0.162	362.4	399.1		0.779

a) Mixture did not recrystallize.

Table S4. Experimental solid-liquid equilibrium data (water-free basis mole fraction of betaine, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system betaine (1) + urea (2) + water (3) with roughly 10% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.897	11.0	0.509	0.058	0.433	481.1	481.0	1.00	
0.800	11.4	0.456	0.114	0.430	435.3	469.6	0.696	
0.699	10.8	0.418	0.179	0.403	395.2	460.8	0.458	
0.600	10.7	0.368	0.245	0.387	372.3	448.8	0.371	
0.500	11.2	0.309	0.308	0.383	b)	432.9		
0.401	11.4	0.252	0.376	0.372	b)	416.0		
0.300	10.6	0.199	0.465	0.336	b)	397.9		
0.202	10.7	0.137	0.540	0.324	246.4 ^{a)}	393.8		0.111
0.100	11.0	0.069	0.620	0.311	346.3	400.6		0.756

a) Data measured using DSC.

b) Mixture did not recrystallize.

Table S5. Experimental solid-liquid equilibrium data (water-free basis mole fraction of ChCl, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system ChCl (1) + urea (2) + water (3) with roughly 1% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.898	1.21	0.824	0.094	0.082	538.5	487.9	1.10	
0.789	1.09	0.734	0.196	0.070	473.3	440.1	1.09	
0.699	1.30	0.644	0.278	0.078	436.4	396.0	1.13	
0.601	1.80	0.541	0.360	0.099	379.1	349.5	1.12	
0.498	1.56	0.458	0.462	0.081	330.5	356.6	1.09	
0.399	1.68	0.367	0.553	0.080	a)	368.2		
0.299	1.06	0.285	0.667	0.048	316.5	377.8		0.435
0.205	1.24	0.195	0.754	0.051	352.1	387.7		0.674
0.101	1.01	0.097	0.866	0.037	380.4	397.8		0.852

a) Mixture did not recrystallize.

Table S6. Experimental solid-liquid equilibrium data (water-free basis mole fraction of ChCl, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system ChCl (1) + urea (2) + water (3) with roughly 2% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.895	2.06	0.776	0.091	0.133	529.7	461.8	1.15	
0.795	2.04	0.696	0.180	0.125	468.2	420.7	1.13	
0.696	2.06	0.613	0.268	0.119	431.2	381.7	1.17	
0.598	2.21	0.527	0.354	0.119	377.3	343.2	1.15	
0.496	2.46	0.436	0.442	0.122	326.0	359.5	1.12	
0.400	2.34	0.356	0.535	0.109	a)	369.5		
0.299	2.01	0.273	0.640	0.087	295.4	379.1		0.305
0.201	2.02	0.185	0.735	0.080	322.7	388.8		0.440
0.101	2.05	0.094	0.833	0.073	350.8	398.1		0.600

a) Mixture did not recrystallize.

Table S7. Experimental solid-liquid equilibrium data (water-free basis mole fraction of ChCl, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system ChCl (1) + urea (2) + water (3) with roughly 5% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.902	5.69	0.626	0.068	0.306	523.6	387.4	1.42	
0.796	6.01	0.554	0.142	0.305	464.1	354.8	1.41	
0.697	5.55	0.506	0.220	0.274	428.9	350.0	1.41	
0.599	5.71	0.440	0.294	0.266	377.8	359.0	1.38	
0.498	6.04	0.367	0.370	0.262	324.2	368.1	1.31	
0.398	5.78	0.303	0.459	0.238	a)	375.7		
0.332	5.74	0.257	0.517	0.226	a)	381.0		
0.201	4.98	0.165	0.654	0.181	329.9	390.9		0.556
0.101	5.15	0.084	0.746	0.170	361.7	399.1		0.780

a) Mixture did not recrystallize.

Table S8. Experimental solid-liquid equilibrium data (water-free basis mole fraction of ChCl, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system ChCl (1) + urea (2) + water (3) with roughly 10% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.898	11.2	0.467	0.053	0.480	520.5	355.3	1.88	
0.797	10.7	0.438	0.112	0.450	458.4	359.2	1.76	
0.700	11.7	0.379	0.162	0.459	421.0	366.7	1.84	
0.589	10.4	0.349	0.243	0.408	374.9	370.4	1.72	
0.498	10.4	0.303	0.306	0.391	319.8	375.7	1.56	
0.400	10.3	0.253	0.379	0.368	a)	381.4		
0.285	10.3	0.186	0.468	0.346	a)	388.6		
0.203	10.9	0.134	0.525	0.342	310.5	394.1		0.498
0.099	10.1	0.070	0.634	0.296	342.6	400.5		0.699

a) Mixture did not recrystallize.

Table S9. Experimental solid-liquid equilibrium data (water-free basis mole fraction of ChCl, x_1^{wfb} , weight percentage of water in the ternary mixture, w_3 , mole fraction of each component in the ternary mixture, x_i , experimental melting temperature, T , ideal melting temperature, T^{id} , and activity coefficients, γ_i) for the ternary system ChCl (1) + urea (2) + water (3) with roughly 3% of water, measured in this work at atmospheric pressure.

x_1^{wfb}	w_3 (%)	x_1	x_2	x_3	T /K	T^{id} /K	γ_1	γ_2
0.301	3.11	0.262	0.608	0.130	308.9	380.4		0.416
0.199	3.15	0.175	0.704	0.121	327.7	389.8		0.498
0.103	3.08	0.092	0.801	0.107	355.3	398.3		0.665

S2. References

¹ D.O. Abranches, L.P. Silva, M.A.R. Martins, S.P. Pinho, and J.A.P. Coutinho, ChemSusChem **13**, 4916 (2020).