Supporting Information

Design and characterization of sugar-based deep eutectic solvents using COSMO-RS

Liliana P. Silva,[a] Luis Fernandez,[b] João H. F. Conceição,[a] Mónia A. R. Martins,[a,c,d] Adriel Sosa,[b] Juan Ortega,[b] Simão P. Pinho,[c,d] João A. P. Coutinho,[a*]

[a]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal;

[b]Laboratorio de Termodinamica y Fisicoquímica de Fluidos, Universidad de Las Palmas de Gran Canaria, 35071 – Parque Científico-Tecnológico, Canary Islands, Spain;

[c]Associate Laboratory LSRE-LCM, Department of Chemical and Biological Technology, Polytechnic Institute of Bragança, 5300-253 Bragança, Portugal;

[d]Mountain Research Center – CIMO, Polytechnic Institute of Bragança, 5301-855 Bragança, Portugal.

*Corresponding author: jcoutinho@ua.pt. Phone: +351 234370200. Fax: +351 234370084.

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Table S1. Water content in [Ch]Cl + Sugars mixtures for density and viscosity measurements.

System	Water wt%
[Ch]Cl + Glucose	8.05
[Ch]Cl + Fructose	5.29
[Ch]Cl + Fructose + Glucose	7.51
[Ch]Cl + Xylose	9.24
[Ch]Cl + Mannose	3.02
[Ch]Cl + Mannose + Xylose	7.73

Table S2. Experimental SLE data (x_1,T) and activity coefficients for eutectic mixtures composed of sugar (1) + sugar (2) at atmospheric pressure.[a]

x_1	T / K	γ_1	x_1	T / K	γ_2
Sucrose(1)+Glucose(2)					
Sucrose phase			Glucose phase		
0.402	410.88	1.093	0.101	416.58	1.032
0.451	421.15	1.128	0.204	408.65	0.979
0.500	428.38	1.135	0.302	406.12	1.056
0.598	439.15	1.127	0.355	402.58	1.057
0.698	444.48	1.055			
0.802	455.15	1.103			
0.900	458.42	1.041			
Sucrose(1)+Fructose(2)					
Sucrose phase			Fructose phase		
0.302	383.85	1.052	0.110	379.5	0.926
0.401	400.15	0.953	0.203	367.35	0.744
0.499	417.15	0.962			
0.600	432.15	1.003			
0.699	440.15	0.980			
0.801	451.15	1.030			
0.899	455.15	0.984			
Glucose(1)+Fructose(2)					
Glucose phase			Fructose phase		
0.299	370.55	1.108	0.100	377.85	0.876
0.401	382.05	1.073	0.200	377.15	0.967
0.500	390.85	1.049			
0.601	403.45	1.156			
0.700	405.65	1.042			
0.800	413.82	1.092			
0.900	418.15	1.067			

[a]Data obtained using the melting points device. Standard uncertainties are $u(T)$ = 1.8 K, $u_r(p)$ = 0.05 and $u_r(x)$ = 0.002.

Table S3. Experimental SLE data (x_1, x_2, T) and activity coefficients for eutectic mixtures composed of sugar (1) + sugar (2) + sugar (3) at atmospheric pressure.[a]

x_1	x_2	T / K	γ_1	x_1	x_2	T / K	γ_2	x_1	x_2	T / K	γ_3
Sucrose phase				Glucose phase				Fructose phase			
Sucrose(1)+ [0.50Glucose(2)+0.50Fructose(3)]											
0.311	0.345	398.15	1.199	0.000	0.500	392.45	1.087				
0.399	0.301	413.35	1.140	0.111	0.445	387.88	1.103				
0.503	0.249	420.85	1.007	0.204	0.398	384.45	1.141				
0.598	0.201	428.35	0.949								
0.700	0.150	434.15	0.888								
0.699	0.151	441.38	1.000								
0.803	0.099	448.65	0.984								
0.901	0.050	456.95	1.013								
Sucrose(1)+ [0.25Glucose(2)+0.75Fructose(3)]											
0.300	0.175	391.52	1.150					0.000	0.250	374.62	0.973
0.400	0.150	395.93	0.908					0.120	0.220	370.35	0.989
0.500	0.125	411.65	0.888					0.201	0.200	366.28	0.978
0.600	0.100	428.69	0.950					0.251	0.187	379.38	1.471
0.800	0.050	439.08	0.841								
0.900	0.025	448.52	0.876								
Sucrose(1)+ [0.75Glucose(2)+0.25Fructose(3)]											
0.361	0.479	401.48	1.076	0.000	0.750	408.48	1.035				
0.400	0.450	411.38	1.107	0.130	0.653	404.52	1.090				
0.500	0.375	417.12	0.960	0.199	0.601	400.05	1.072				
0.550	0.338	429.17	1.045	0.302	0.524	394.82	1.094				

0.600	0.300	443.35	1.204								
0.700	0.225	449.45	1.144								
0.800	0.150	456.15	1.125								
0.900	0.075	458.55	1.044								
Sucrose(1)+ [0.10Glucose(2)+0.90Fructose(3)]											
0.300	0.070	392.05	1.157					0.000	0.100	382.15	0.987
0.410	0.059	401.25	0.945					0.102	0.090	375.78	0.931
0.500	0.050	408.85	0.855					0.201	0.080	372.45	0.959
0.600	0.040	426.85	0.924					0.262	0.074	381.35	1.310
0.700	0.030	437.40	0.935								
0.800	0.020	443.87	0.911								
0.900	0.010	453.05	0.947								
Sucrose(1)+ [0.90Glucose(2)+0.10Fructose(3)]											
0.368	0.569	406.02	1.119	0.000	0.900	417.15	1.044				
0.410	0.531	414.22	1.123	0.100	0.810	416.83	1.152				
0.500	0.450	422.77	1.042	0.204	0.716	407.95	1.072				
0.600	0.360	443.75	1.212	0.310	0.621	402.35	1.092				
0.700	0.270	448.82	1.132								
0.800	0.180	452.95	1.064								
0.900	0.090	459.25	1.057								

[a]Data obtained using the melting points device. Standard uncertainties are $u(T) = 1.8$ K, $u_r(p) = 0.05$ and $u_r(x) = 0.002$.

Table S4. Experimental SLE data (x_1,T) data and activity coefficients for eutectic mixtures composed of [Ch]Cl (1) + sugar (2) at atmospheric pressure.[a,b]

x_1	T / K	γ_1	x_1	T / K	γ_2
[Ch]Cl phase			Sugar phase		
[Ch]Cl(1) + Glucose(2)					
0.501	330.48	0.992	0.101	402.45	0.700
0.608	374.95	0.984	0.200	390.22	0.583
0.700	428.55	1.016	0.310	365.92	0.351
0.800	477.28	1.006	0.411	350.52	0.259
0.898	535.92	1.009			
[Ch]Cl(1) + Fructose(2)					
0.497	327.62	0.986	0.101	370.62	0.822
0.600	374.58	0.997	0.201	361.85	0.751
0.700	437.62	1.042	0.301	354.42	0.713
0.800	490.75	1.036	0.388	334.85	0.480
0.899	539.75	1.015			
[Ch]Cl(1) + Xylose(2)					
0.498	320.62	0.952	0.102	405.78	0.722
0.599	379.45	1.017	0.201	381.62	0.448
0.699	439.22	1.048	0.293	359.82	0.277
0.799	487.45	1.031	0.399	341.72	0.186
0.896	540.15	1.019			
[Ch]Cl(1) + Mannose(2)					
0.501	332.52	1.001	0.101	391.75	0.848
0.600	377.52	1.008	0.200	377.85	0.722
0.700	438.88	1.046	0.300	364.48	0.618
0.798	496.65	1.051	0.401	353.58	0.562
0.900	547.75	1.028			
[Ch]Cl(1) + Arabinose(2)					
0.598	367.68	0.973	0.100	402.78	0.511
0.699	428.72	1.018	0.201	381.58	0.318
0.801	492.65	1.040	0.300	359.72	0.183
0.900	539.75	1.014	0.394	341.52	0.112
			0.503	322.22	0.064
[Ch]Cl(1) + Sucrose(2)					
0.600	370.52	0.982	0.107	431.45	0.473
0.700	411.82	0.968	0.201	404.58	0.225
0.800	477.88	1.007	0.302	386.22	0.134
0.900	541.95	1.017	0.395	369.65	0.081
			0.494	343.65	0.031

[a]Melting points device; standard uncertainties are $u(T)$ = 0.9 K and $u_r(x)$ = 0.002. [b]Oil bath method (composition range of 0.4 to 0.8); standard uncertainties are $u(T)$ = 1.8 K, $u_r(p)$ = 0.05 and $u_r(x)$ = 0.002.

Table S5. Experimental SLE data (x_1, x_2, T) data and activity coefficients for eutectic mixtures composed of [Ch]Cl (1) + sugar (2) + sugar (3) at atmospheric pressure.[a]

x_1	x_2	T / K	γ_1	x_1	x_2	T / K	γ_2	x_1	x_2	T / K	γ_3
[Ch]Cl (1) + Fructose (2) + Glucose(3)											
[Ch]Cl phase				Fructose phase				Glucose phase			
[Ch]Cl (1) + [0.33Fructose + 0.67Glucose] (2)											
0.702	0.125	388.65	0.895					0.000	0.404	406.29	1.241
0.796	0.083	438.85	0.919					0.103	0.357	395.72	1.083
0.898	0.040	503.52	0.948					0.201	0.319	367.46	0.643
								0.299	0.281	361.55	0.642
								0.399	0.258	352.02	0.631
								0.487	0.213	343.77	0.596
								0.594	0.169	336.74	0.64
[Ch]Cl (1) + [0.50Fructose + 0.50Glucose] (2)											
0.699	0.148	398.82	0.930					0.095	0.453	385.75	1.035
0.792	0.102	444.58	0.938					0.201	0.399	372.39	0.864
0.898	0.049	504.38	0.950					0.298	0.354	366.22	0.862
								0.402	0.302	360.12	0.881
								0.498	0.249	354.51	0.906
								0.584	0.209	341.69	0.822
[Ch]Cl (1) + [0.67Fructose+ 0.33Glucose] (2)											
0.698	0.202	389.02	0.902					0.000	0.670	379.56	1.232
0.799	0.134	438.35	0.915					0.102	0.599	385.52	1.556
0.893	0.067	515.28	0.976					0.200	0.534	376.57	1.428

								0.300	0.465	352.66	0.934
								0.395	0.399	339.56	0.786
								0.498	0.335	326.12	0.708
								0.600	0.267	308.92	0.594
[Ch]Cl (1) + Mannose(2) + Xylose (3)											
[Ch]Cl phase				Mannose phase				Xylose phase			
[Ch]Cl (1) + [0.33Mannose+ 0.67Xylose] (2)											
0.695	0.100	339.17	0.745					0.000	0.329	393.55	0.916
0.798	0.067	432.02	0.900					0.100	0.296	387.38	0.920
0.899	0.033	521.02	0.980					0.198	0.266	379.92	0.917
								0.300	0.231	372.38	0.928
								0.396	0.196	356.76	0.831
								0.501	0.165	338.92	0.769
								0.595	0.132	325.56	0.769
[Ch]Cl (1) + [0.50Mannose+ 0.50Xylose] (2)											
0.602	0.200	341.71	0.870					0.000	0.491	394.58	1.228
0.698	0.148	376.95	0.864					0.100	0.448	388.48	1.251
0.795	0.104	422.72	0.880					0.203	0.402	375.74	1.163
0.897	0.052	517.92	0.977					0.300	0.350	365.37	1.111
								0.409	0.286	345.61	0.933
								0.485	0.251	334.28	0.906
[Ch]Cl (1) + [0.67Mannose+ 0.33Xylose] (2)											
0.701	0.178	363.28	0.817	0.000	0.601	407.59	1.682				
0.792	0.122	419.88	0.876	0.100	0.536	402.72	1.728				
0.891	0.062	502.68	0.954	0.201	0.477	384.38	1.398				
				0.296	0.419	364.09	1.108				

0.389	0.361	351.77	1.035
0.501	0.300	337.34	0.969
0.589	0.246	320.86	0.892

[a]Data obtained using the melting points device. Standard uncertainties are $u(T) = 1.8$ K, $u_r(p) = 0.05$ and $u_r(x) = 0.002$.

Table S6. Quality factors for the consistency tests as proposed by Kang et al.[1] and Cunico et al.[2]

System	Kang et al.[1]	Cunico et al.[2]	
	Q_1	Q_2	Q_3
Sucrose+Glucose	0.634	0.375	0.784
Sucrose+Fructose	0.581	0.085	0.557
Glucose+Fructose	0.565	0.126	0.673
[Ch]Cl+Sucrose	0.522	0.103	0.32
[Ch]Cl+Glucose	0.535	0.116	0.638
[Ch]Cl+Fructose	0.524	0.21	0.429
[Ch]Cl+Arabinose	0.517	0.075	0.407
[Ch]Cl+Mannose	0.548	0.093	0.548
[Ch]Cl+Xylose	0.756	0.304	0.544

Table S7. Experimental and ideal eutectic points for sugar + sugar mixtures.

System		exp		Ideal	
Comp. 1	Comp. 2	x_1^e	T^e	x_1^e	T^e
Sucrose	Glucose	0.36	402.58	0.37	399.04
Sucrose	Fructose	0.20	367.35	0.29	374.15
Glucose	Fructose	0.30	370.55	0.34	371.69

Table S8. Experimental eutectic points (x^e,T^e) and values estimated by excess Gibbs energy models for sugar+[Ch]Cl mixtures.

System		Exp		Ideal mix.		NRTL		mRK	
Comp. 1	Comp. 2	x_1^e	T^e	x_1^e	T^e	x_1^e	T^e	x_1^e	T^e
[Ch]Cl	Glucose	0.50	330.48	0.62	382.73	0.57	321.04	0.52	328.81
[Ch]Cl	Fructose	0.50	327.62	0.56	356.05	0.58	327.76	0.49	327.23
[Ch]Cl	Sucrose	0.49	343.65	0.66	403.51	0.57	332.79	0.46	348.79
[Ch]Cl	Xylose	0.50	320.62	0.62	384.07	0.56	316.92	0.49	321.84
[Ch]Cl	Mannose	0.50	332.52	0.57	363.79	0.58	351.58	0.50	332.68
[Ch]Cl	Arabinose	0.50	322.22	0.64	393.8	0.57	321.84	0.49	318.40

Table S9. Estimated parameters for the excess Gibbs energy models used.

[Ch]Cl +	Sucrose	Glucose	Fructose	Arabinose	Mannose	Xylose
			NRTL			
Δg_{120}	-7.425	-2.247	4.315	-7.775	4.107	-4.948
Δg_{121}	6.247	-0.440	-6.579	4.998	-5.060	2.294
Δg_{210}	-3.338	0.837	2.762	0.902	-0.479	0.914
Δg_{211}	6.030	0.617	-2.575	0.590	0.376	0.560
$s(T)$ (K)	12	15	16	16	18	21
			mRK			
$k_g^{2\text{-}1}$	0.168	0.401	0.344	0.356	0.353	0.355
g_0 (J/mol)	-7375	-9473	-7129	-15306	-4566	-11161
$s(T)$ (K)	12	3	7	8	5	6

Table S10. Tuned parameters of COSMO-RS.

cmf	chb	whb	dhb
0.492	1.074	≈0	4.094

Table S11. Experimental eutectic points (x^e,T^e) for sugar+[Ch]Cl mixtures estimated by COSMO-RS assuming $\Delta_m Cp$ = 0 J·mol^{-1}·K^{-1} for all compounds.

System		Original COSMO-RS		Modified COSMO-RS	
Comp. 1	Comp. 2	x_1^e	T^e	x_1^e	T^e
[Ch]Cl	Glucose	0.65	304.59	0.65	322.88
[Ch]Cl	Fructose	0.65	290.60	0.65	308.13
[Ch]Cl	Sucrose	0.72	254.63	0.67	355.28
[Ch]Cl	Xylose	0.64	316.24	0.64	330.40
[Ch]Cl	Mannose	0.64	209.70	0.63	282.95
[Ch]Cl	Arabinose	0.67	347.08	0.72	316.81

Table S12. Eutectic point of [Ch]Cl (1)+sugar (2)+sugar (3) solutions, estimated with the tuned COSMO-RS model, assuming $\Delta_m Cp$ = 0 J·mol^{-1}·K^{-1} for all compounds.

		Sugar (3)											
		Fructose			Glucose			Mannose			Xylose		
		x_1	x_2	T / K	x_1	x_2	T / K	x_1	x_2	T / K	x_1	x_2	T / K
Sugar (2)	Arabinose	0.636	0.044	304.8	0.642	0.078	318.2	0.636	0.012	281.0	0.631	0.103	323.7
	Fructose	-	-	-	0.621	0.131	299.1	0.628	0.079	275.3	0.628	0.266	300.1
	Glucose	-	-	-	-	-	-	0.631	0.051	277.7	0.630	0.211	310.1
	Mannose	-	-	-	-	-	-	-	-	-	0.591	0.322	295.2

Table S13. Eutectic points of the ternary systems sucrose(1)+glucose(2)+fructose(3), [Ch]Cl(1)+mannose(2)+xylose(3) and [Ch]Cl(1)+fructose(2)+glucose(3) estimated using the tuned COSMO-RS.

System	x_1	x_2	x_3	T / K
[Ch]Cl+Mannose+Xylose	0.59	0.32	0.09	295.20
[Ch]Cl+Fructose+Glucose	0.62	0.13	0.25	299.06

Table S14. Density, ρ / g·cm^{-3}, of the dried systems at different temperatures and at 0.10 MPa.

	ρ / g·cm^{-3}					
[Ch]Cl +	**Glucose**	**Fructose**	**Fructose + Glucose**	**Xylose**	**Mannose**	**Mannose + Xylose**
$x_{[Ch]Cl}$ / **T / K**	0.50	0.50	0.62	0.50	0.50	0.59
303.15			1.2696			1.2567
305.15			1.2686			
308.15			1.2670			1.2541
313.15			1.2643			1.2516
318.15			1.2618	1.2690		1.2490
323.15		1.2888	1.2591	1.2668		1.2466
328.15		1.2861		1.2637		
333.15	1.2618	1.2833	1.2539	1.2615	1.2973	1.2415
338.15	1.2602			1.2584	1.2956	
343.15	1.2568	1.2778	1.2487	1.2562	1.2920	1.2364
348.15	1.2552				1.2903	
353.15	1.2518	1.2721	1.2433	1.2506	1.2865	1.2311
363.15	1.2472	1.2661	1.2375	1.245	1.2804	1.2257
373.15	1.2427	1.2604	1.2325	1.2398	1.2735	1.2210

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

Table S15. Density, ρ / g·cm^{-3}, of the [Ch]Cl+sugar systems containing water at different temperatures and at 0.10 MPa.

	ρ / g·cm^{-3}					
[Ch]Cl +	**Glucose**	**Fructose**	**Fructose + Glucose**	**Xylose**	**Mannose**	**Mannose + Xylose**
$x_{[Ch]Cl}$ / **T / K**	0.50	0.50	0.62	0.50	0.50	0.59
293.15	1.2721	1.2959	1.2480	1.2591	1.2990	1.2445
298.15		1.2931	1.2454	1.2563	1.2962	1.2418
303.15	1.2667	1.2896	1.2426	1.2535	1.2937	1.2391
313.15	1.2612	1.2840	1.2372	1.2479	1.2885	1.2337
323.15	1.2559	1.2782	1.2316	1.2424	1.2831	1.2284
333.15	1.2506	1.2723	1.2263	1.2372	1.2776	1.2233
343.15	1.2453	1.2664	1.2211	1.2318	1.2721	1.2183
353.15	1.2396	1.2604	1.2157	1.2261	1.2664	1.2128

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

Table S16. Viscosity, η / **mPa·s**, of the dried systems at different temperatures and at 0.10 MPa.

	η / mPa·s					
[Ch]Cl +	**Glucose**	**Fructose**	**Fructose + Glucose**	**Xylose**	**Mannose**	**Mannose + Xylose**
$x_{[Ch]Cl}$ / **T / K**	0.50	0.50	0.62	0.50	0.50	0.59
308.15			22377.00			18586.00
313.15			13361.00			12031.00
318.15			8319.60	5999.90		7039.70
323.15		5586.90	5310.00	3850.60		4651.50
328.15		3630.30		2493.90		
333.15	2781.40	2384.60	2350.90	1679.90	6619.40	2039.70
338.15	1892.00			1190.70	4178.30	
343.15	1295.60	1131.60	1141.10	810.07	2752.50	1001.90
348.15	918.51				1845.20	
353.15	666.47	583.48	601.39	424.88	1274.60	531.75
363.15	369.98	327.52	340.95	243.88	647.54	
373.15	216.83	199.59	205.59	146.28	356.01	299.13

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

Table S17. Viscosity, η / **mPa·s**, of the [Ch]Cl+sugar systems containing water at different temperatures and at 0.10 MPa.

	η / mPa·s					
[Ch]Cl +	**Glucose**	**Fructose**	**Fructose + Glucose**	**Xylose**	**Mannose**	**Mannose + Xylose**
$x_{[Ch]Cl}$ / **T / K**	0.50	0.50	0.62	0.50	0.50	0.59
293.15	8897.90	15051.00	2894.50	1433.40	16453.00	1477.00
298.15	5250.60	8696.00	1872.80	938.97	9157.10	977.02
303.15	3213.70	5061.20	1241.90	632.62	5521.60	666.14
313.15	1341.10	2028.40	597.78	311.29	2151.10	333.35
323.15	623.97	913.44	315.11	167.97	951.07	182.33
333.15	319.88	455.37	181.70	98.17	465.38	107.39
343.15	178.31	244.44	111.63	61.43	248.41	67.43
353.15	109.64	142.06	72.56	40.70	143.41	44.70

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

Table S18. Kamlet-Taft solvatochromic parameters of the [Ch]Cl-based mixtures investigated in this work at 323.15 K, along with the standard deviations, and of other common solvents[3] (standard temperature and pressure).

		β	π*	α
[Ch]Cl +	Xylose + 9% Water	0.39 ± 0.01	1.18 ± 0.01	1.15
	Xylose	0.23 ± 0.01	1.13 ± 0.01	-
	Fructose + 9% Water	0.53 ± 0.03	1.12 ± 0.02	1.13
	Fructose	0.42 ± 0.04	1.07 ± 0.01	-
	Glucose + 9% Water	0.48 ± 0.02	1.15 ± 0.02	1.15
	Mannose + 9% Water	0.37 ± 0.01	1.18 ± 0.01	1.16
	Sucrose + 9% Water	0.36 ± 0.01	1.25 ± 0.01	1.27
	Mannose + Xylose + 9% Water	0.46 ± 0.03	1.11 ± 0.01	1.05
	Mannose + Xylose	0.33 ± 0.01	1.11 ± 0.01	-
	Fructose + Glucose + 9% Water	0.50 ± 0.01	1.15 ± 0.01	1.15
	Fructose + Glucose	0.52 ± 0.03	1.10 ± 0.02	-
Other solvents[3]	Water	0.14	1.09	1.17
	Ethanol	0.75	0.51	0.83
	Methanol	0.66	0.58	0.93
	Acetone	0.48	0.71	0.08
	Heptane	0.00	-0.08	0.00
	Cyclohexane	0.00	0.00	0.00
	o-xylene	0.16	0.48	0.00

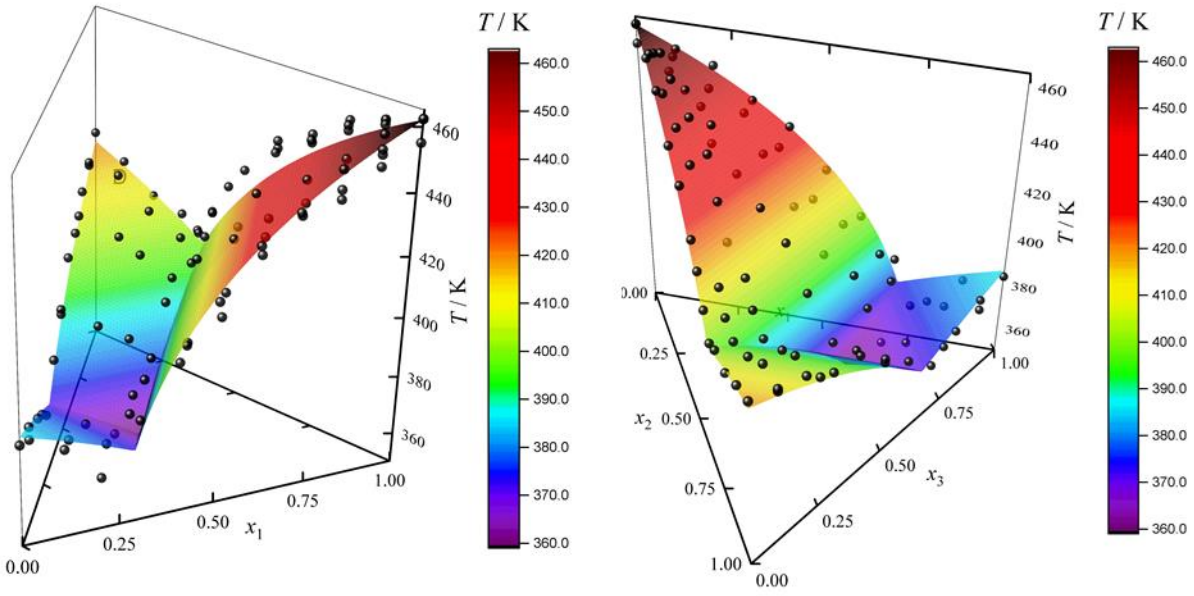

Figure S1. Different perspectives of the solid-liquid phase diagram of the ternary mixture sucrose (1)+glucose (2)+fructose (3). Symbols (●) represent the experimental data.

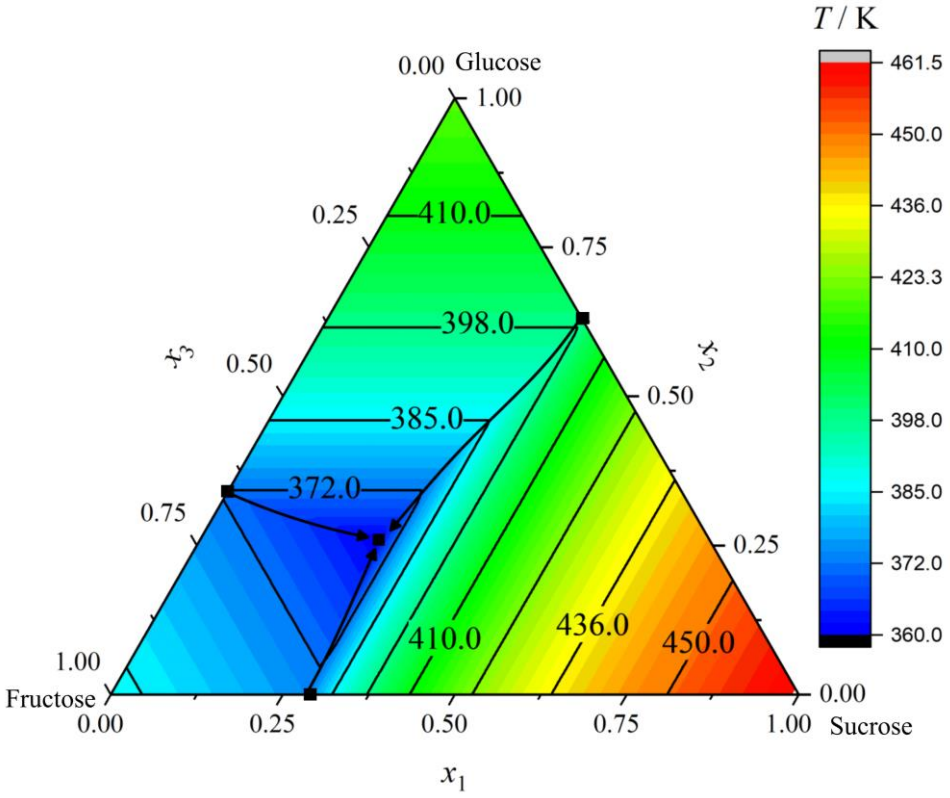

Figure S2. Plane projection of the 3D solid-liquid phase diagram of the ternary mixture sucrose (1)+glucose (2)+fructose (3). (■) represents the locus of the eutectic points of the binary and the ternary systems..

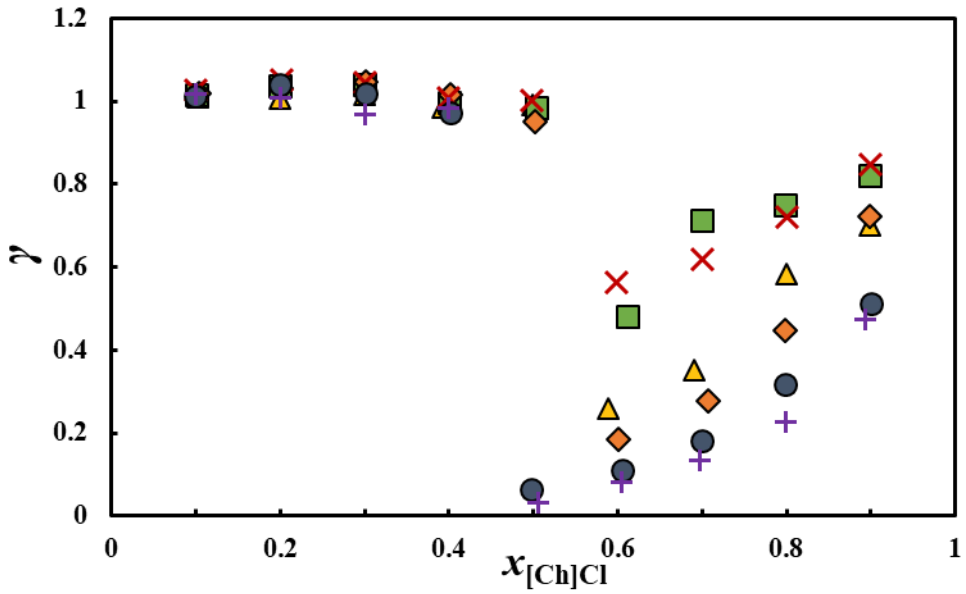

Figure S3. Experimental activity coefficients of [Ch]Cl and: (▲) Glucose; (■) Fructose; (♦) Xylose; (×) Mannose; (●) Arabinose and (+) Sucrose calculated from SLE data.

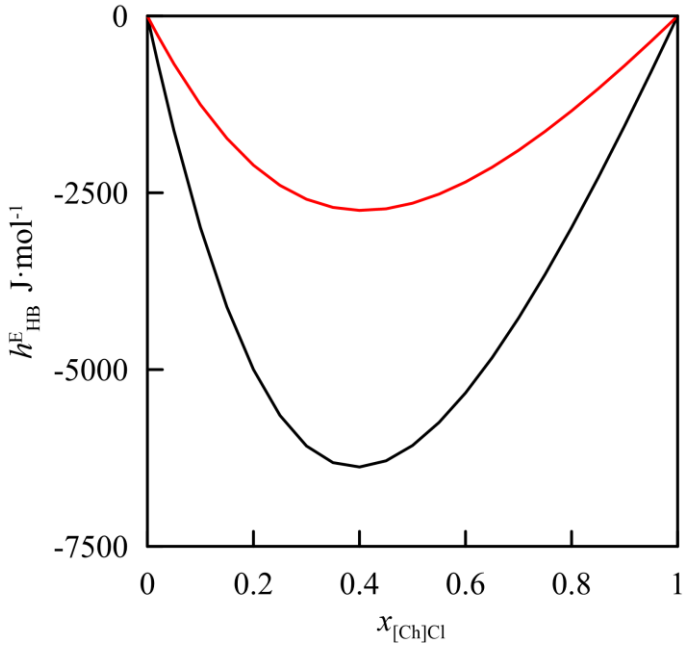

Figure S4. Comparison of the estimated contribution of the hydrogen bond interaction to the total excess enthalpy for the solution [Ch]Cl (1)+glucose (2) at 298.15 K. Legend: (—) original COSMO-RS; (—) tuned COSMO-RS.

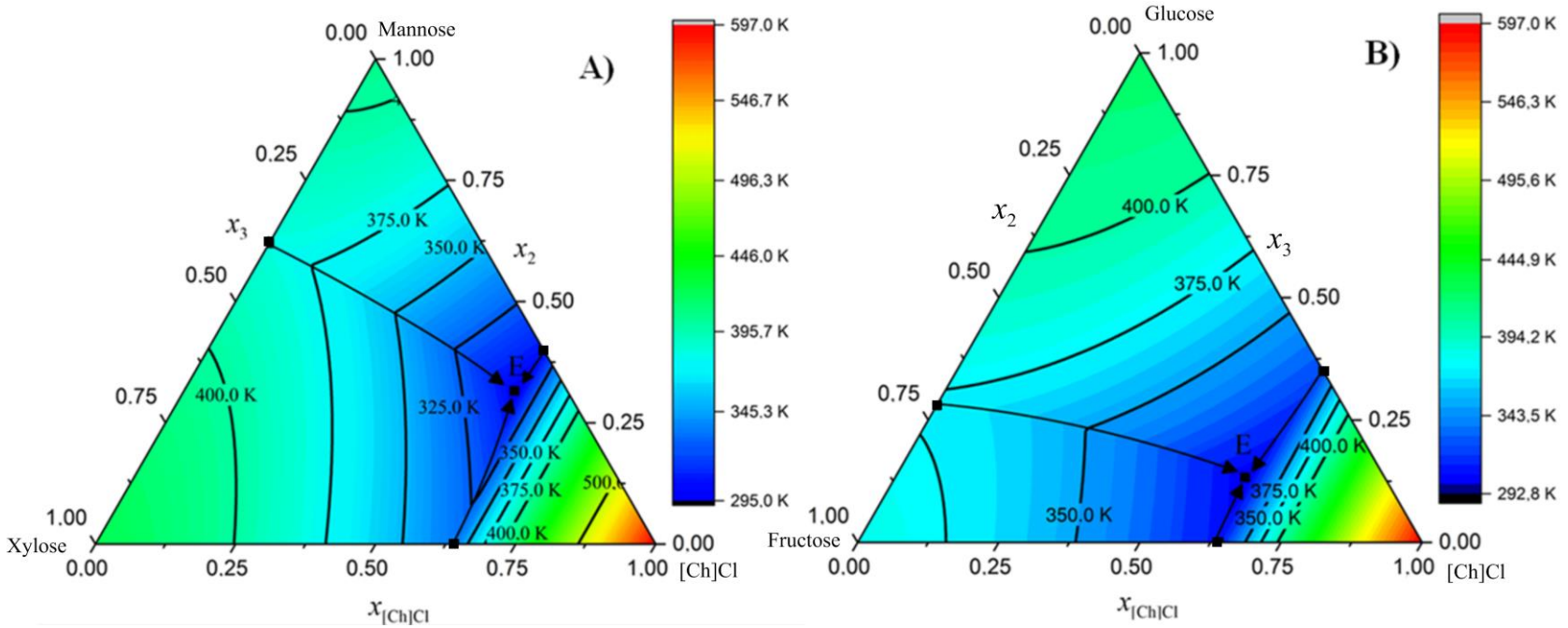

Figure S5. Plane projections of the 3D SLE phase diagrams: A) [Ch]Cl(1)+mannose(2)+xylose(3); B) [Ch]Cl(1)+fructose(2)+glucose(3), with the locus of eutectic points represented by E.

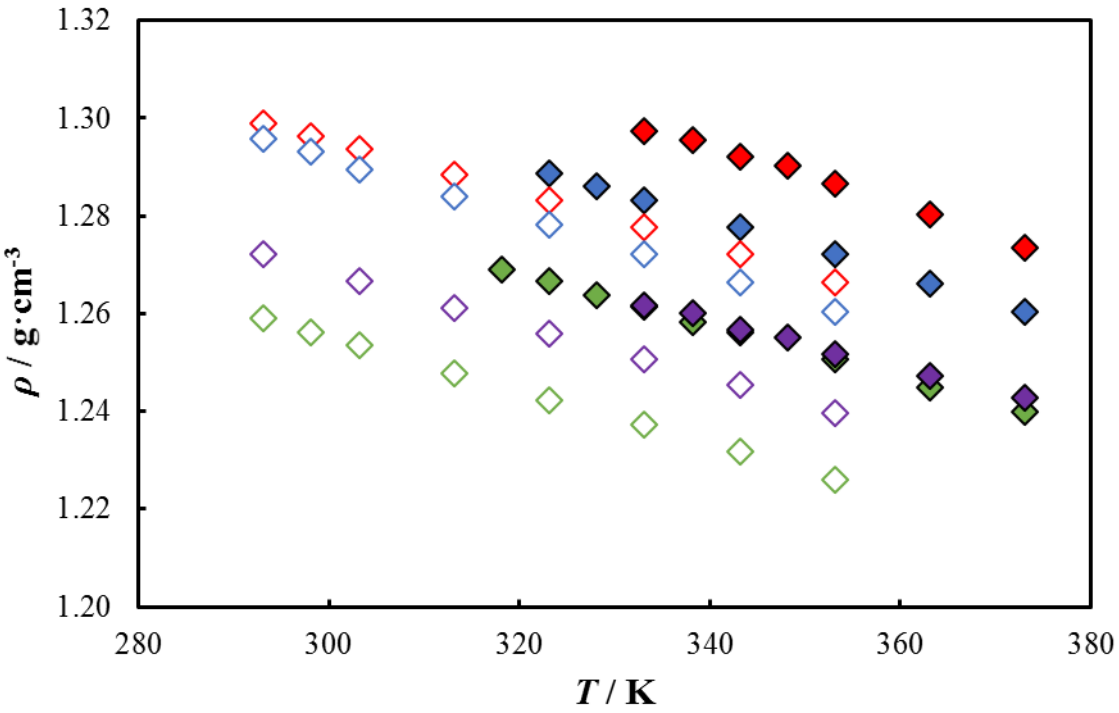

Figure S6. Density of the binary systems [Ch]Cl+sugars as a function of temperature. The full markers correspond to the dried systems and the empty markers to the same mixtures with water: (♦) mannose; (♦) fructose; (♦) glucose; (♦) xylose.

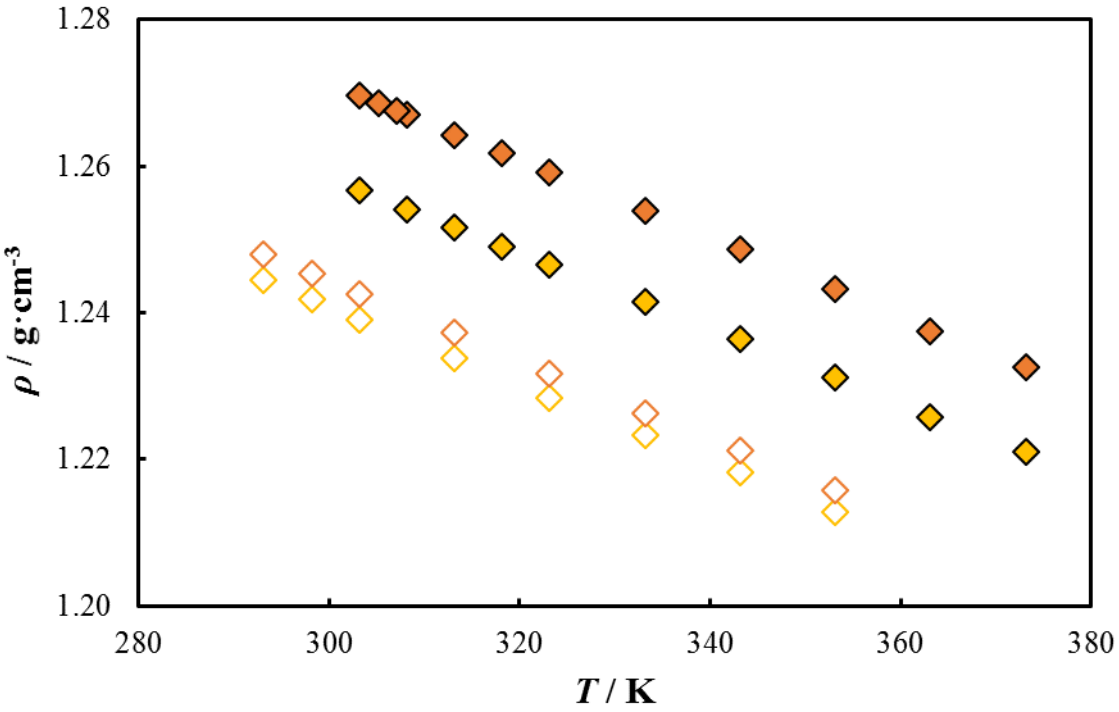

Figure S7. Density of the ternary systems [Ch]Cl+sugar+sugar as a function of temperature. The full markers correspond to the dried systems and the empty markers to the same mixture with water: (♦) [Ch]Cl+fructose+glucose; (♦) [Ch]Cl+mannose+xylose.

Excess Gibbs energy (g^E) models

According to the NRTL, the excess Gibbs energy is, for a binary system, given by:[4]

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}} + \frac{\tau_{21} G_{21}}{x_2 + x_1 G_{21}}\right]; \; G_{ij} = \exp(-0.47\tau_{ij}) \qquad \text{(S1)}$$

where x_i is the mole fraction of the component *i*, *R* is the ideal gas constant and *T* is the absolute temperature. The parameters τ_{ij} are considered as temperature dependent according to:

$$\tau_{ij} = \Delta g_{ij0} + \Delta g_{ij1}\left(\frac{298.15}{T}\right) \qquad \text{(S2)}$$

being the parameters Δg_{ij0} and Δg_{ij1} between species *i* and *j*, estimated from experimental data.

Furthermore, a modified Redlick-Kister equation based on the concept of active fraction[5] was also be used to model the liquid phase behavior. The expression for the excess Gibbs energy of a binary mixture is given by:

$$g^E = z_1(1 - z_1)(g_0 + g_1 z_1); \; z_1 = \frac{x_1}{x_1 + k_g^{2-1} x_2} \qquad \text{(S3)}$$

where g_0, g_1 and k_g^{2-1} are parameters to be obtained by fitting experimental data. For the systems studied in this work, g_1 is taken as zero, without any lost of accuracy. As this model is not as well known as NRTL, the expressions for the activity coefficients are given below:

$$\ln g_1 = \left[z_1\left(1 - z_1\right) + \frac{\left(1 - x_1\right)\left(1 - 2z_1\right)k_g^{2-1}}{\left(x_1 + k_g^{2-1} x_2\right)^2} \right] \frac{g_0}{RT} \qquad \text{(S4)}$$

$$\ln g_2 = \left[z_1\left(1 - z_1\right) - \frac{x_1\left(1 - 2z_1\right)k_g^{2\text{-}1}}{\left(x_1 + k_g^{2\text{-}1}x_2\right)^2} \right] \frac{g_0}{RT} \quad \text{(S5)}$$

The estimation of the parameters of the two models was carried using the deterministic Nedler-Mead method,[6] by minimizing the objective function:

$$s(T) = \left[\frac{\sum \left(T_{exp} - T_{cal}\right)^2}{m} \right]^{0.5} \quad \text{(S6)}$$

where T_{exp} and T_{cal} are the experimental and calculated absolute temperatures, respectively, and m is the total number of experimental data points for each system.

Conductor-like Screening Model for Real Solvents: COSMO-RS

COSMO-RS[7] is a predictive tool that uses a statistical thermodynamic approach based on the results of quantum chemical calculations. The model can be used to predict the phase behaviour of mixtures without any experimental information.[8,9]

Here, the experimental SLE data gathered were used to perform a fine-tuning of some of the COSMO-RS parameters (the pre-factor of the misfit interaction, *cmf*, the hydrogen bond interaction, *chb*, and the hydrogen bond temperature dependency parameters, *whb* and *dhb*) in order to improve the quality of the description.

The procedure schematized in **Figure S8** is based on modelling equations (eqs. S3-S5), used to calculate the activity coefficients as a reference for the parameter fitting. For each system, the mRK model was selected since it gave better description of phase diagram (Figure 3 and Table S9). The objective function (eq. S7), based on the residuals between the activity coefficients by COSMO-RS values (γ_i^{est}) and those calculated by mRK (γ_i^{calc}), was used to drive the search.

$$OF = \frac{1}{N}\sum_j \sum_{i_j} \sum_k^N w\left(x_{e,i_j}\right)\left(ln\gamma_{i_j,k}^{est} - ln\gamma_{i_j,k}^{calc}\right)^2 \quad \text{(S7)}$$

In equation S7 the sum is extended through every data point *k* of each component *i* belonging to *j*-th system of the [Ch]Cl+sugar system. $w(x_{e,i})$ is a step-shaped weighting

function settled to minimize the differences between calculated and estimated activity coefficients beyond the eutectic composition.

$$w\left(x_{e,i_j}\right) = \begin{cases} 1 \; if \; x_i \leq x_{e,i_j} \\ 0 \; otherwise \end{cases} \tag{S8}$$

To refine the solution, the Nelder-Mead Simplex algorithm[6] was applied, where the function tolerance and the Euclid norm of variable vector were selected as stopping criteria. The default COSMO-RS parameterization was used as starting approximation.

This procedure was applied to avoid solving the SLE equation (1) in each step of the iteration, reducing drastically the optimization time. The use of γ_i^{calc} was preferred over the γ_i^{exp} because it was not possible to obtain values of γ_i^{exp} for both compounds in the full composition range. This choice does not introduce any difficulty due to the good agreement obtained between the experimental SLE and that calculated by the mRK model.

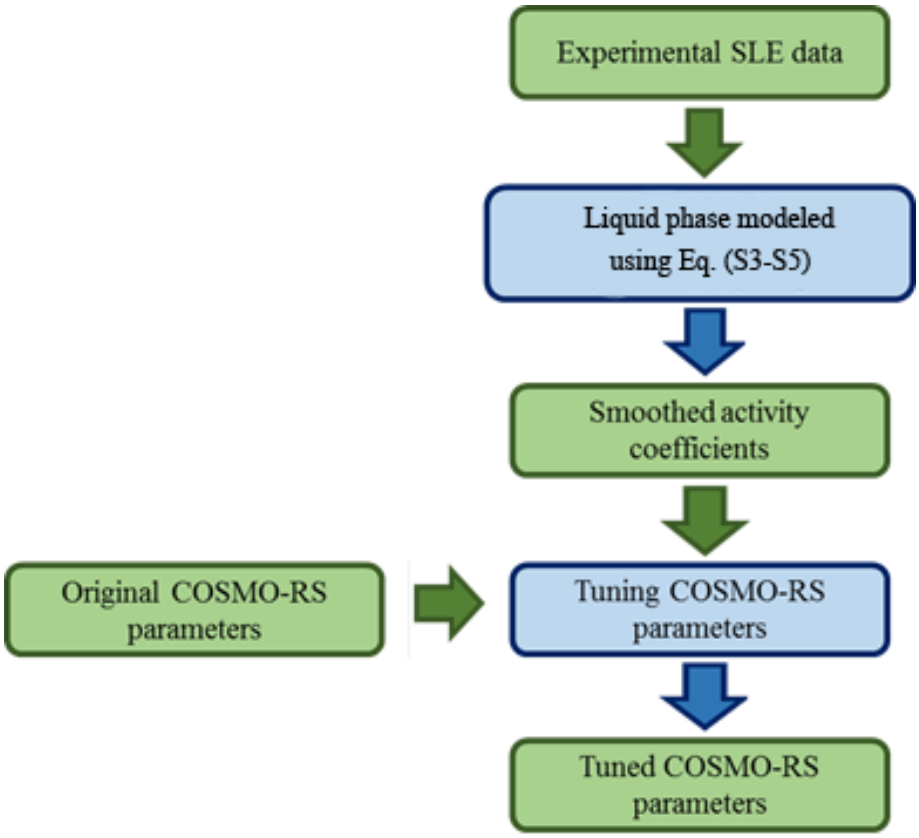

Figure S8. Procedure used to tune the COSMO-RS parameters.

Kamlet-Taft Solvatochromic Parameters

The dipolarity/polarizability, π*, and the hydrogen-bond acceptor basicity, β, solvatochromic parameters were determined from the experimental measurements according with the following equations:

$$\pi^* = \frac{\nu_{N,N(mixture)} - \nu_{N,N(cyclohexane)}}{\nu_{N,N(DMSO)} - \nu_{N,N(cyclohexane)}} \quad \text{(S9)}$$

$$\beta = \frac{\left(\Delta\nu_{N,N(mixture)} - \Delta\nu_{N,N(cyclohexane)}\right) \times 0.76}{\Delta\nu_{N,N(DMSO)} - \Delta\nu_{N,N(cyclohexane)}} \quad \text{(S10)}$$

$$\Delta\nu = \Delta\nu_{N,N} - \Delta\nu_{4N} \quad \text{(S11)}$$

$$\nu = \frac{1}{\lambda_{\max\ probe}} \times 10^{-4} \quad \text{(S12)}$$

where ν is the experimental wavenumber, and $\lambda_{\max\ probe}$ is the maximum wavelength of the probe. Subscripts *N*,*N* and 4*N* represent the probes *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline, respectively. The subscripts cyclohexane and DMSO indicate the corresponding reference values for these solvents.

The hydrogen-bond donor acidity, α, was estimated using the ^{13}C NMR chemicals shifts, $\delta(C_i)$ (in ppm), of the carbons atoms of pyridine-*N*-oxide in positions i = 2 and 4:

$$\alpha = -0.15 \times d_{24} + 2.32 \quad \text{(S13)}$$

where $d_{24} = \delta_4 - \delta_2$.[10]

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