Supporting Information

Characterization and modelling of the liquid phase of deep eutectic solvents based on fatty acids/alcohols and choline chloride

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1. Experimental data

Table S1. Experimental (x_1,T) and calculated (γ_i) data of the solid-liquid equilibria for eutectic mixtures composed of fatty alcohols (1) + [Ch]Cl (2) at atmospheric pressure. [a]

x_1	T / K	γ_2	x_1	T / K	γ_1
1-Tetradecanol (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, 1-Tetradecanol		
0.107	520.08	0.99	0.581	303.15	1.04
0.165	494.78	1.00	0.712	306.55	1.04
0.204	483.52	1.03	0.798	310.32	1.16
0.258	456.58	1.03	0.891	310.92	1.07
0.289	443.85	1.04	1	311.72	1
0.357	414.08	1.06			
0.400	390.25	1.05			
0.449	353.18	1.00			
0.495	331.62	0.99			
0.539	319.48	1.02			
1-Hexadecanol (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, 1-Hexadecanol		
0.056	536.25	0.96	0.592	320.78	1.31
0.102	513.25	0.97	0.604	320.95	1.30
0.140	488.25	0.96	0.668	322.28	1.29
0.192	451.65	0.94	0.694	322.55	1.27
0.250	415.78	0.91	0.792	322.73	1.12
0.319	371.45	0.87	0.868	323.35	1.07
0.409	335.42	0.86	1	324.38	1
0.417	334.62	0.87			
0.500	318.55	0.94			
1-Octadecanol (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, 1-Octadecanol		
0.061	541.55	0.97	0.498	328.32	1.44
0.099	510.18	0.96	0.508	328.48	1.43
0.112	508.55	0.97	0.597	329.98	1.36
0.150	477.25	0.95	0.606	329.52	1.29
0.159	480.75	0.96	0.681	330.58	1.24
0.200	456.75	0.96	0.698	330.55	1.21
0.202	460.15	0.97	0.795	331.58	1.14
0.249	413.48	0.91	0.797	331.12	1.10
0.250	413.78	0.91	0.850	332.20	1.12
0.252	418.65	0.92	0.902	332.42	1.07
0.315	383.65	0.90	1	332.92	1
0.350	373.95	0.92			

0.368	363.25	0.91
0.400	339.48	0.86
0.401	341.25	0.87
0.413	344.82	0.90
0.433	333.68	0.89

[a]Melting points device, standard uncertainties, u, are $u(T) = 1.3$ K, $u_r(p) = 0.05$, $u_r(x) = 0.002$.

Table S2. Experimental (x_1,T) and calculated (γ_i) data of the solid-liquid equilibria for eutectic mixtures composed of fatty acids (1) + [Ch]Cl (2) at atmospheric pressure. [a]

Capric acid (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, Capric acid		
0.062	543.95	0.98	0.658	305.45	1.56
0.104	520.95	0.98	0.704	304.10	1.39
0.150	499.80	0.99	0.788	304.45	1.26
0.214	473.55	1.02	0.899	304.60	1.11
0.239	453.70	1.00	1	304.75	1
0.325	427.85	1.05			
0.358	413.70	1.06			
0.408	395.55	1.09			
0.460	373.60	1.10			
0.515	343.30	1.09			
0.544	328.75	1.08			
0.601	304.70	1.09			
Lauric acid (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, Lauric acid		
0.047	548.53	0.97	0.655	313.20	1.28
0.123	513.35	0.99	0.703	313.38	1.20
0.160	505.70	1.02	0.802	315.88	1.17
0.208	483.78	1.03	0.900	316.48	1.07
0.252	473.40	1.07	1	317.50	1
0.309	444.35	1.08			
0.342	423.45	1.06			
0.439	373.75	1.06			
0.503	343.85	1.06			
0.554	324.20	1.08			
0.589	316.05	1.13			
Myristic acid (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, Myristic acid		
0.054	562.60	1.00	0.594	325.13	1.53
0.100	536.70	1.01	0.684	325.75	1.37

0.156	504.25	1.01	0.689	325.95	1.37
0.208	475.83	1.01	0.785	326.33	1.23
0.255	451.33	1.02	0.792	326.20	1.21
0.294	429.53	1.01	0.892	326.98	1.12
0.333	413.52	1.02	0.899	326.65	1.09
0.403	374.53	1.00	1	327.03	1
0.421	373.62	1.03			
0.498	327.68	0.98			
0.509	323.30	0.98			
0.551	317.03	1.04			
0.554	317.40	1.04			
Palmitic Acid (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, Palmitic acid		
0.105	539.52	1.02	0.600	331.03	1.21
0.150	517.95	1.03	0.634	331.95	1.21
0.197	502.18	1.06	0.693	333.20	1.18
0.250	473.58	1.06	0.744	333.75	1.14
0.327	443.48	1.10	0.812	334.60	1.09
0.348	438.48	1.12	0.842	335.05	1.08
0.397	418.85	1.15	0.896	335.28	1.03
0.445	393.63	1.15	1	336.84	1
0.446	393.88	1.16			
0.470	377.63	1.14			
0.551	338.85	1.15			
Stearic Acid (1) + [Ch]Cl (2)					
Solid Phase, [Ch]Cl			Solid Phase, Stearic acid		
0.104	543.68	1.03	0.614	339.55	1.25
0.156	523.92	1.05	0.703	340.68	1.18
0.213	493.68	1.06	0.811	341.72	1.09
0.254	483.82	1.09	0.892	342.45	1.04
0.305	463.58	1.12	1	343.67	1
0.350	443.85	1.14			
0.404	433.78	1.21			
0.446	408.60	1.21			
0.495	388.62	1.25			
0.548	355.52	1.23			

[a]Melting points device, standard uncertainties, u, are $u(T) = 1.3$ K, $u_r(p) = 0.05$, $u_r(x) = 0.002$.

2. Consistency Tests

The thermodynamic consistency of the SLE phase diagrams measured in this work was verified using the methodologies proposed by Kang et al.[15] and Cunico et al.[16]. The former checks if the mixture data asymptote to the pure components through the quality factor, Q_1:

$$Q_1 = 0.25\sum_{i=1}^{2}\left(F_{T,i} + F_{S,i}\right) \qquad (1)$$

where the temperature factor, F_T, and the slope factor, F_S, are taken as:

$$\left.\begin{array}{l} if\ \Delta T_{m,i} \le 2 \rightarrow F_{T,i} = 1 \\ else \rightarrow F_{T,i} = 2/\Delta T_{m,i} \end{array}\right\} \qquad (2)$$

$$\left.\begin{array}{l} if\ \Delta \text{slope}_i \le 0.8 \rightarrow F_{S,i} = 1 \\ else \rightarrow F_{S,i} = 0.8/\Delta \text{slope}_i \end{array}\right\} \qquad (3)$$

$\Delta T_{m,i}$ and Δslope_i are the relative difference between the experimental and calculated values for the melting temperature, $T_{m,i}$,of the pure component, i, and slope of its solubility curve when $x_i \rightarrow 1$ [$\text{slope} = \left(dx_i/dT\right)_{i,x=1}$], respectively. The experimental values are obtained from pure component data and the calculated are estimated from correlations of the SLE data (see [15] for the specific details).

The method proposed by Cunico et al.[16] combines a "pure-component" test and a "point-to-point" test, generating two independent quality factors, Q_2 and Q_3 respectively.

Q_2 is expressed as:

$$Q_2 = \left[\frac{2}{1000\left(\Delta t_1 + \Delta t_2\right)} - \frac{U}{10}\right] \qquad (4)$$

Where the factors Δt_i are the normalized error between experimental and calculated melting temperatures and U is an uncertainty factor, calculated as the sum of the absolute uncertainty of each experimental measurement.

The point-to-point quality factor is obtained from the normalized root squared mean error, *nRSME* (Equation 6), of an adequate fit to the equilibrium data (the PC-SAFT results were considered) and is given by Equation 5.

$$Q_3 = \left[\frac{1}{1+100 \cdot nRSME} \right] \qquad (5)$$

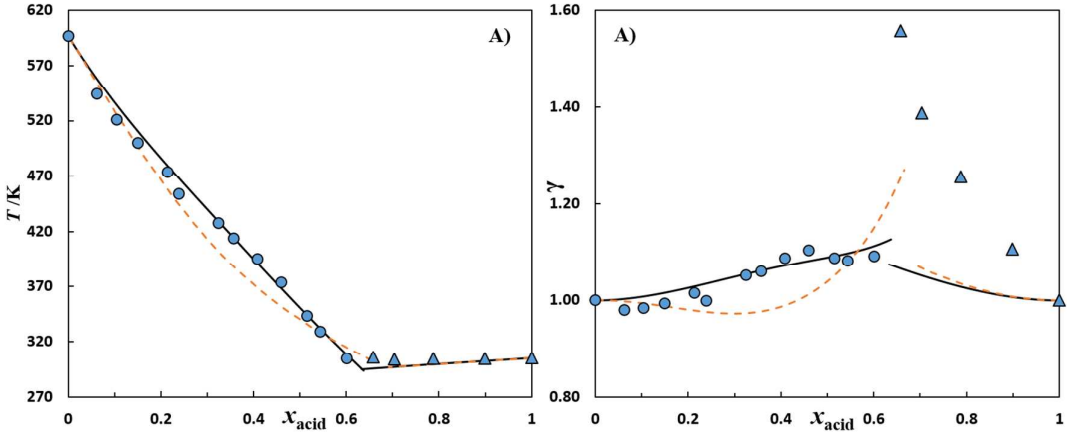
$$nRSME_T = \left[\sum_{i=1}^{n} \left(\frac{T_{i,exp} - T_{i,cal}}{T_{i,exp}} \right)^2 \Big/ n \right]^{0.5} \qquad (6)$$

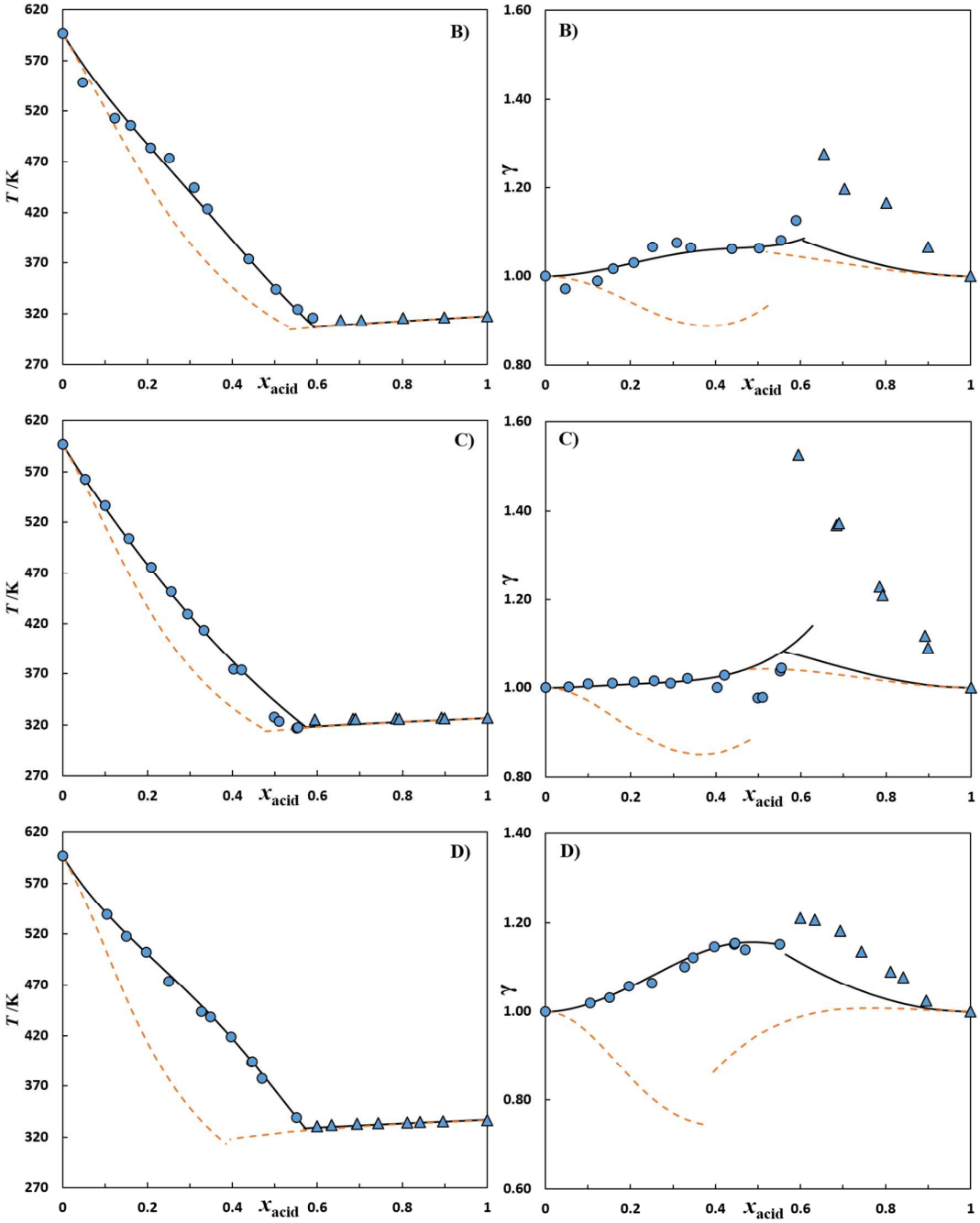
The value of the quality factors, Q_i, suggest the consistency degree of the experimental data, so that the greater their values, more consistent is the experimental data. The range of possible values of the quality factors Q_1 and Q_3 are between 0 (completely inconsistent data) and 1 (completely consistent data).

Table S3. Results of consistency tests.

	Q_1	Q_2	Q_3
[Ch]Cl+ 1-tetradecanol	0.762	0.058	0.429
[Ch]Cl+ 1-hexadecanol	0.667	0.042	0.407
[Ch]Cl+ 1-octadecanol	0.633	0.042	0.422
[Ch]Cl+ capric acid	0.587	0.049	0.348
[Ch]Cl+ lauric acid	0.764	0.037	0.388
[Ch]Cl+ myristic acid	0.766	0.056	0.510
[Ch]Cl+ palmitic acid	0.766	0.094	0.617
[Ch]Cl+ stearic acid	0.768	0.093	0.500

3. PC-SAFT results (Prediction vs Correlation)




B)
C)
D)
T /K
γ
x_{acid}
620
570
520
470
420
370
320
270
1.60
1.40
1.20
1.00
0.80
0.60
0
0.2
0.4
0.6
0.8
1

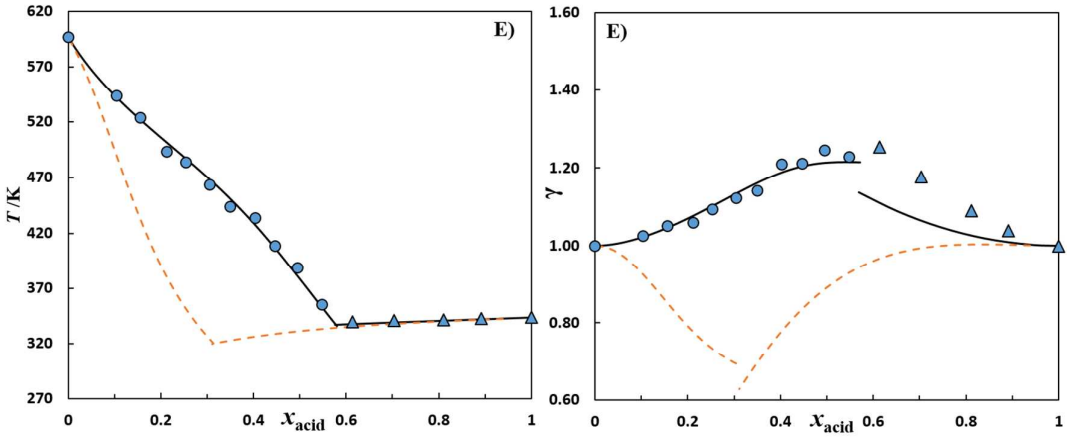
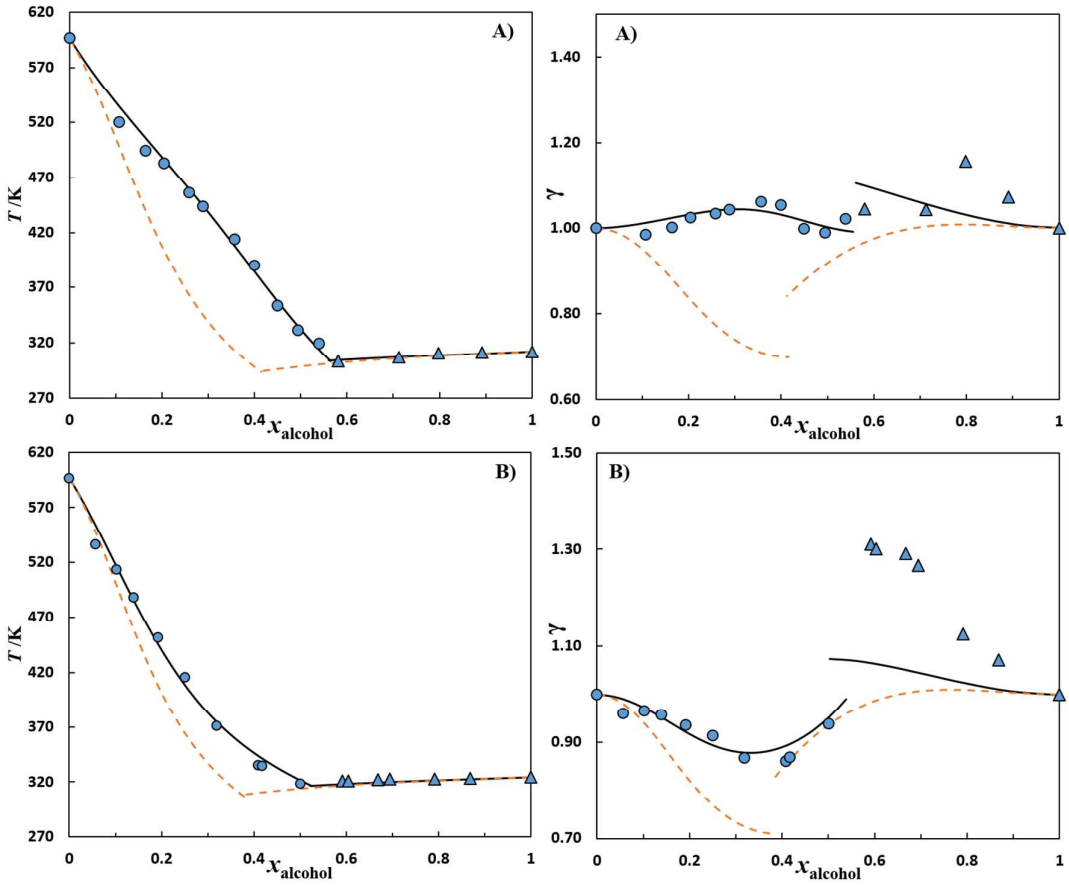


Figure S1. Solid-liquid phase diagrams for the binary mixtures composed of [Ch]Cl and A) capric acid B) lauric acid C) myristic acid D) palmitic acid E) stearic acid. ▲ and ● represent the fatty acid and [Ch]Cl experimental solubility curves measured in this work while the solid and dashed lines depict the PC-SAFT correlations and predictions (k_{ij}=0) respectively.



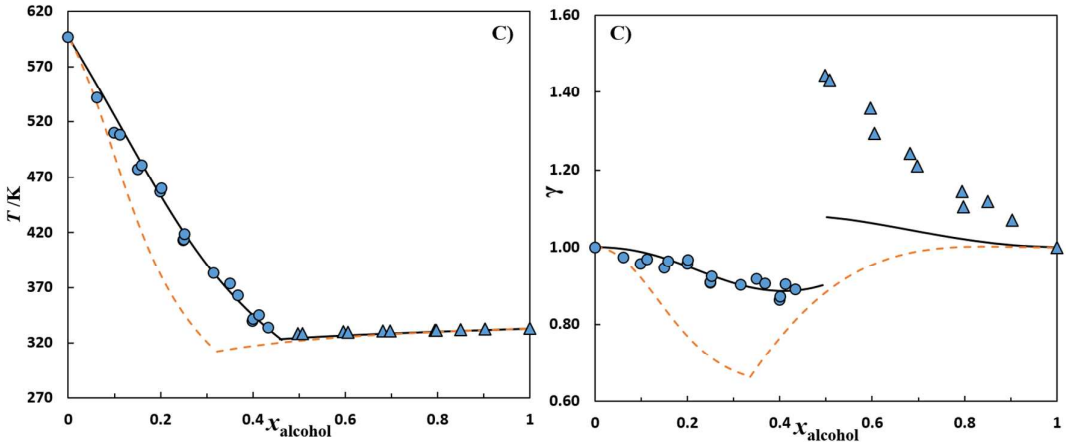


Figure S2. Solid-liquid phase diagrams for the binary mixtures composed of [Ch]Cl and A) 1-tetradecanol B) 1-hexadecanol C) 1-octadecanol. ▲ and ● represent the fatty acid and [Ch]Cl experimental solubility curves measured in this work while the solid and dashed lines depict the PC-SAFT correlations and predictions (k_{ij}=0) respectively.