Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Anatomy of a Deep Eutectic Solvent: Structural Properties of Choline Chloride:Sesamol 1:3 compared to Reline

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Electronic Supplementary Information

Table S1. Number of molecules and box dimensions used to build the simulated MD systems for the ChCl:sesamol 1:3 and reline DESs.

DES	ChCl	Sesamol	Urea	Box edge (Å)
ChCl:sesamol 1:3	1390	4170	-	99.989
Reline	2782	-	5564	99.998

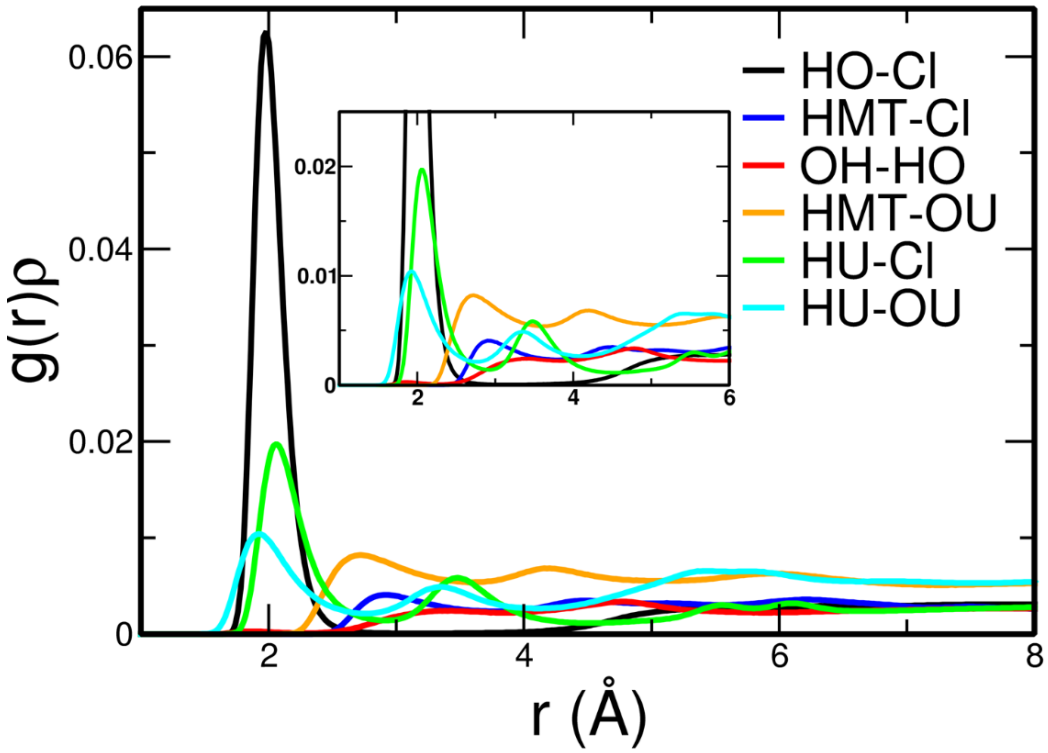

Figure S1. Radial distribution functions multiplied by the numerical densities of the observed atoms, *g(r)ρ's*, calculated from the MD simulations of reline. The reference and observed atom names are employed according to the nomenclature shown in Figure 1 of the main manuscript.

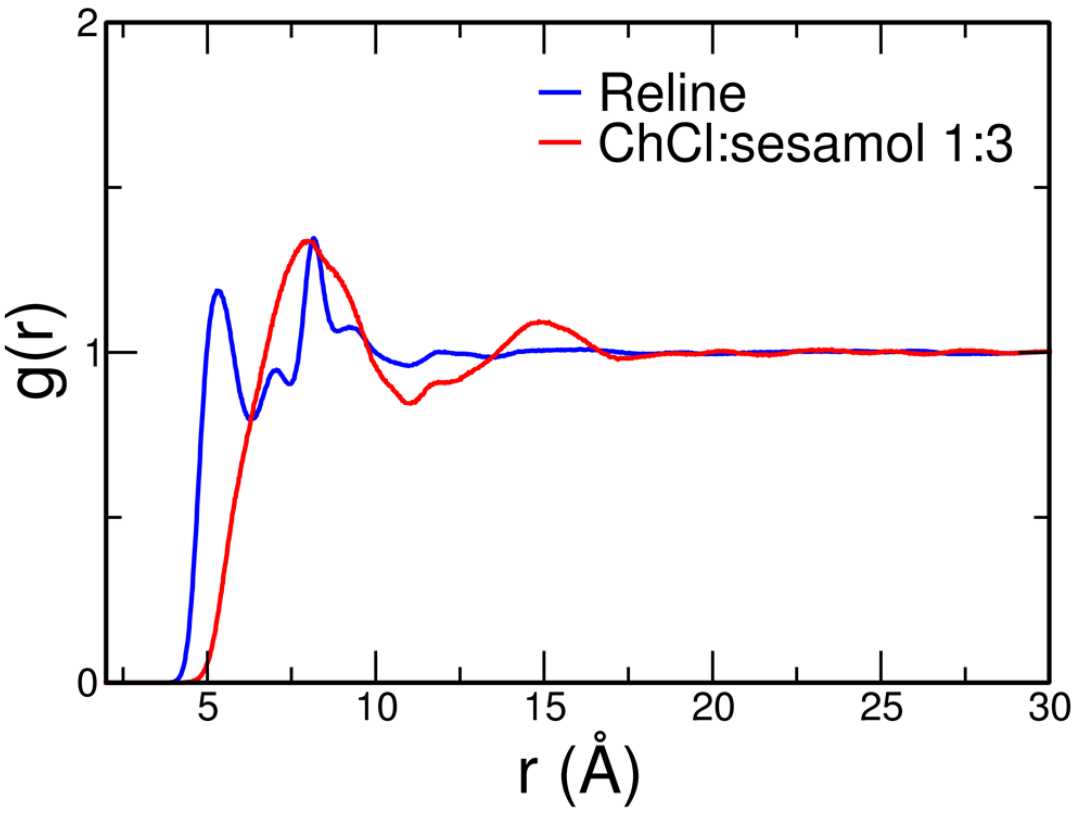

Figure S2. Chloride-chloride radial distribution functions *g(r)'s* calculated from the MD simulations of the ChCl:sesamol 1:3 and reline DESs.

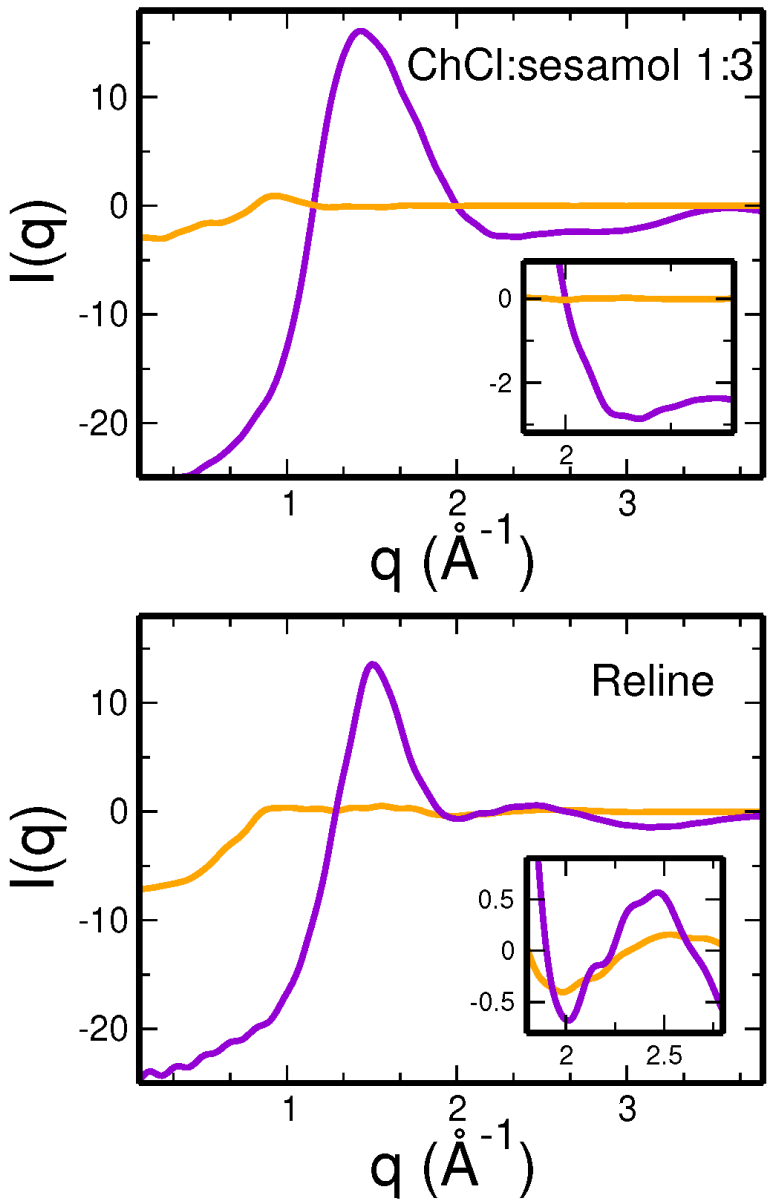

Figure S3. Comparison between the total theoretical structure factors (violet curves) and the partial structure factors due to the Cl-Cl contribution (orange curves) calculated from the MD simulations of the ChCl:sesamol 1:3 DES (top panel) and reline (bottom panel).

Section S1: Derivative spectra of the SWAXS data and estimate of the peak onsets

To better appreciate the differences between the position of the x-ray scattering peak onsets of the two systems investigated, we used a graphical approach assisted by the calculation of the first and second derivative of the SWAXS data. This was done by first resampling the experimental data with a fixed q spacing of 0.01 $Å^{-1}$, and then applying a smoothing and differentiation protocol with the Savitzky-Golay method implemented in Matlab ("sgolay", https://it.mathworks.com/help/signal/ref/sgolay.html). The Savitzky-Golay filter was applied with a polynomial of order 3 and a moving window of 31 points.

For each SWAXS profile, two possible values of the peak onset were estimated, according to two possible operative definitions:

i) According to the first approach (solid lines in panels a,b,c of Figure S4 and symbols “x” in panel a), we started with finding the first point in which the second derivative goes from positive to negative values and crosses the zero axis (Fig. S4c), *i.e*. the position of the first inflection point of the SWAXS peak (1.15 $Å^{-1}$ and 1.28 $Å^{-1}$ for ChCl:sesamol 1:3 and reline, respectively). The value of the first derivative at this inflection point was used to plot the tangent line to the scattering peak through that point (Fig. S4a, solid oblique lines). A local baseline was estimated by fitting the data points with $q < 0.2$ $Å^{-1}$ (horizontal dashed line in Fig. S4a). Finally, the intersection between the baseline and the tangent, was considered as the peak onset (symbols “x” in Figure S4a and its inset).

ii) A second estimate, considered more representative of the aspect that we wanted to comment in the manuscript, was based on finding the q value at which the second derivative reaches zero going towards q values lower than the inflection point (dotted lines in Fig. S4c). In correspondence of this point at lower q with zero second derivative, the same procedure described above was applied to find an alternative estimate of the onset, which considers the initial deviation of the scattering data from the flat background, with much lower slope. The onset positions according to this second approach (“*” symbols in Fig. S4a and its inset) would be 0.17 $Å^{-1}$ and 0.45 $Å^{-1}$ for ChCl:sesamol 1:3 and reline, respectively.

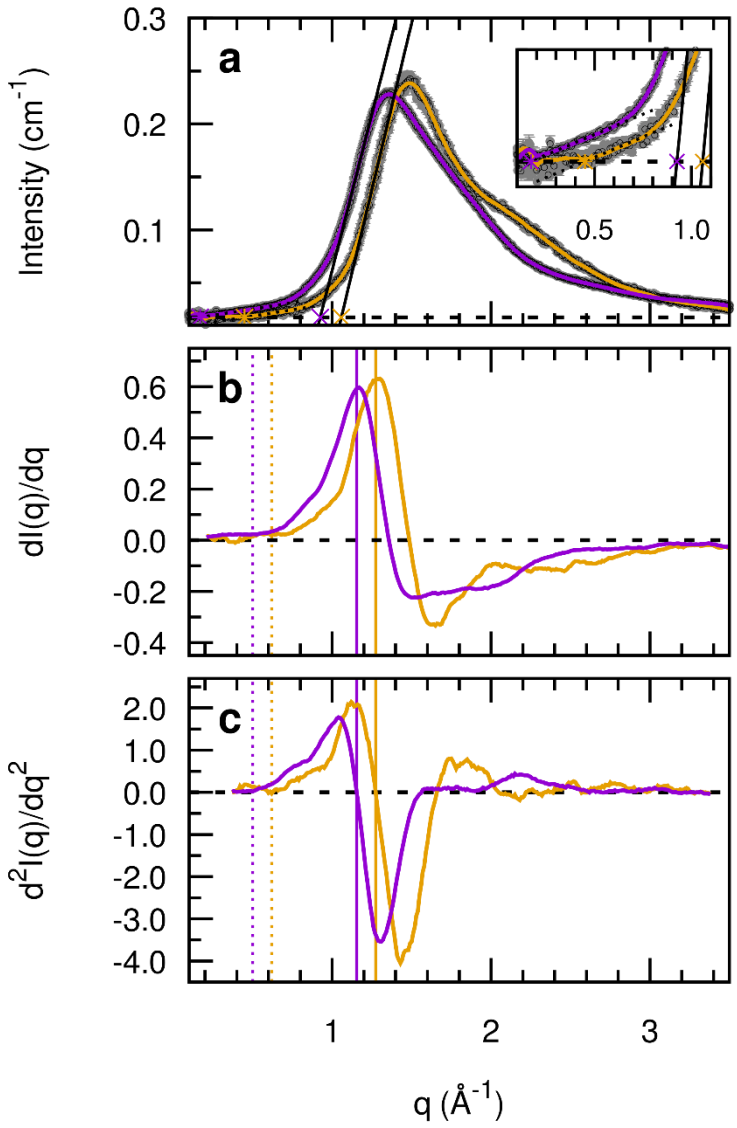

Figure S4: Estimate of peak onset points for the SWAXS data of reline (orange) and ChCl:sesamol 1:3 (purple) employing the first (b) and second (c) derivatives of the smoothed data (a). In (a) the experimental data are shown as empty black circles and grey error-bars, whereas the smoothed data are shown as solid lines.