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

Iodine speciation in deep eutectic solvents

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Supplementary information

EXAFS fitting model decisions for the concentration series

To fit the EXAFS data, a series of models were used with the parameters having different levels of constraints. The first model involved fitting a single σ^2 value for each of the I*–Cl and I*–I scattering paths. The second model permitted variation of σ^2 for only the I*–I scattering paths, whereas the third model permitted variation of σ^2 for all scattering paths. The fit indexes for the three models were compared for each series fit, and if the fit index did not decrease significantly with the larger number of allowed fitting parameters (e.g. by an order of magnitude), then the fitting model with fewer free parameters was used. This process provided access to maximum information from the spectra while avoiding fitting a model to the noise.

For the concentration series of iodine in EG: ChCl, 12Prop: ChCl, Gly: ChCl, and LacA: ChCl, a single fitted value of σ^2 was used for the I*–Cl scattering paths. Despite the high error in σ^2 for the I*–Cl scattering paths, the presence of chloride in the Gly: ChCl and LacA: ChCl fitting models for the 0.01 mol dm^{-3} iodine system is still required for a good fit (a factor of 10 better than a chloride-free model).

For the I*–I scattering paths in EG: ChCl, the change in fit index between models one and two was negligible, supporting the hypothesis that the iodine species and ratio of species does not change with concentration in EG: ChCl. For the I*–I scattering paths in 12Prop: ChCl, Gly: ChCl, and LacA: ChCl the fit index changed significantly between models one and two, indicating that there was a change in the type and amount of iodine-iodine bonding.

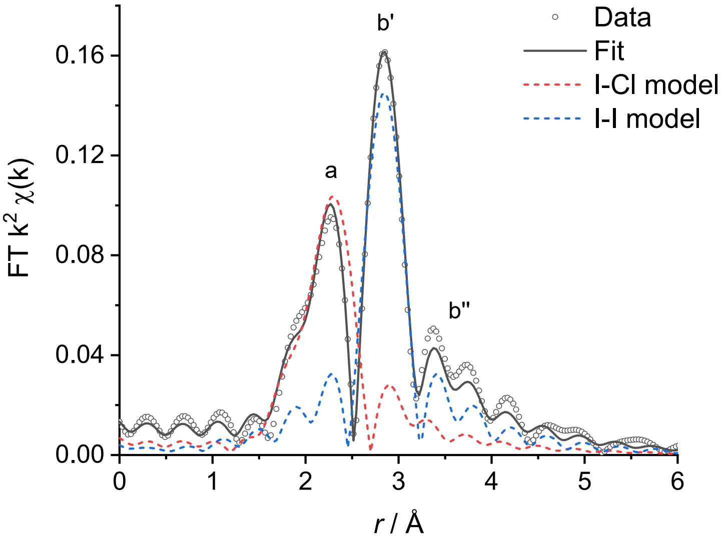
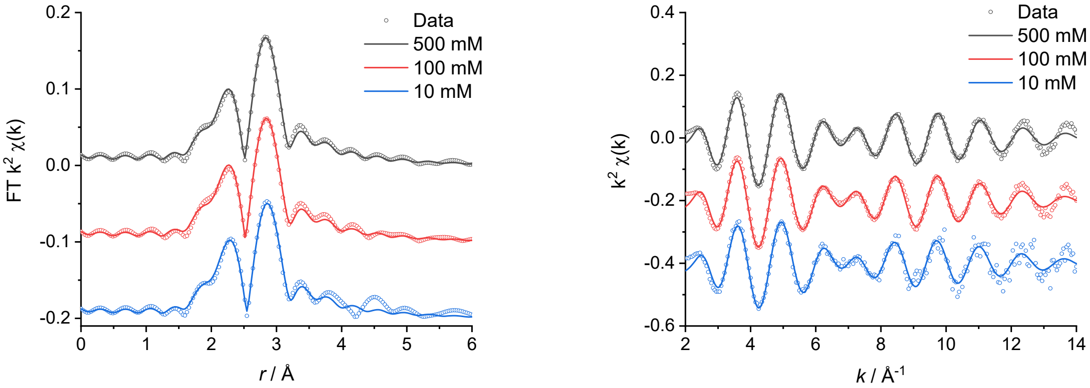
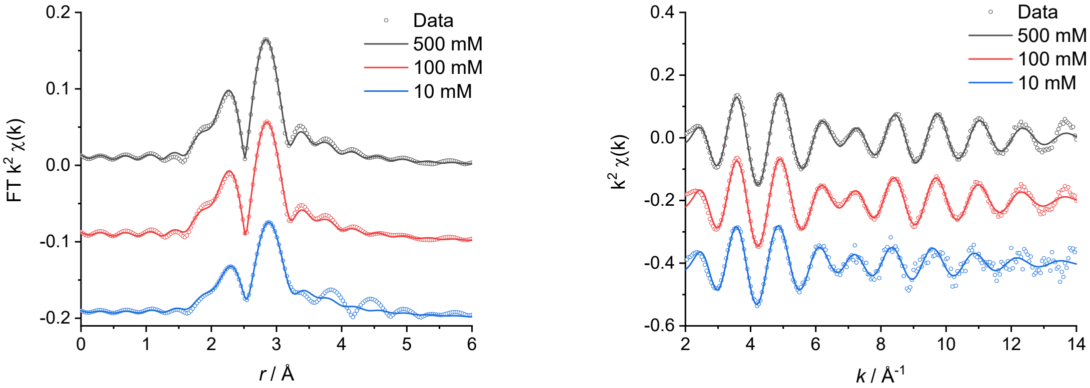


Figure S1: Fourier transform plot of data (circles), fit (solid line) and scattering path models (dashed lines) for the example of 0.1 mol dm^{-3} iodine in EG: ChCl. Note that the "fringes" below 0.02 on the Y-axis are related to the Fourier transform process, and can be considered "noise". The I–I scattering path was used for phase correction.

a) EG: ChCl



b) 12Prop: ChCl



c) Gly: ChCl

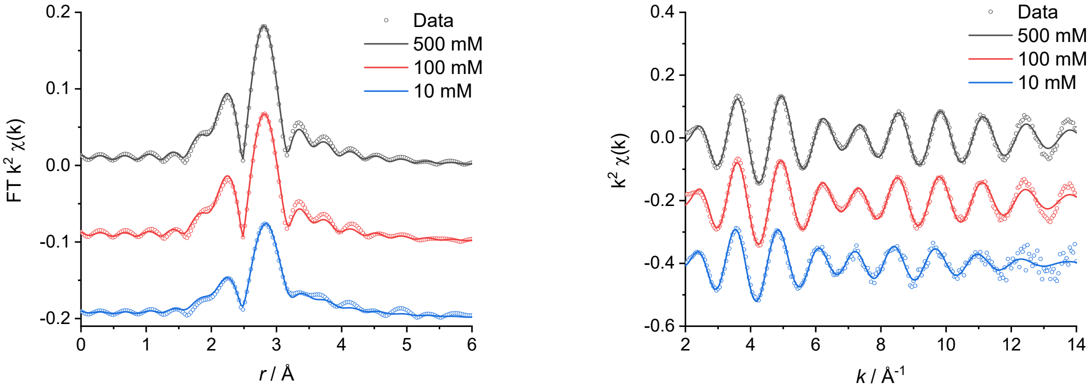
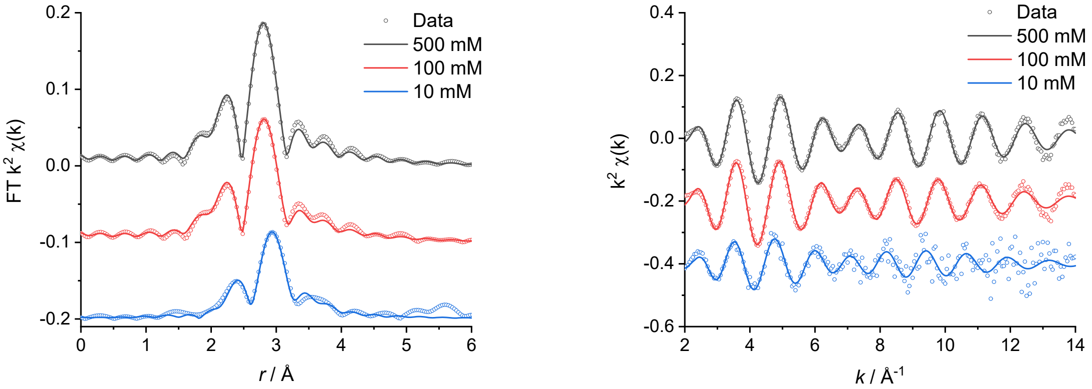
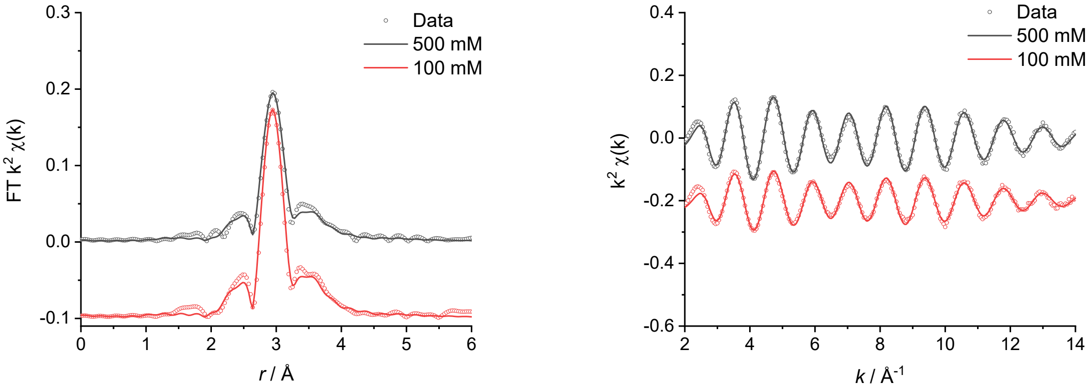


Figure S2: Fourier transforms (left) and k^2-weighted EXAFS (right) for solutions containing different concentrations of iodine in DESs formed with different HBDs: a) EG: ChCl, b) 12Prop: ChCl, c) Gly: ChCl, d) LacA: ChCl, e) LevA: ChCl, f) OxA: ChCl, and g) U: ChCl. Data are circles, data fits are lines. Spectra are offset for clarity. The I–I scattering path was used for phase correction.

d) LacA: ChCl



e) LevA: ChCl



f) OxA: ChCl

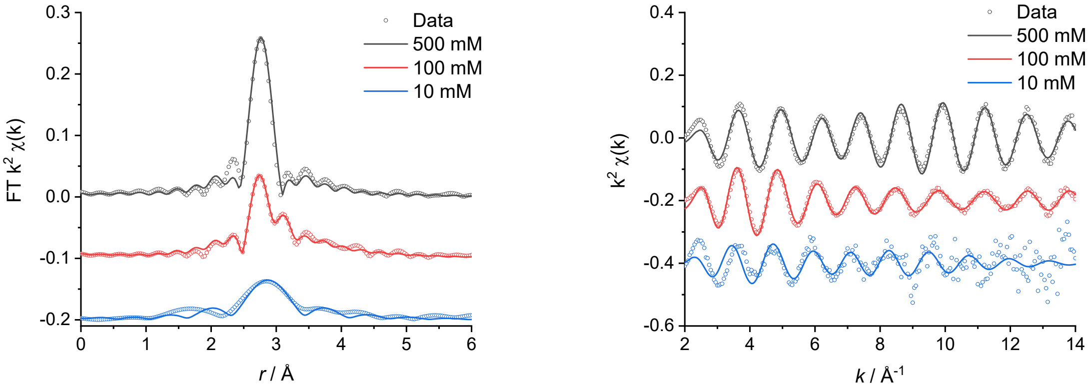


Figure S2 cont.: Fourier transforms (left) and k^2-weighted EXAFS (right) for solutions containing different concentrations of iodine in DESs formed with different HBDs: a) EG: ChCl, b) 12Prop: ChCl, c) Gly: ChCl, d) LacA: ChCl, e) LevA: ChCl, f) OxA: ChCl, and g) U: ChCl. Data are circles, data fits are lines. Spectra are offset for clarity. The I–I scattering path was used for phase correction.

g) U: ChCl

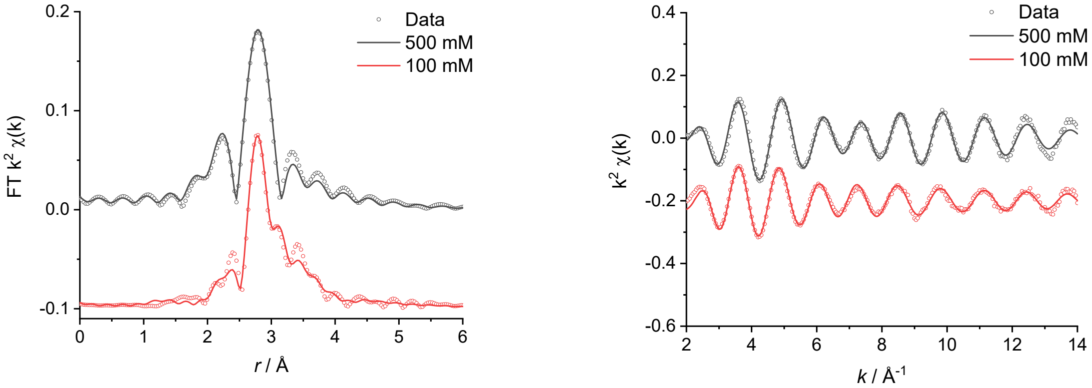
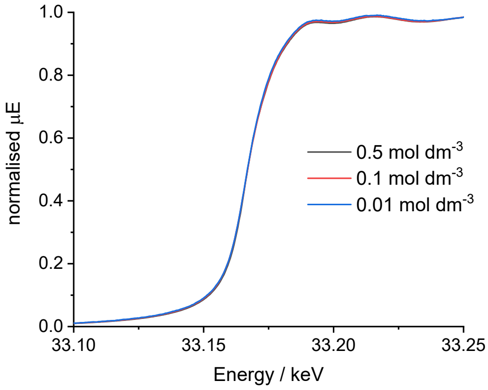
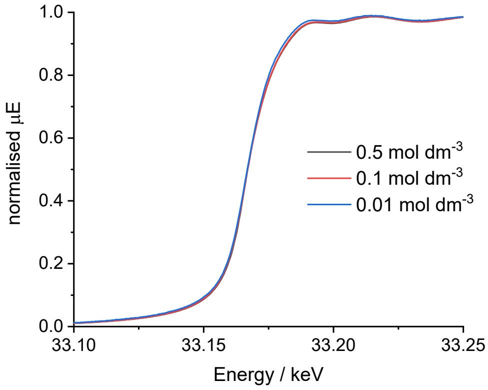


Figure S2 cont.: Fourier transforms (left) and k^2-weighted EXAFS (right) for solutions containing different concentrations of iodine in DESs formed with different HBDs: a) EG: ChCl, b) 12Prop: ChCl, c) Gly: ChCl, d) LacA: ChCl, e) LevA: ChCl, f) OxA: ChCl, and g) U: ChCl. Data are circles, data fits are lines. Spectra are offset for clarity. The I–I scattering path was used for phase correction.

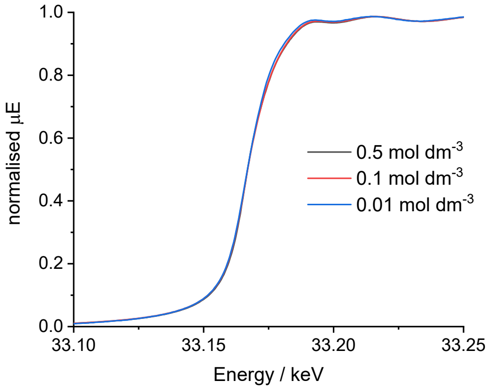
a) EG: ChCl



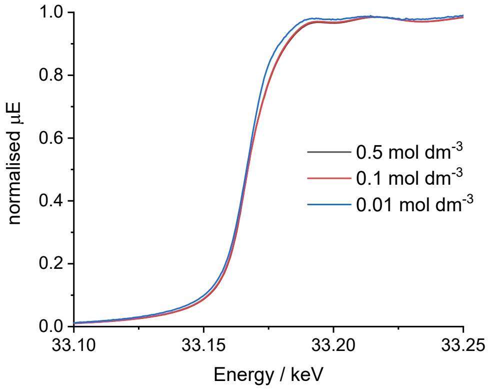
b) 12Prop: ChCl



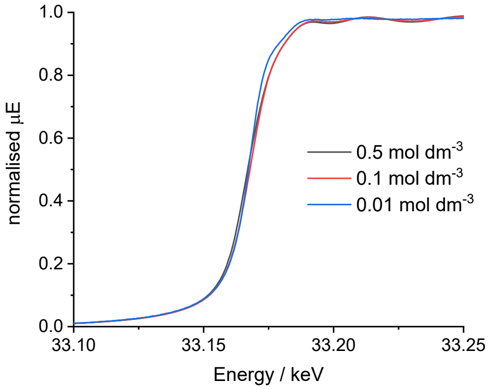
c) Gly: ChCl



d) LacA: ChCl



e) LevA: ChCl



f) OxA: ChCl

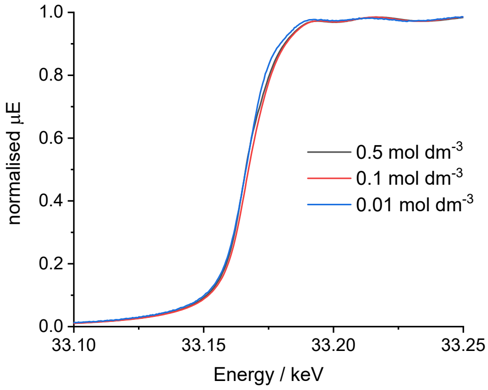


Figure S3: Normalised XANES plots of for solutions containing different concentrations of iodine in DESs formed with different HBDs: a) EG: ChCl, b) 12Prop: ChCl, c) Gly: ChCl, d) LacA: ChCl, e) LevA: ChCl, f) OxA: ChCl, and g) U: ChCl.

g) U: ChCl

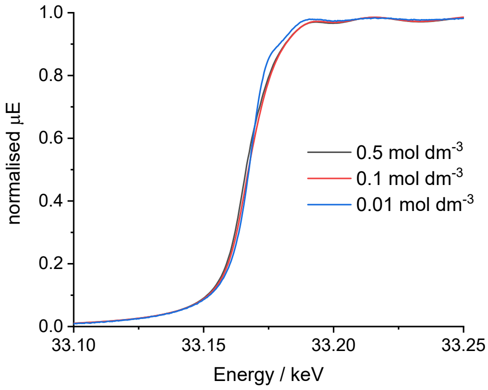


Figure S3 cont.: Normalised XANES plots of for solutions containing different concentrations of iodine in DESs formed with different HBDs: a) EG: ChCl, b) 12Prop: ChCl, c) Gly: ChCl, d) LacA: ChCl, e) LevA: ChCl, f) OxA: ChCl, and g) U: ChCl.

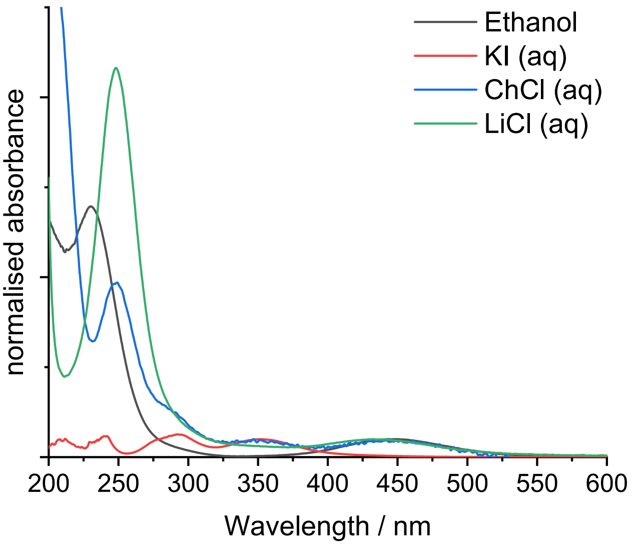


Figure S4: UV-vis spectra for reference solutions of iodine in KI (I_3^-), ChCl (predicted I_2Cl^-), LiCl (predicted I_2Cl^-) and ethanol (I_2), normalised to the 350 or 450 nm maximum.

Table S1: Karl Fischer titration results for the water content in the DES stock solutions. Errors are presented in brackets as the standard error of three measurements.

Solvent	**Water Content / wt.%**
EG: ChCl	1.20(3)
12Prop: ChCl	1.22(2)
Gly: ChCl	0.94(1)
LacA: ChCl	11.4(2)
OxA: ChCl	17.3(1)
U: ChCl	1.07(2)
LevA: ChCl	2.01(7)

Table S2: UV-vis absorption maxima for solutions of iodine in different DES environments at low concentration (5 to 20 mol dm^{-3}). Maxima values were obtained from Gaussian peak fitting in Origin. Proposed species ratios assume that molar extinction coefficients for all species are similar.

Solvent	**Wavelength / nm**	**Proposed species present**
KI (aq)	289, 353	$[I_3]^-$
ChCl (aq)	…, 247, 285, 344, 446	$[I_2Cl]^- + [I_3]^- + I_2$
LiCl (aq)	…, 248, (286), 439	$[I_2Cl]^-$ + (trace $[I_3]^-$) +I_2
Ethanol	230, 449	I_2
EG: ChCl	226, 260, 282, 358, 384	$3[I_2Cl]^- : 2[I_3]^-$
12Prop: ChCl	227, 260, 285, 358, 395	$3[I_2Cl]^- : 2[I_3]^-$
Gly: ChCl	219, 260, 288, 359, 385	$[I_2Cl]^- : [I_3]^-$
LacA: ChCl	…, 258, 291, 361, 371	$[I_2Cl]^- : [I_3]^-$
OxA: ChCl	…, 257, 291, 360, *ca.* 410	$[I_2Cl]^- : 2[I_3]^-$
U: ChCl	218, 261, 279, 365, *ca.* 410	$5[I_2Cl]^- : 2[I_3]^-$
LevA: ChCl	295, 365	$[I_3]^-$