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

Supplementary Information

Bulk Nanostructure of a Deep Eutectic Solvent with An Amphiphilic Hydrogen Bond Donor

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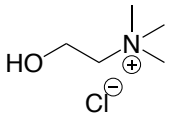
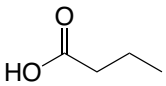
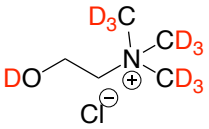
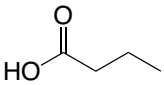
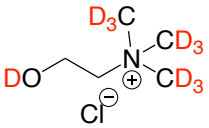
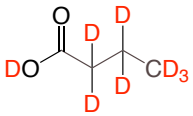
Table S1. Deuteration scheme of each pure DES contrast measured by neutron diffraction and deuterium (D) is marked red on the chemical structures. The deuteration scheme of choline chloride (ChCl) and butyric acid (BuOOH) in the DES + water is the same as the pure DES, except contrasts are labelled: H-ChCl:H-BuOOH:H_2O, d-ChCl:H-BuOOH:H_2O and d-ChCl:d-BuOOH:H_2O, respectively.

Contrast label	Choline chloride	Butyric acid
H-ChCl:H-BuOOH		
d-ChCl:H-BuOOH		
d-ChCl:d-BuOOH		

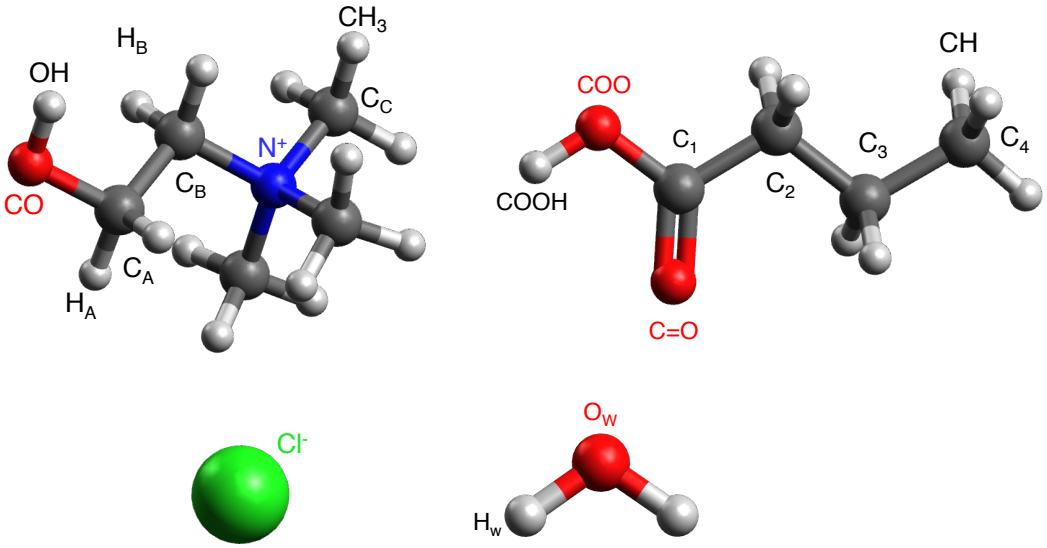


Fig. S1. Atomic labels for choline, butyric acid, chloride, and water in this study. Atoms are shown in CPK colouring.

Table S2. Box parameters used in EPSR refinement. Atomic density is the number of atoms in the EPSR refinement box divided by the cubic box length. This was calculated from the bulk experimental density and stoichiometry in each DES. The box size is the total number of molecules (or ions) in the box, and N choline, N chloride, N butyric acid and N water are the number of molecules in the box based on the eutectic composition of 1:3.9 (approximately 1:4).

System	Atomic density (atoms Å^{-3})	Box size (molecules)	N choline	N chloride	N butyric acid	N water
Pure DES	0.0962	4000	678	678	2644	-
DES + water	0.0967	4000	448	448	1741	1363

Table S3. Initial Lennard-Jones (12-6 potential) parameters based on Lorentz and Berthelot mixing rules for EPSR modelling.[1–3] Atomic labels (see Fig. S1), element, dispersion energy (ε), effective size (σ), and partial charge is tabulated.

Label	Element	ε (kJ mol^{-1})	σ (Å)	Charge (e$^-$)
		Choline (Ch$^+$)		
C_A	C	0.2763	3.50	0.23
C_B	C	0.2763	3.50	-0.11
C_C	C	0.2763	3.50	-0.38
H_A	H	0.1256	2.50	0.04
H_B	H	0.1256	2.50	0.13
CH_3	H	0.1256	2.50	0.19
OH	H[a]	0.0000	0.00	0.45
N^+	N	0.7000	3.20	0.16
CO	O	0.7118	3.07	-0.65
		Butyric acid (BuOOH)		
C_1	C	0.4393	3.75	0.52
C_2 & C_3	C	0.2761	3.50	-0.12
C_4	C	0.2761	3.50	-0.18
CH	H	0.1255	2.50	0.06
C=O	O	0.8786	2.96	-0.53
COO	O	0.7113	3.00	-0.44
COOH	H[a]	0.0000	0.00	0.45
		Chloride (Cl$^-$)		
Cl^-	Cl	0.62	3.77	-1.00
		Water (H_2O)		
O_W	O	0.6500	3.17	-0.85
H_W	H[a]	0.0000	0.00	0.42

[a] – exchangeable proton(s).

AFM force curves

Measurements of the normal force versus separation curve was performed on a freshly cleaved mica surface using a Veeco Nanoscope IV Atomic Force Microscope (AFM). The experimental procedure involved moving the mica surface towards the AFM tip while simultaneously detecting the cantilever deflection as a function of separation following a previously described method.[4]

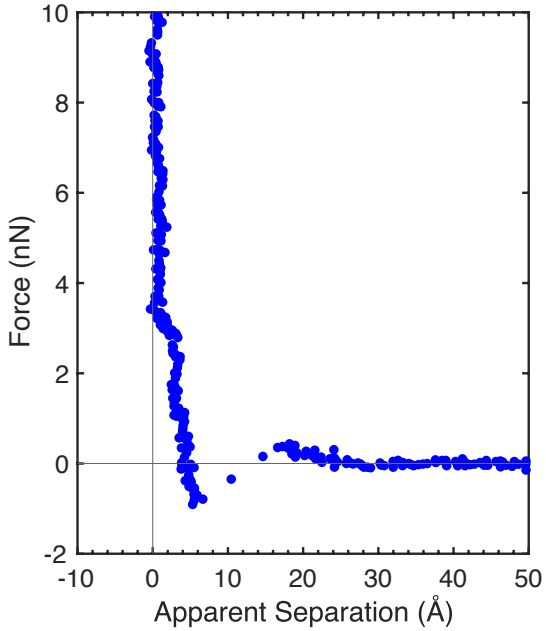


Fig. S2. Representative normal force-separation profiles (force curve) of an AFM tip approaching mica immersed in 1:4:3 ChCl:BuOOH:H_2O (10 wt% water) at 25 °C. The first discontinuity occurs at 25 Å which approximately matches the real space repeat length observed from neutron diffraction (27 Å).

Additional Pair Distribution Functions

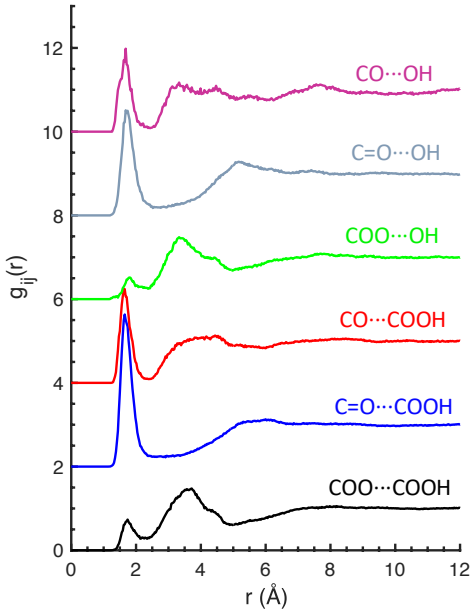


Fig. S3. Additional Pair distribution functions (PDFs) of H-bond interactions in the pure DES. Each first shell coordination number is low, and falls below 0.4. PDFs scaled verically for clarity and labeled as above.

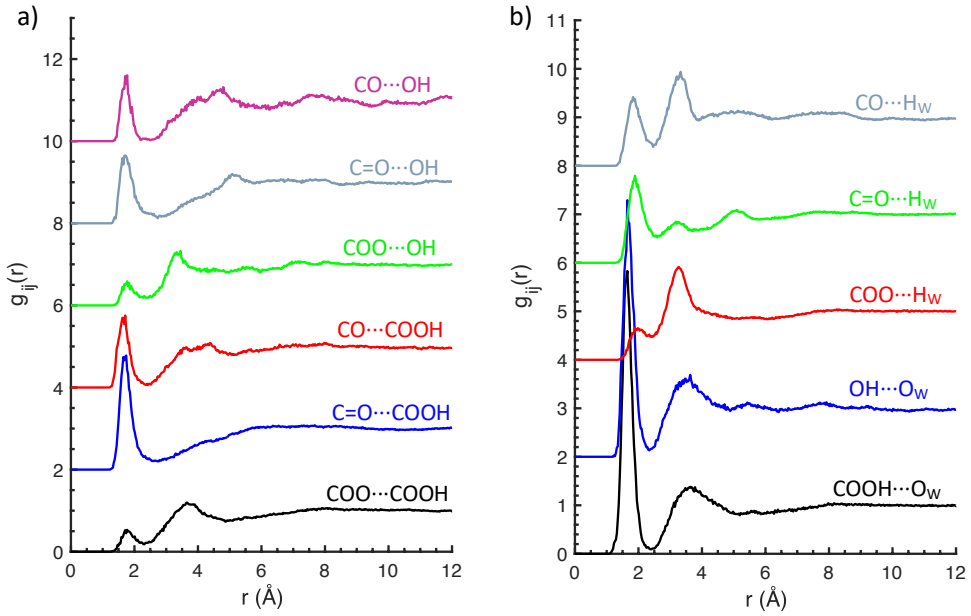


Fig. S4. Additional PDFs of a) DES-DES H-bond interactions and b) water-DES H-bond interactions in the DES + water. Each first shell coordination number is low, and falls below 0.4. PDFs scaled verically for clarity and labeled as above.

References

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2 S. V. Sambasivarao and O. Acevedo, *J. Chem. Theory Comput.*, 2009, **5**, 1038–1050.

3 S. Lenton, N. H. Rhys, J. J. Towey, A. K. Soper and L. Dougan, *Nat Commun*, 2017, **8**, 919.

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