Electronic Supplementary Information for Heterogeneity in Hydrophobic Deep Eutectic Solvents: SAXS Prepeak and Local Environments

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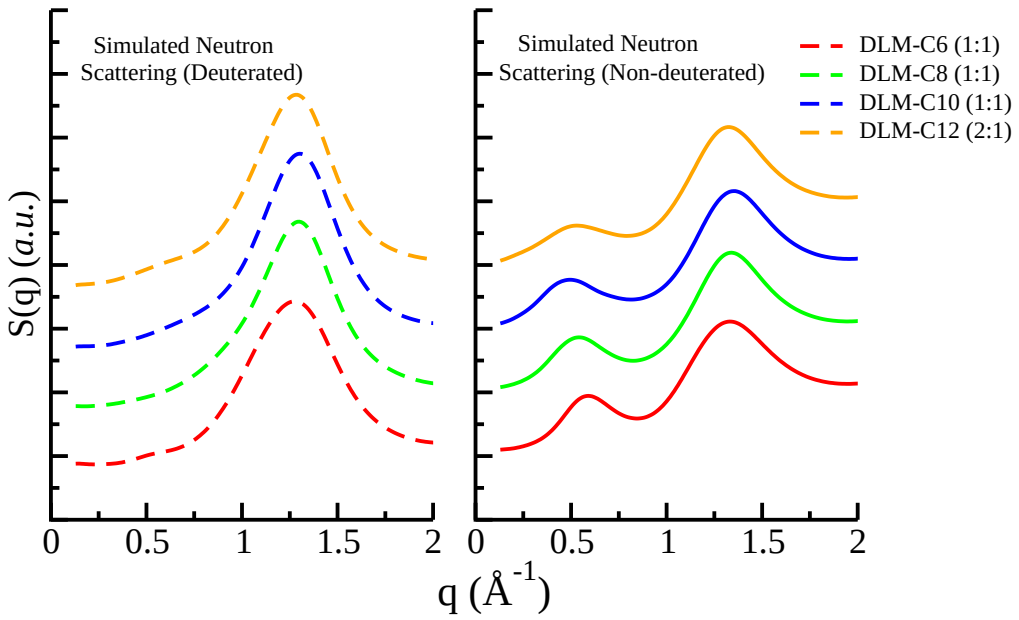
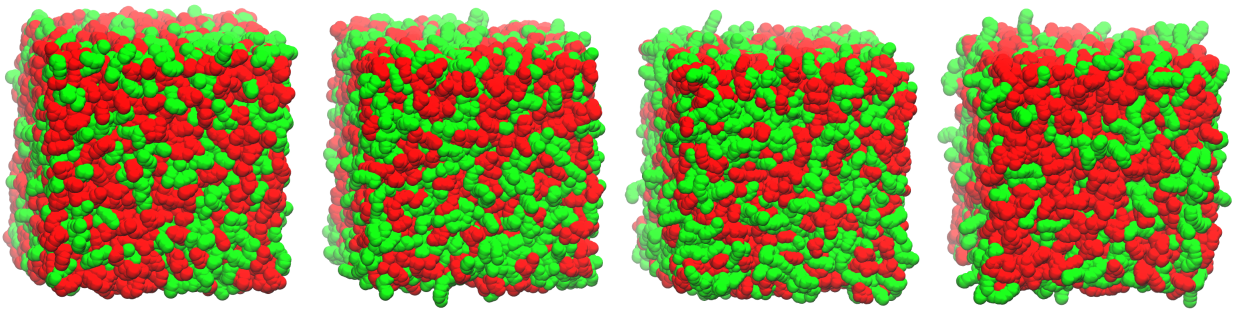


Figure S1: Simulated total neutron scattering structure function, S(q), of the four HDESs. Left panel refers to simulated neutron scattering when all hydrogens are deuterated and right panel when hydrogens were not deuterated. These S(q)s are calculated using equation 16 from the work of Liu et al. (Ref. 71 of the main article). For clarity, S(q)s are offset vertically.



(a) (b) (c) (d)

Figure S2: Equilibrium simulation cells snapshot of (a) DL-menthol:hexanoic acid (1:1), (b) DL-menthol:octanoic acid (1:1), (c) DL-menthol:decanoic acid (1:1) and (d) DL-menthol:dodecanoic acid (2:1) system. Here, red and green color refer to DL-menthol and organic acids, respectively.

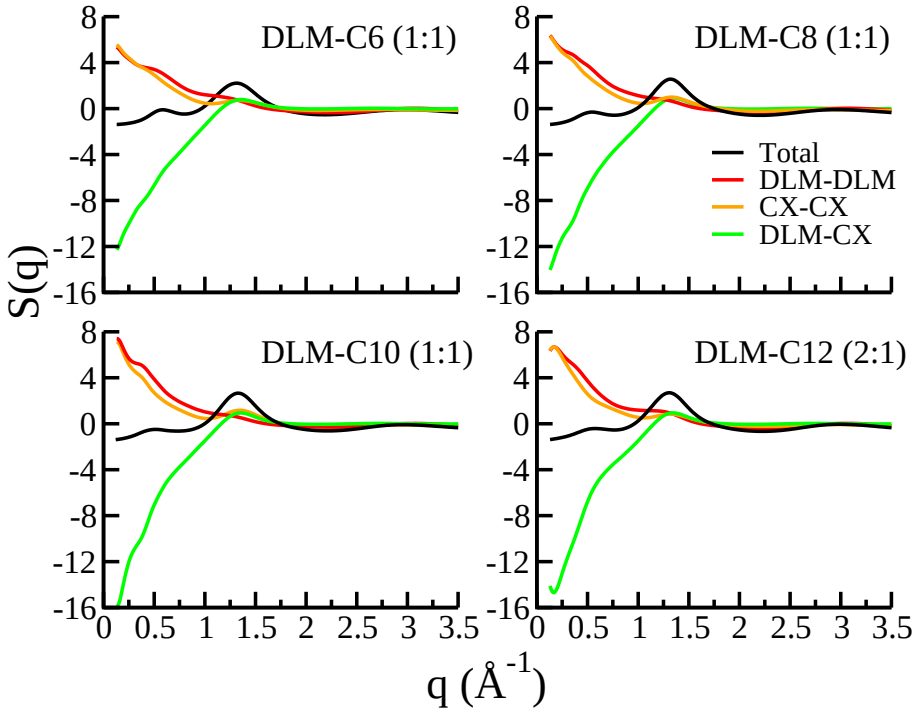
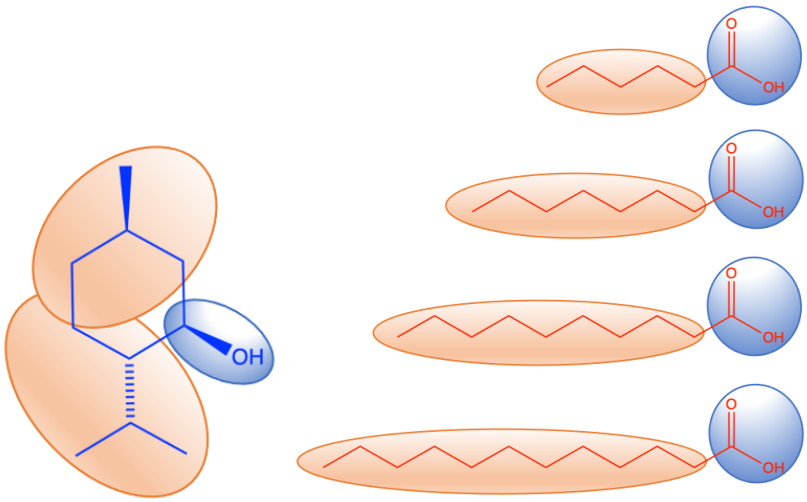


Figure S3: Simulated species wise partial X-ray scattering structure function, S(q), of the four HDESs. CX represents organic acids where, X=6, 8, 10 and 12. DLM represents DL-menthol species.

Table S1: Peak positions of first minimum (r_{min}) and their corresponding coordination number (n_{coord}) for different RDF pairs.

RDF Pair	r_{min}	n_{coord}
O_{C6}-HO_{C6}	0.264	0.502
O_{C8}-HO_{C8}	0.262	0.506
O_{C10}-HO_{C10}	0.266	0.518
O_{C12}-HO_{C12}	0.266	0.360
OH_{DLM}-HO_{C6}	0.266	0.466
OH_{DLM}-HO_{C8}	0.266	0.461
OH_{DLM}-HO_{C10}	0.266	0.451
OH_{DLM}-HO_{C12}	0.268	0.307
O_{C6}-HO_{DLM}	0.254	0.441
O_{C8}-HO_{DLM}	0.254	0.437
O_{C10}-HO_{DLM}	0.254	0.428
O_{C12}-HO_{DLM}	0.256	0.595
OH_{DLM}-HO_{DLM}(C6)	0.260	0.403
OH_{DLM}-HO_{DLM}(C8)	0.260	0.408
OH_{DLM}-HO_{DLM}(C10)	0.258	0.408
OH_{DLM}-HO_{DLM}(C12)	0.260	0.555
OH_{C6}-HO_{DLM}	0.252	0.040
OH_{C8}-HO_{DLM}	0.252	0.038
OH_{C10}-HO_{DLM}	0.250	0.036
OH_{C12}-HO_{DLM}	0.252	0.050
OH_{C6}-HO_{C6}	0.248	0.019
OH_{C8}-HO_{C8}	0.244	0.017
OH_{C10}-HO_{C10}	0.246	0.017
OH_{C12}-HO_{C12}	0.248	0.011
$C6_T$-$C6_T$	0.696	2.631
$C8_T$-$C8_T$	0.704	2.601
$C10_T$-$C10_T$	0.712	2.498
$C12_T$-$C12_T$	0.724	1.730



(a) (b)

Figure S4: Chemical structures of (a) DL-menthol (DLM) (b) hexanoic (C6), octanoic (C8), decanoic (C10) and dodecanoic (C12) acids, shown from top to bottom, respectively. Polar part in HDESs are shaded in blue and refers to COOH group in acids and in DLM the OH group and carbon and hydrogen directly attached to OH. The alkyl chain in acids and other remaining atoms of DLM are referred to apolar part of HDESs, which is shaded in orange.

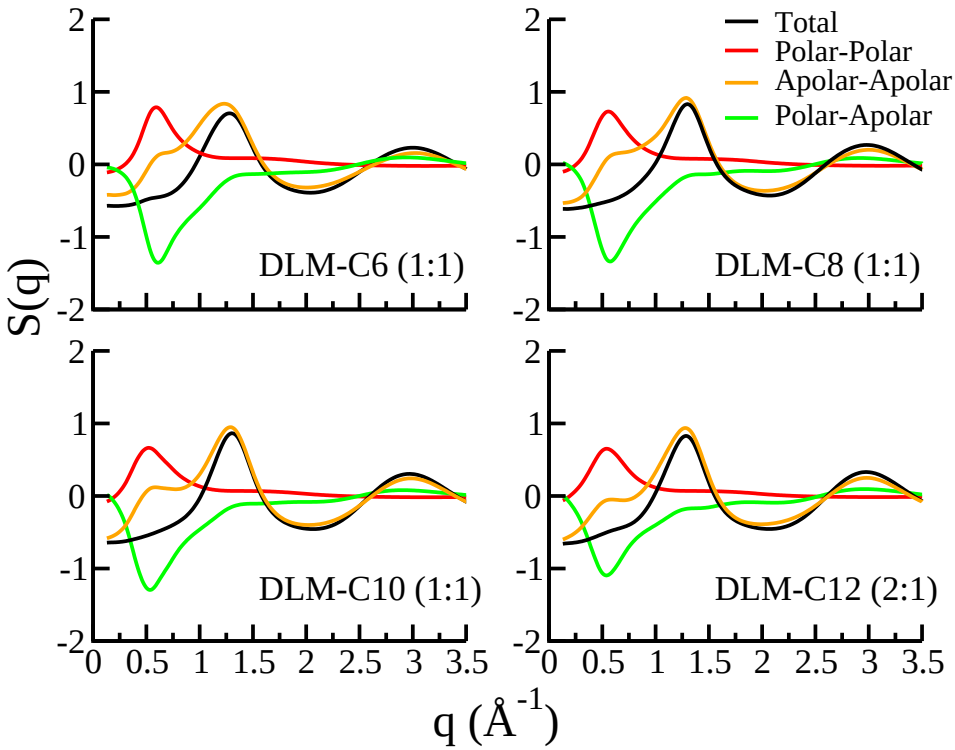


Figure S5: Simulated total and partial S(q)s without weighting the contributions with radiation-specific weights for the four HDESs.

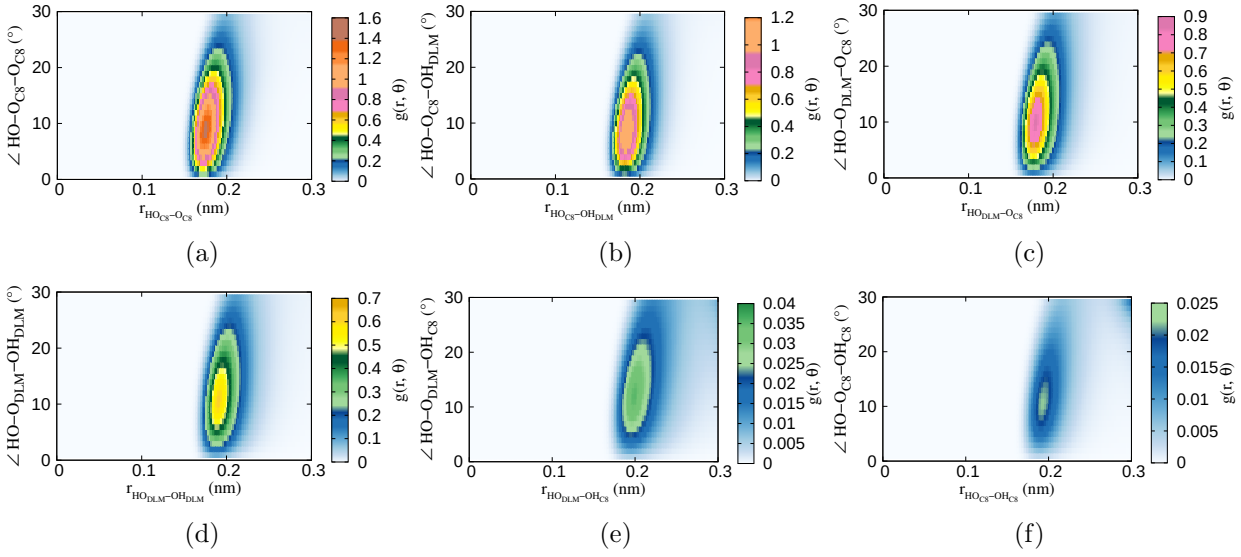


Figure S6: Angle-resolved radial distribution functions, $g(r, \theta)$, for H-D-A angle and H-A distance in DLM-C8 (1:1) HDES. Here, HO_{DLM} and OH_{DLM} are the hydroxyl hydrogen and oxygen atoms of DL-menthol, respectively. OH_{C8}, HO_{C8} and O_{C8} are the hydroxyl oxygen, hydroxyl hydrogen, and, carbonyl oxygen atoms of octanoic acid, respectively.

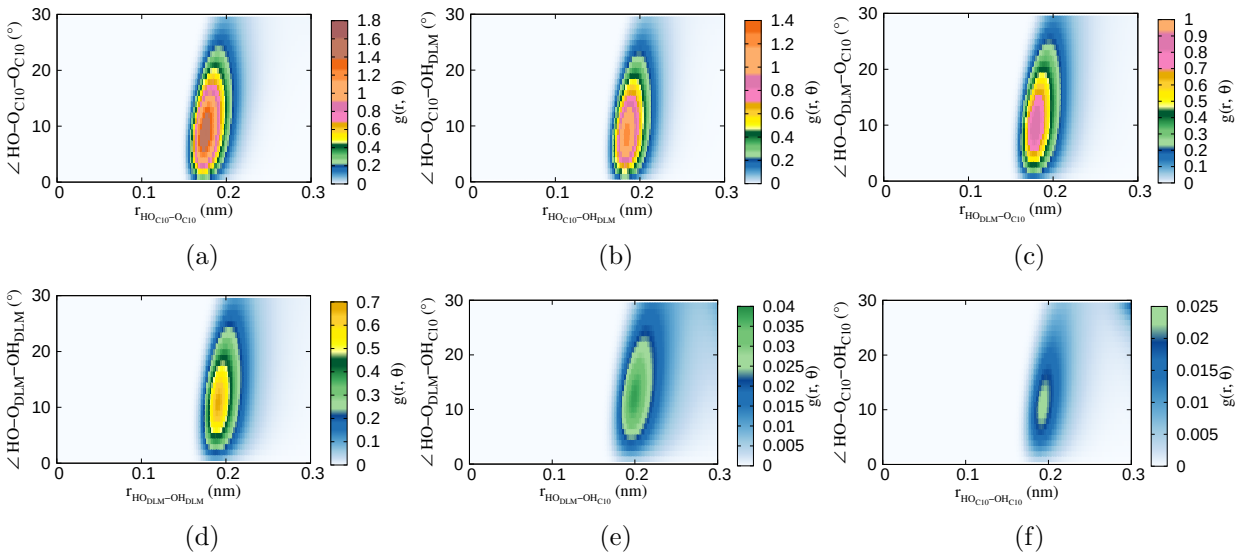


Figure S7: Angle-resolved radial distribution functions, $g(r, \theta)$, for H-D-A angle and H-A distance in DLM-C10 (1:1) HDES. Here, HO_{DLM} and OH_{DLM} are the hydroxyl hydrogen and oxygen atoms of DL-menthol, respectively. OH_{C10}, HO_{C10} and O_{C10} are the hydroxyl oxygen, hydroxyl hydrogen, and, carbonyl oxygen atoms of decanoic acid, respectively.