Supporting Information for: "Interfacial Properties of Hydrophobic Deep Eutectic Solvents with Water"

Hirad S. Salehi, Othonas A. Moultos, and Thijs J. H. Vlugt[*]

Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, Leeghwaterstraat 39, 2628CB Delft, The Netherlands

E-mail: t.j.h.vlugt@tudelft.nl

In this supporting information, molecular structures and force field parameters used in Molecular Dynamics (MD) simulations of mixtures of hydrophobic DESs with water are presented, as well as additional simulation details and results. The following DESs were considered in the simulations: Tetrabutylammonium chloride-decanoic acid (TBAC-dec), thymol-decanoic acid (Thy-dec), and DL-menthol-decanoic acid (Men-dec). In these DESs, tetrabutylammonium chloride (a salt composed of tetrabutylammonium cation and chloride anion), thymol, and DL-menthol are the hydrogen bond acceptors (HBAs), respectively, and decanoic acid is the hydrogen bond donor (HBD) component. The HBA:HBD molar ratios of 1:2, 1:2, and 2:1 were used for TBAC-dec, Thy-dec, and Men-dec, respectively. For the DL-menthol (HBA) component of Men-dec, an equimolar mixture of enantiomers D-menthol and L-menthol was used. The all-atom non-polarizable Generalized AMBER force field (GAFF)[1] was used for all DESs. Bonded interactions, including bond-stretching, bond-bending, torsions, and improper torsions, as well non-bonded interactions, i.e., Lennard-Jones (LJ) and

electrostatic interactions, were used to model inter- and intramolecular interactions. The SPC/E model[2] was used for water, and the SHAKE algorithm[3,4] was used to keep the bond lengths and angles of the water molecules fixed. For the chloride anion, the LJ parameters by Fox and Kollman[5] were used. To compute the LJ interactions between non-identical atom types, the Lorentz-Berthelot mixing rules[3] were used. Partial atomic charges were obtained from quantum mechanical calculations at the HF/6-31G* level of theory and the restrained electrostatic potential (RESP)[6] method, using the Gaussian 09 Rev.B.01 software[7] and the R.E.D-III.52 tools.[8] The influence of charge scaling on the computed DES/water interfacial properties was investigated by considering different charge scaling factors f_q. For TBAC-dec, charge scaling factors of 0.6, 0.7, 0.8, or 0.9 were used for the cation and anion. For Thy-dec, two sets of charge scaling factors were used: 0.7 for thymol and 1 for decanoic acid (denoted by '$f_q = 0.7/1$'), and 0.8 for both thymol and decanoic acid (denoted by '$f_q = 0.8/0.8$'). For Men-dec, charge scaling factors of 0.8 for DL-menthol and 1 for decanoic acid were used. The listed partial charges in Tables S1, S5, S9 and S14 of this document are the unscaled charges, and should therefore be multiplied by the proper scaling factors when used in simulations. To prevent atomic overlaps, the LJ parameters $\epsilon = 0.001\,\text{kcal.mol}^{-1}$ and $\sigma = 0.1\,\text{Å}$ were used for unprotected hydroxyl hydrogen atoms in DES and water molecules.

The structures and atom labels for all molecules (except for the chloride anion) are presented in Figures S1 to S5, and the force field parameters of all the molecules are listed in Tables S1 to S17. For all DES/water mixtures, the numbers of molecules and the HBA:HBD molar ratios used in the simulations are listed in Table S19. Additional MD simulation results are presented for density profiles in Figures S6 to S10, and hydrogen bond number densities in Figures S11 to S13.

Molecular Structures
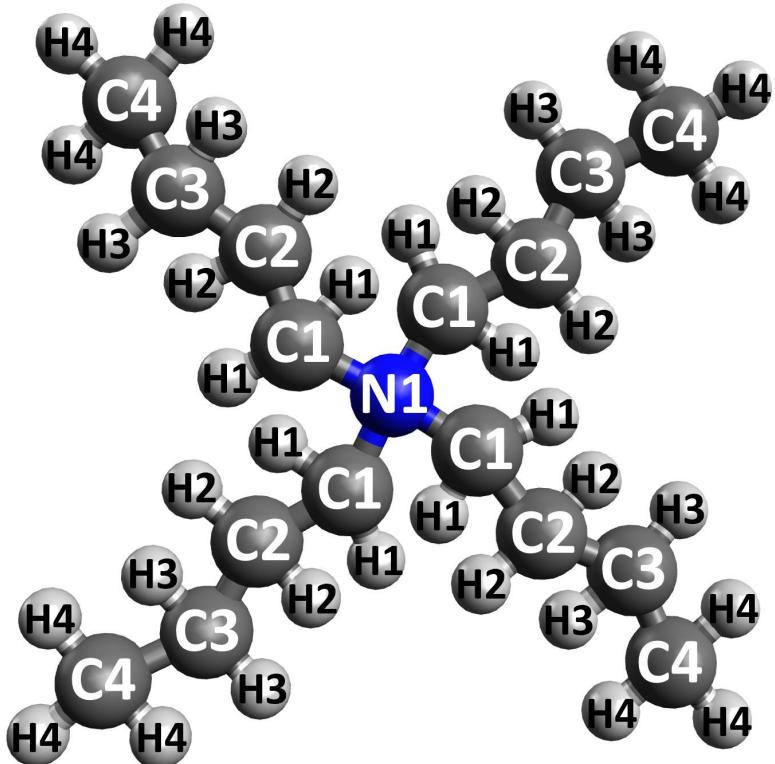
Figure S1: Structure and atom labels of the TBA cation.
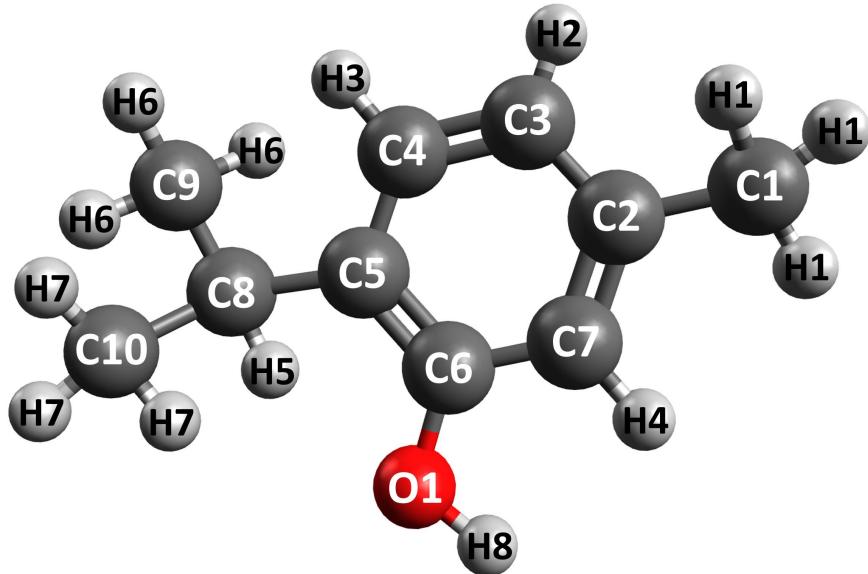

**Figure S2:** Structure and atom labels of thymol.
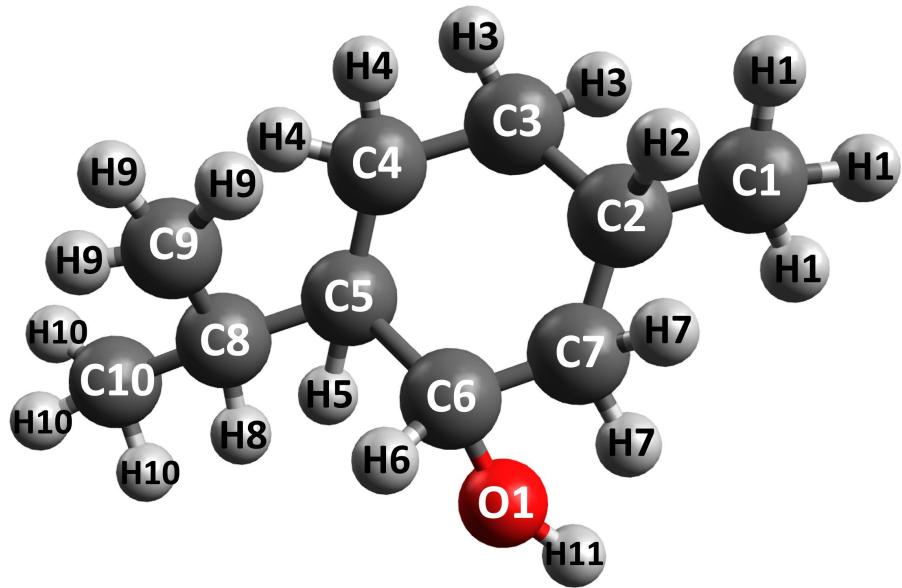
**Figure S3:** Structure and atom labels of menthol.
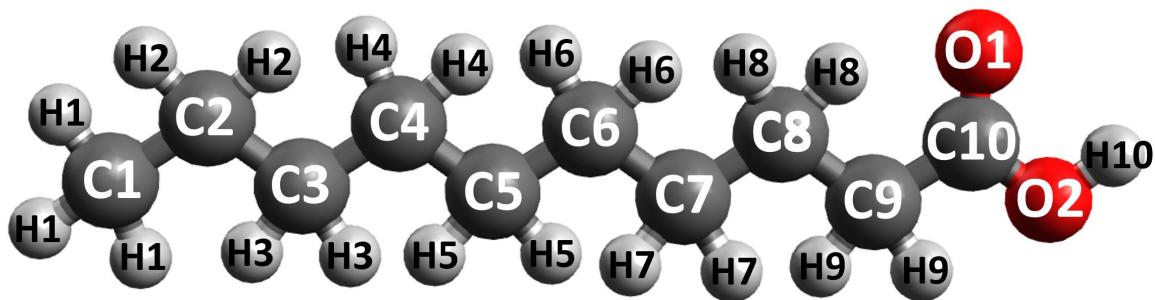

Figure S4: Structure and atom labels of decanoic acid.
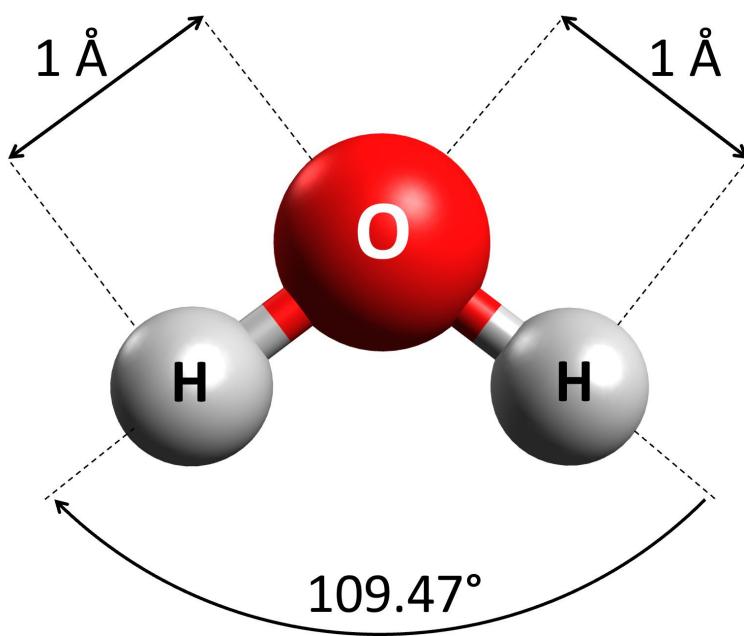
Figure S5: Structure and atom labels of water (the SPC/E model[2]).

Force Field Parameters for TBAC

Table S1: GAFF atom types and non-bonded parameters for tetrabutylammonium chloride (TBAC).[1] The LJ energy is calculated as: $E_{\mathrm{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The atom labels are defined in Figure S1. The listed charges are the unscaled values (+1 for tetrabutylammonium and -1 for chloride), and should therefore be multiplied by the proper scaling factors when used in simulations.

atom label	GAFF atom type	$q/[e^-]$	$\epsilon/[\mathrm{kcal.mol}^{-1}]$	$\sigma/[\mathrm{\mathring{A}}]$
C1	c3	-0.0048	0.1094	3.3997
C2	c3	-0.0178	0.1094	3.3997
C3	c3	-0.0096	0.1094	3.3997
C4	c3	-0.1069	0.1094	3.3997
H1	hx	0.0663	0.0157	1.9600
H2	hc	0.0368	0.0157	2.6495
H3	hc	0.0284	0.0157	2.6495
H4	hc	0.0419	0.0157	2.6495
N1	n4	0.0016	0.1700	3.2500
Cl	cl	-1.0000	0.2650	3.4709

Table S2: Bond-stretching interaction parameters for the TBA cation.[1] The bond-stretching energy is calculated according to: $E_{\text{stretching}}(r) = k_{\text{r}}(r - r_0)^2$.

bond type	$k_{\text{r}}/[\text{kcal.mol}^{-1}.\text{Å}^{-2}]$	$r_0/[\text{Å}]$
c3-c3	303.1	1.535
c3-hc	337.3	1.092
c3-hx	338.7	1.091
c3-n4	293.6	1.499

Table S3: Bond-bending interaction parameters for the TBA cation.[1] The bond-bending energy is calculated according to: $E_{\text{bending}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/[\text{kcal.mol}^{-1}.\text{rad}^{-2}]$	θ_0
c3-c3-c3	63.2	110.63
c3-c3-hc	46.4	110.05
c3-c3-hx	46.0	111.74
c3-c3-n4	66.0	108.93
c3-n4-c3	62.8	110.64
hc-c3-hc	39.4	108.35
hx-c3-hx	39.0	110.74
hx-c3-n4	49.0	107.91

Table S4: Dihedral parameters for the TBA cation.[1] The dihedral energy is calculated according to: $E_{\text{dihedral}}(\phi) = A_0 + A_1 \cos(\phi) + A_2 \cos^2(\phi) + A_3 \cos^3(\phi)$, where for each dihedral a-b-c-d, ϕ is the angle between the planes a-b-c and b-c-d.

dihedral type	A_0/[kcal.mol^{-1}]	A_1/[kcal.mol^{-1}]	A_2/[kcal.mol^{-1}]	A_3/[kcal.mol^{-1}]
c3-c3-c3-c3	0.8800	-0.7400	-0.5000	0.7200
c3-c3-c3-hc	0.1600	-0.4800	0.0000	0.6400
c3-c3-c3-hx	0.1556	-0.4667	0.0000	0.6222
c3-c3-c3-n4	0.1556	-0.4667	0.0000	0.6222
c3-c3-n4-c3	0.1556	-0.4667	0.0000	0.6222
hc-c3-c3-hc	0.1500	-0.4500	0.0000	0.6000
hc-c3-c3-hx	0.1556	-0.4667	0.0000	0.6222
hc-c3-c3-n4	0.1556	-0.4667	0.0000	0.6222
hx-c3-n4-c3	0.1556	-0.4667	0.0000	0.6222

Force Field Parameters for Thymol

Table S5: GAFF atom types and non-bonded parameters for thymol.[1] The LJ energy is calculated as: $E_{\text{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The atom labels are defined in Figure S2. The listed charges are the unscaled values, and should therefore be multiplied by the proper scaling factors when used in simulations.

atom label	GAFF atom type	$q/[\text{e}^-]$	$\epsilon/[\text{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
C1	c3	-0.1835	0.1094	3.3997
C2	ca	0.0799	0.0860	3.3997
C3	ca	-0.2007	0.0860	3.3997
C4	ca	-0.3135	0.0860	3.3997
C5	ca	0.0679	0.0860	3.3997
C6	ca	0.1919	0.0860	3.3997
C7	ca	-0.2712	0.0860	3.3997
C8	c3	0.2411	0.1094	3.3997
C9	c3	-0.2008	0.1094	3.3997
C10	c3	-0.2008	0.1094	3.3997
H1	hc	0.0678	0.0157	2.6495
H2	ha	0.1507	0.0150	2.5996
H3	ha	0.1999	0.0150	2.5996
H4	ha	0.1442	0.0150	2.5996
H5	hc	0.0211	0.0157	2.6495
H6	hc	0.0385	0.0157	2.6495
H7	hc	0.0385	0.0157	2.6495
H8	ho	0.4403	0.0010	0.1000
O1	oh	-0.6009	0.2104	3.0665

Table S6: Bond-stretching interaction parameters for thymol.[1] The bond-stretching energy is calculated according to: $E_{\text{stretching}}(r) = k_{\text{r}}(r - r_0)^2$.

bond type	$k_{\text{r}}/[\text{kcal.mol}^{-1}.\text{Å}^{-2}]$	$r_0/[\text{Å}]$
c3-c3	303.1	1.535
c3-hc	337.3	1.092
ho-oh	369.6	0.974
ca-c3	323.5	1.513
ca-ca	478.4	1.387
ca-oh	386.1	1.362
ca-ha	344.3	1.087

Table S7: Bond-bending interaction parameters for thymol.[1] The bond-bending energy is calculated according to: $E_{\text{bending}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/[\text{kcal.mol}^{-1}.\text{rad}^{-2}]$	θ_0
c3-c3-c3	63.2	110.63
c3-c3-hc	46.4	110.05
hc-c3-hc	39.4	108.35
ca-c3-hc	47.0	110.15
ca-ca-ca	67.2	119.97
ca-ca-c3	63.8	120.63
ca-ca-ha	48.5	120.01
ca-oh-ho	48.9	109.47
ca-ca-oh	69.8	119.94
ca-c3-c3	62.5	114.61

Table S8: Dihedral parameters for thymol.[1] The dihedral energy is calculated according to: $E_{\text{dihedral}}(\phi) = A_0 + A_1 \cos(\phi) + A_2 \cos^2(\phi) + A_3 \cos^3(\phi)$, where for each dihedral a-b-c-d, ϕ is the angle between the planes a-b-c and b-c-d.

dihedral type	$A_0/[\text{kcal.mol}^{-1}]$	$A_1/[\text{kcal.mol}^{-1}]$	$A_2/[\text{kcal.mol}^{-1}]$	$A_3/[\text{kcal.mol}^{-1}]$
c3-c3-c3-hc	0.1600	-0.4800	0.0000	0.6400
hc-c3-c3-hc	0.1500	-0.4500	0.0000	0.6000
c3-c3-ca-ca	0.0000	0.0000	0.0000	0.0000
c3-ca-ca-ca	7.2500	0.0000	-7.2500	0.0000
c3-ca-ca-ha	7.2500	0.0000	-7.2500	0.0000
c3-ca-ca-oh	7.2500	0.0000	-7.2500	0.0000
ca-c3-c3-hc	0.1556	-0.4667	0.0000	0.6222
ca-ca-ca-ca	7.2500	0.0000	-7.2500	0.0000
ca-ca-ca-oh	7.2500	0.0000	-7.2500	0.0000
ca-ca-oh-ho	1.8000	0.0000	-1.8000	0.0000
ha-ca-ca-ha	7.2500	0.0000	-7.2500	0.0000
ha-ca-ca-oh	7.2500	0.0000	-7.2500	0.0000
hc-c3-ca-ca	0.0000	0.0000	0.0000	0.0000
ca-ca-ca-ha	7.2500	0.0000	-7.2500	0.0000
c3-ca-ca-ca [a]	2.2000	0.0000	-2.2000	0.0000
ha-ca-ca-ca [a]	2.2000	0.0000	-2.2000	0.0000
oh-ca-ca-ca [a]	2.2000	0.0000	-2.2000	0.0000

[a] These are improper dihedrals. The energy functional form for improper dihedrals is the same as for the (proper) dihedrals. However, for each improper dihedral a-b-c-d, the angle ϕ is defined as the angle between the planes a-b-c and a-c-d.

Force Field Parameters for DL-Menthol

Table S9: GAFF atom types and non-bonded parameters for D-menthol.[1] The LJ energy is calculated as: $E_{\mathrm{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The atom labels are defined in Figure S3. The listed charges are the unscaled values, and should therefore be multiplied by the proper scaling factors when used in simulations.

atom label	GAFF atom type	$q/[\mathrm{e}^-]$	$\epsilon/[\mathrm{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
C1	c3	-0.1819	0.1094	3.3997
C2	c3	0.1651	0.1094	3.3997
C3	c3	-0.0985	0.1094	3.3997
C4	c3	-0.1855	0.1094	3.3997
C5	c3	-0.0084	0.1094	3.3997
C6	c3	0.1368	0.1094	3.3997
C7	c3	-0.1807	0.1094	3.3997
C8	c3	0.1673	0.1094	3.3997
C9	c3	-0.1985	0.1094	3.3997
C10	c3	-0.1985	0.1094	3.3997
H1	hc	0.0394	0.0157	2.6495
H2	hc	-0.0076	0.0157	2.6495
H3	hc	0.0361	0.0157	2.6495
H4	hc	0.0639	0.0157	2.6495
H5	hc	0.0370	0.0157	2.6495
H6	h1	0.1171	0.0157	2.4714
H7	hc	0.0571	0.0157	2.6495
H8	hc	0.0082	0.0157	2.6495
H9	hc	0.0417	0.0157	2.6495
H10	hc	0.0417	0.0157	2.6495
H11	ho	0.3972	0.0010	0.1000
O1	oh	-0.6517	0.2104	3.0665

Table S10: GAFF atom types and non-bonded parameters for L-menthol.[1] The LJ energy is calculated as: $E_{\mathrm{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The atom labels are defined in Figure S3. The listed charges are the unscaled values, and should therefore be multiplied by the proper scaling factors when used in simulations.

atom label	GAFF atom type	$q/[\mathrm{e}^-]$	$\epsilon/[\mathrm{kcal.mol}^{-1}]$	$\sigma/[\mathrm{\mathring{A}}]$
C1	c3	-0.1783	0.1094	3.3997
C2	c3	0.1580	0.1094	3.3997
C3	c3	-0.0982	0.1094	3.3997
C4	c3	-0.1892	0.1094	3.3997
C5	c3	-0.0082	0.1094	3.3997
C6	c3	0.1331	0.1094	3.3997
C7	c3	-0.1716	0.1094	3.3997
C8	c3	0.1690	0.1094	3.3997
C9	c3	-0.1997	0.1094	3.3997
C10	c3	-0.1997	0.1094	3.3997
H1	hc	0.0387	0.0157	2.6495
H2	hc	-0.0059	0.0157	2.6495
H3	hc	0.0366	0.0157	2.6495
H4	hc	0.0651	0.0157	2.6495
H5	hc	0.0374	0.0157	2.6495
H6	h1	0.1171	0.0157	2.4714
H7	hc	0.0555	0.0157	2.6495
H8	hc	0.0081	0.0157	2.6495
H9	hc	0.0420	0.0157	2.6495
H10	hc	0.0420	0.0157	2.6495
H11	ho	0.3965	0.0010	0.1000
O1	oh	-0.6509	0.2104	3.0665

Table S11: Bond-stretching interaction parameters for DL-menthol.[1] The bond-stretching energy is calculated according to: $E_{\text{stretching}}(r) = k_{\text{r}}(r - r_0)^2$.

bond type	$k_{\text{r}}/[\text{kcal.mol}^{-1}.\text{Å}^{-2}]$	$r_0/[\text{Å}]$
c3-c3	303.1	1.535
c3-hc	337.3	1.092
ho-oh	369.6	0.974
c3-h1	335.9	1.093
c3-oh	314.1	1.426

Table S12: Bond-bending interaction parameters for DL-menthol.[1] The bond-bending energy is calculated according to: $E_{\text{bending}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/[\text{kcal.mol}^{-1}.\text{rad}^{-2}]$	θ_0
c3-c3-c3	63.2	110.63
c3-c3-hc	46.4	110.05
hc-c3-hc	39.4	108.35
c3-c3-h1	46.4	110.07
c3-c3-oh	67.7	109.43
c3-oh-ho	47.1	108.16
h1-c3-oh	51.0	109.88

Table S13: Dihedral parameters for DL-menthol.[1] The dihedral energy is calculated according to: $E_{\text{dihedral}}(\phi) = A_0 + A_1 \cos(\phi) + A_2 \cos^2(\phi) + A_3 \cos^3(\phi)$, where for each dihedral a-b-c-d, ϕ is the angle between the planes a-b-c and b-c-d.

dihedral type	$A_0/[\text{kcal.mol}^{-1}]$	$A_1/[\text{kcal.mol}^{-1}]$	$A_2/[\text{kcal.mol}^{-1}]$	$A_3/[\text{kcal.mol}^{-1}]$
c3-c3-c3-hc	0.1600	-0.4800	0.0000	0.6400
c3-c3-c3-c3	0.8800	-0.7400	0.5000	0.7200
hc-c3-c3-hc	0.1500	-0.4500	0.0000	0.6000
c3-c3-c3-h1	0.1556	-0.4667	0.0000	0.6222
c3-c3-c3-oh	0.1556	-0.4667	0.0000	0.6222
h1-c3-c3-hc	0.1556	-0.4667	0.0000	0.6222
h1-c3-oh-ho	0.1667	-0.5000	0.0000	0.6667
hc-c3-c3-oh	0.2500	0.2500	0.0000	0.0000
c3-c3-oh-ho	0.4100	-0.2300	0.0000	0.6400

Force Field Parameters for Decanoic Acid

Table S14: GAFF atom types and non-bonded parameters for decanoic acid.[1] The LJ energy is calculated as: $E_{\mathrm{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The atom labels are defined in Figure S4. The listed charges are the unscaled values, and should therefore be multiplied by the proper scaling factors when used in simulations.

atom label	GAFF atom type	$q/[\mathrm{e}^-]$	$\epsilon/[\mathrm{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
C1	c3	-0.0977	0.1094	3.3997
C2	c3	0.0308	0.1094	3.3997
C3	c3	0.0032	0.1094	3.3997
C4	c3	-0.0033	0.1094	3.3997
C5	c3	0.0023	0.1094	3.3997
C6	c3	0.0138	0.1094	3.3997
C7	c3	-0.0092	0.1094	3.3997
C8	c3	-0.0189	0.1094	3.3997
C9	c3	-0.0228	0.1094	3.3997
C10	c	0.7355	0.0860	3.3997
H1	hc	0.0216	0.0157	2.6495
H2	hc	0.0012	0.0157	2.6495
H3	hc	0.0028	0.0157	2.6495
H4	hc	-0.0025	0.0157	2.6495
H5	hc	-0.0023	0.0157	2.6495
H6	hc	0.0037	0.0157	2.6495
H7	hc	-0.0005	0.0157	2.6495
H8	hc	0.0145	0.0157	2.6495
H9	hc	0.0400	0.0157	2.6495
H10	ho	0.4595	0.0010	0.1000
O1	oh	-0.6752	0.2104	3.0665
O2	o	-0.5966	0.2100	2.9599

Table S15: Bond-stretching interaction parameters for decanoic acid.[1] The bond-stretching energy is calculated according to: $E_{\text{stretching}}(r) = k_r(r - r_0)^2$.

bond type	$k_r/[\text{kcal.mol}^{-1}.\text{Å}^{-2}]$	$r_0/[\text{Å}]$
c-c3	328.3	1.508
c-o	648.0	1.214
c-oh	466.4	1.306
c3-c3	303.1	1.535
c3-hc	337.3	1.092
ho-oh	369.6	0.974

Table S16: Bond-bending interaction parameters for decanoic acid.[1] The bond-bending energy is calculated according to: $E_{\text{bending}}(\theta) = k_\theta(\theta - \theta_0)^2$.

angle type	$k_\theta/[\text{kcal.mol}^{-1}.\text{rad}^{-2}]$	θ_0
c-c3-c3	63.8	110.53
c3-c3-c3	63.2	110.63
c-oh-ho	51.2	107.37
c3-c-o	68.0	123.11
c3-c-oh	69.8	112.20
c3-c3-hc	46.4	110.05
c-c3-hc	47.2	109.68
hc-c3-hc	39.4	108.35
o-c-oh	77.4	122.88

Table S17: Dihedral parameters for decanoic acid.[1] The dihedral energy is calculated according to: $E_{\text{dihedral}}(\phi) = A_0 + A_1 \cos(\phi) + A_2 \cos^2(\phi) + A_3 \cos^3(\phi)$, where for each dihedral a-b-c-d, ϕ is the angle between the planes a-b-c and b-c-d.

dihedral type	$A_0/[\text{kcal.mol}^{-1}]$	$A_1/[\text{kcal.mol}^{-1}]$	$A_2/[\text{kcal.mol}^{-1}]$	$A_3/[\text{kcal.mol}^{-1}]$
c3-c3-c3-hc	0.1600	-0.4800	0.0000	0.6400
c3-c3-c3-c3	0.8800	-0.7400	0.5000	0.7200
c-c3-c3-c3	0.1556	-0.4667	0.0000	0.6222
c-c3-c3-hc	0.1556	-0.4667	0.0000	0.6222
hc-c3-c3-hc	0.1500	-0.4500	0.0000	0.6000
c3-c-oh-ho	4.6000	0.0000	-4.6000	0.0000
o-c-c3-c3	0.0000	0.0000	0.0000	0.0000
o-c-c3-hc	0.8800	1.0400	0.0000	-0.3200
o-c-oh-ho	6.5000	1.9000	-4.6000	0.0000
oh-c-c3-c3	0.0000	0.0000	0.0000	0.0000
oh-c-c3-hc	0.0000	0.0000	0.0000	0.0000
oh-c-o-c3 [a]	2.2000	0.0000	-2.2000	0.0000

[a] This is an improper dihedral. The energy functional form for improper dihedrals is the same as for the (proper) dihedrals. However, for each improper dihedral a-b-c-d, the angle ϕ is defined as the angle between the planes a-b-c and a-c-d.

Force Field Parameters for Water

Table S18: Non-bonded parameters for water (the SPC/E model[2]). The LJ energy is calculated as: $E_{\text{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The atom labels and molecular structure are provided in Figure S5.

atom label	$q/[\text{e}^-]$	$\epsilon/[\text{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
H	0.4100	0.0010	0.1000
O	-0.8200	0.1553	3.166

Additional Simulation Details

Table S19: The numbers of molecules and the HBA:HBD molar ratios used in the MD simulations of DES/water systems. The HBA components of TBAC-dec, Thy-dec, and Men-dec, are tetrabutylammonium chloride, thymol, and DL-menthol, respectively, and the HBD component of all the DESs is decanoic acid. The each molecule of the HBA component of TBAC-dec is composed of 1 cation (tetrabutylammonium) and 1 anion (chloride). For Men-dec, equal amounts of D-menthol and L-menthol were used as the HBA component (racemic mixture), i.e., 180 D-menthol and 180 L-menthol molecules. For all mixtures, the total numbers of atoms ($N_{\text{atoms}}^{\text{tot}}$) and the approximate box dimensions, $L_x \times L_y \times L_z$ (where each box length is in units of Å, and the z-direction is perpendicular to the interface), after equilibration at 363 K and 1 atm, are also listed.

| DES	molar ratio	N_{HBA}	N_{HBD}	N_{water}	$N_{\text{atoms}}^{\text{tot}}$	$L_x \times L_y \times L_z$
TBAC-dec	1:2	180	360	6000	39240	42×42×228
Thy-dec	1:2	180	360	6000	34020	42×42×203
Men-dec	2:1	360	180	6000	34920	42×42×203

Additional Simulation Results
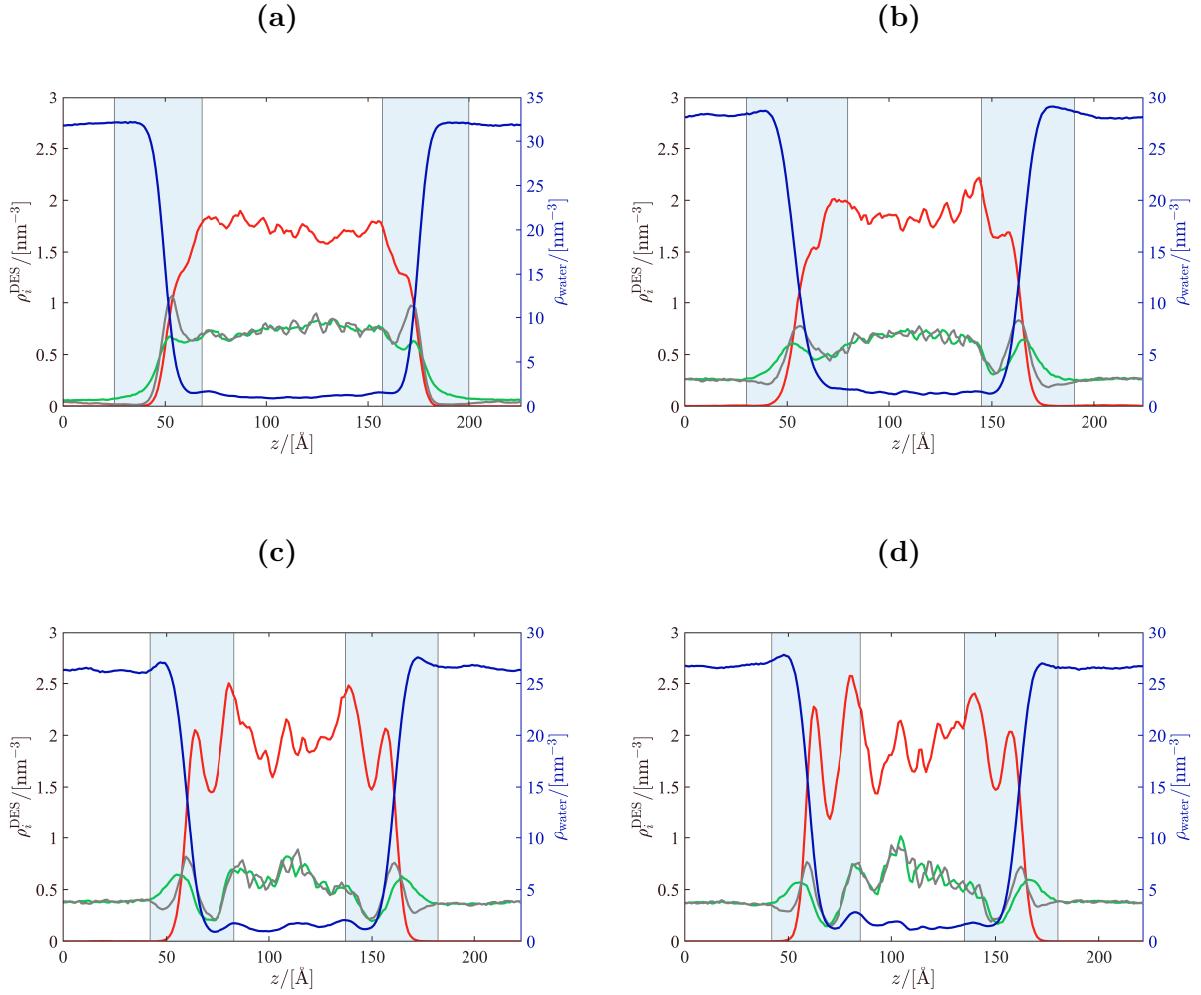
Figure S6: Computed number density profiles (number of molecules per nm^3) of DES components i (left vertical axis) and water (right vertical axis) in the TBAC-dec/water mixture at 343 K and 1 atm, using charge scaling factors of (a) $f_q = 0.6$, (b) $f_q = 0.7$, (c) $f_q = 0.8$, and (d) $f_q = 0.9$ for the HBA. The red, green, gray, and blue colors correspond to decanoic acid (HBD), chloride (anion), choline (cation), and water, respectively. For the density profiles of decanoic acid and choline, the coordinates of the hydroxyl oxygen and the nitrogen atoms were used, respectively. The DES/water interfaces are indicated using blue shaded areas.
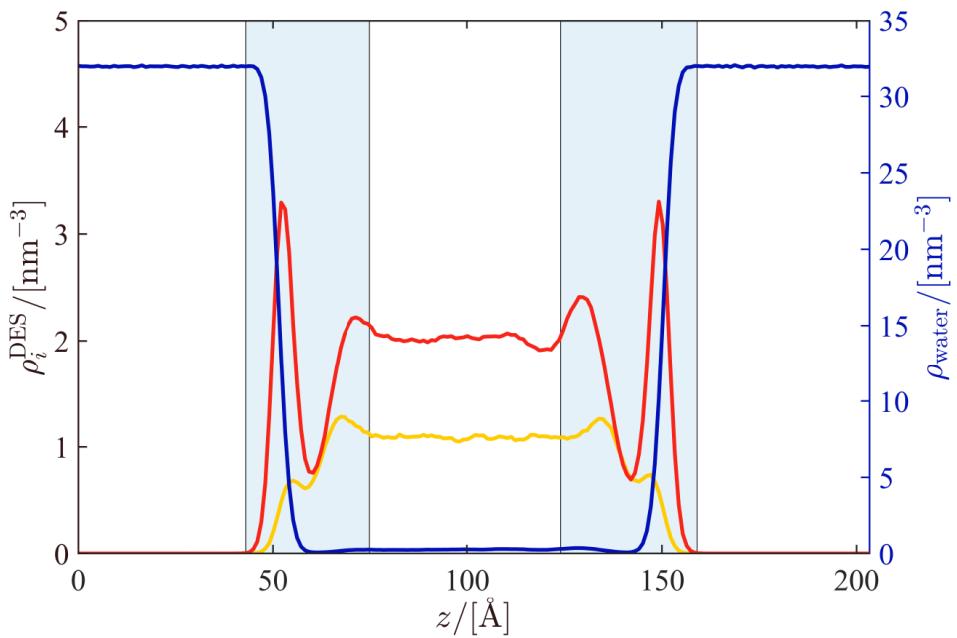
Figure S7: Computed number density profiles (number of molecules per nm^3) of DES components i (left vertical axis) and water (right vertical axis) in the Thy-dec/water mixture at 363 K and 1 atm, using the charge scaling factors $f_q = 0.8/0.8$. The red, yellow, and blue profiles correspond to decanoic acid (HBD), thymol (HBA), and water, respectively. For the density profiles of decanoic acid and thymol, the coordinates of the hydroxyl oxygen atoms were used. The DES/water interfaces are designated using blue shaded areas.
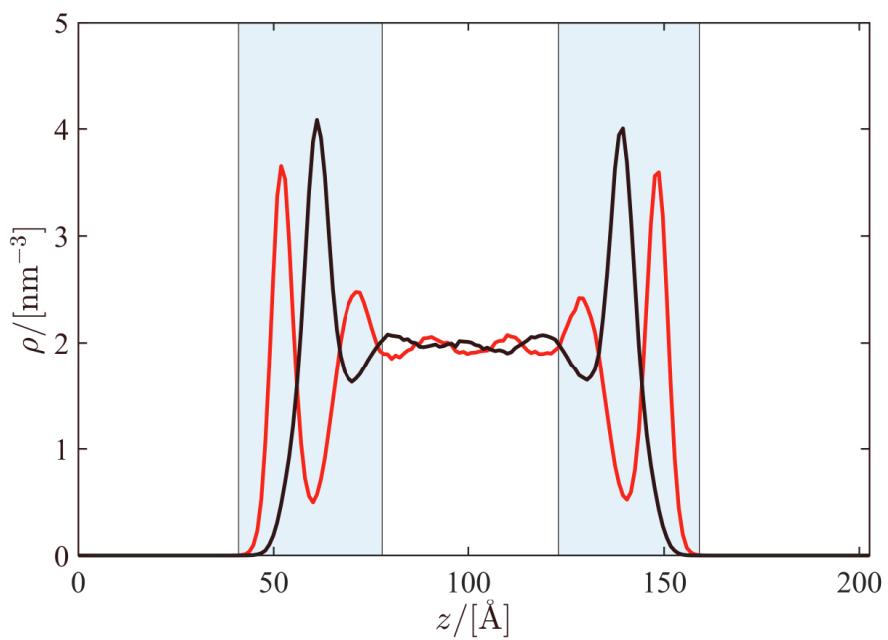
Figure S8: Computed number density profiles (number of molecules per nm^3) for the hydroxyl oxygen (denoted by 'O2' in Figure S4), in red, and the terminal carbon (denoted as 'C1' in Figure S4), in black, of decanoic acid in the Thy-dec/water mixture at 363 K and 1 atm, using the charge scaling factors $f_q = 0.7/1$.

(a)

(b)
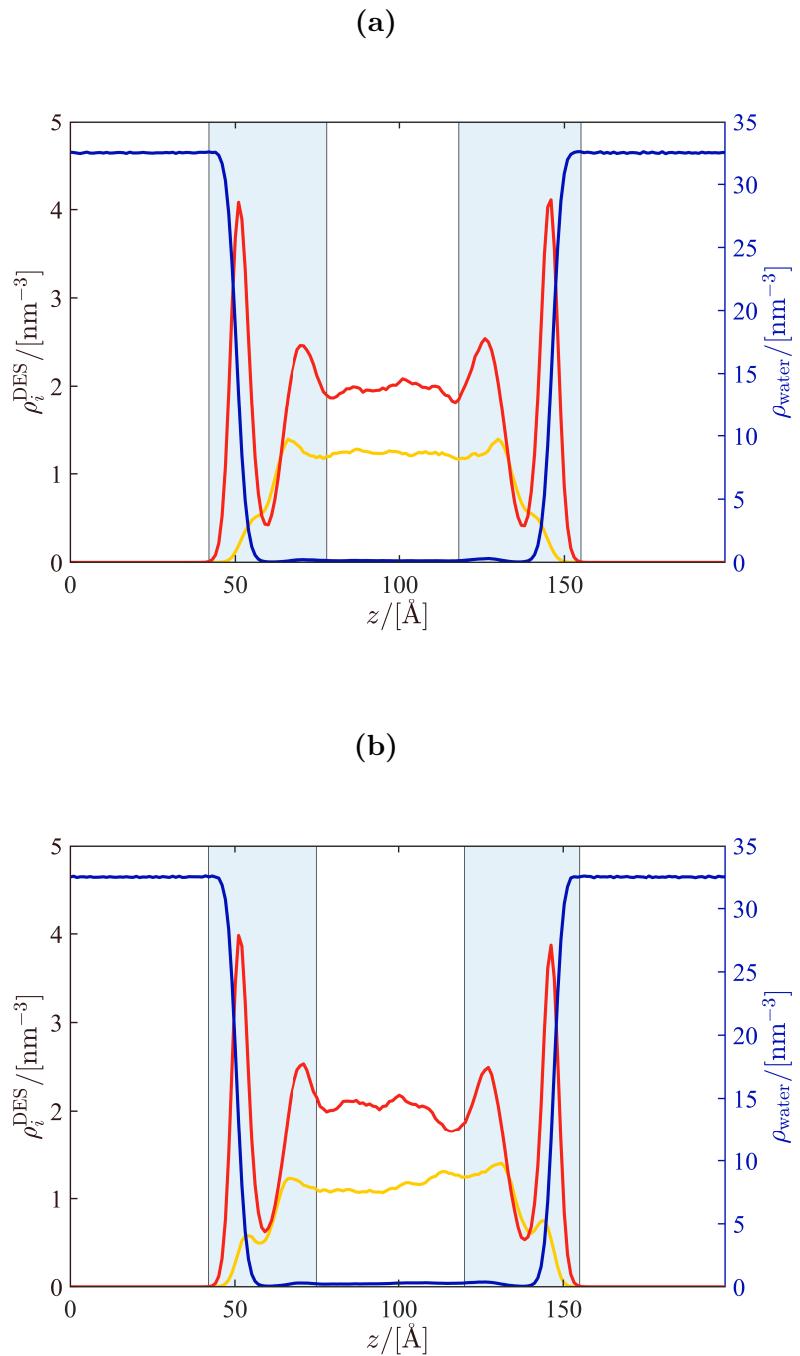
Figure S9: Computed number density profiles (number of molecules per nm³) of DES components i (left vertical axis) and water (right vertical axis) in the Thy-dec/water mixture at 343 K and 1 atm, using the charge scaling factors (a) $f_q = 0.7/1$, and (b) $f_q = 0.8/0.8$. The red, yellow, and blue profiles correspond to decanoic acid (HBD), thymol (HBA), and water, respectively. For the density profiles of decanoic acid and thymol, the coordinates of the hydroxyl oxygen atoms were used. The DES/water interfaces are designated using blue shaded areas.
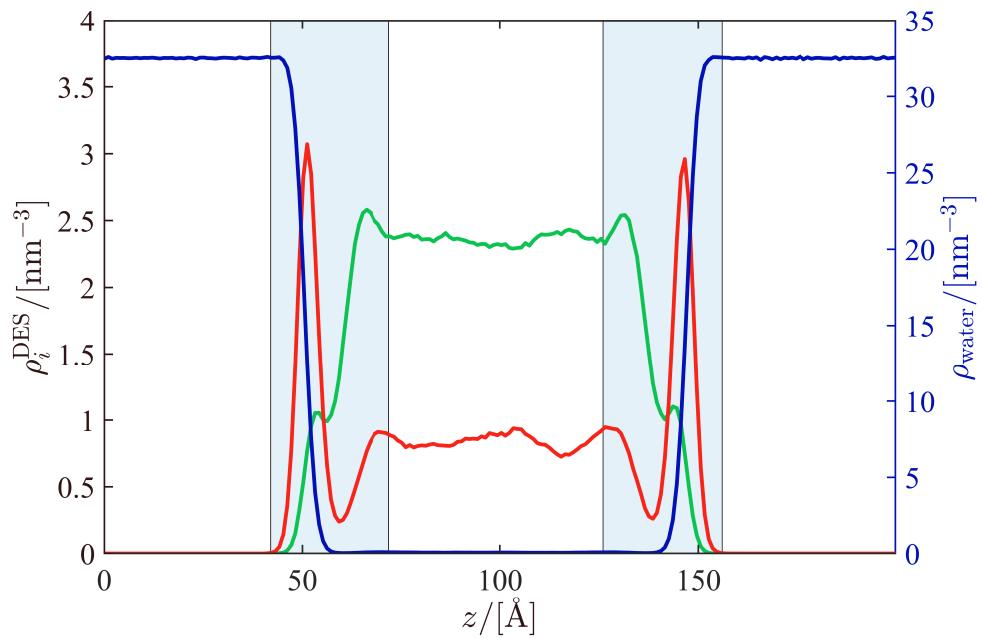
Figure S10: Computed number density profiles (number of molecules per nm^3) of DES components i (left vertical axis) and water (right vertical axis) in the Men-dec/water mixture at 343 K and 1 atm, using the charge scaling factors $f_q = 0.8/1$. The red, green, and blue profiles correspond to decanoic acid (HBD), menthol (HBA), and water, respectively. For the density profiles of decanoic acid and menthol, the coordinates of the hydroxyl oxygen atoms were used. The density profile of menthol includes both D-menthol and L-menthol molecules. The DES/water interfaces are designated using blue shaded areas.
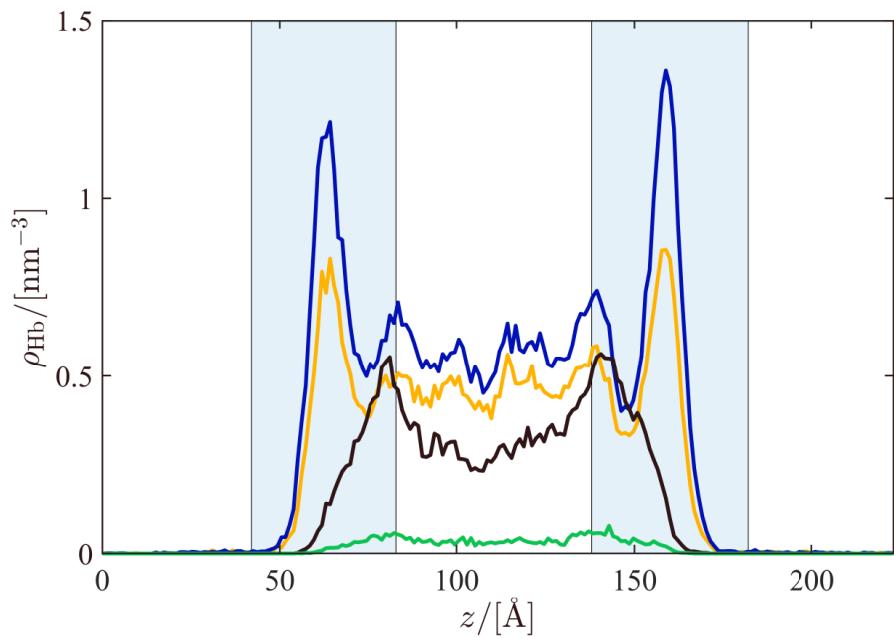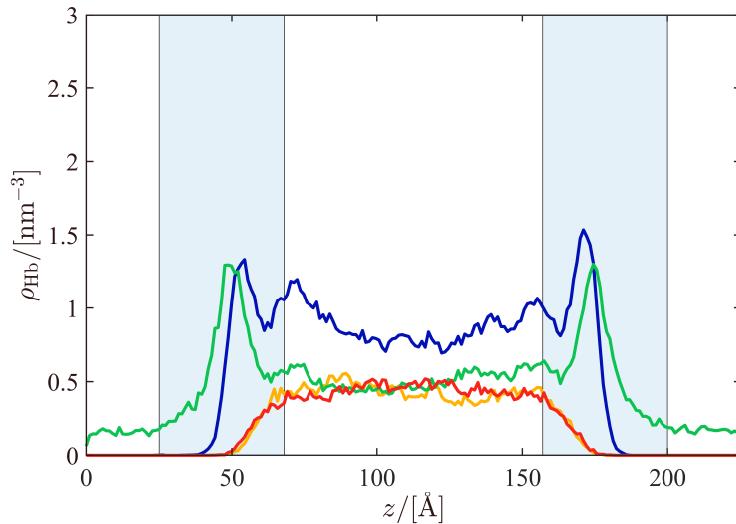
Figure S11: Computed hydrogen bond number densities (number of hydrogen bonds per nm^3) for the TBAC-dec/water system at $363\,\mathrm{K}$ and 1 atm, using the charge scaling factor of f_{q}=0.8. The colors correspond to the different types of hydrogen bonds according to: Blue, between water and the hydroxyl group of decanoic acid; orange, between water and the carbonyl group of decanoic acid; black, between the hydroxyl and carbonyl groups of decanoic acid molecules; and green, between the hydroxyl groups of decanoic acid molecules.

(a)

(b)
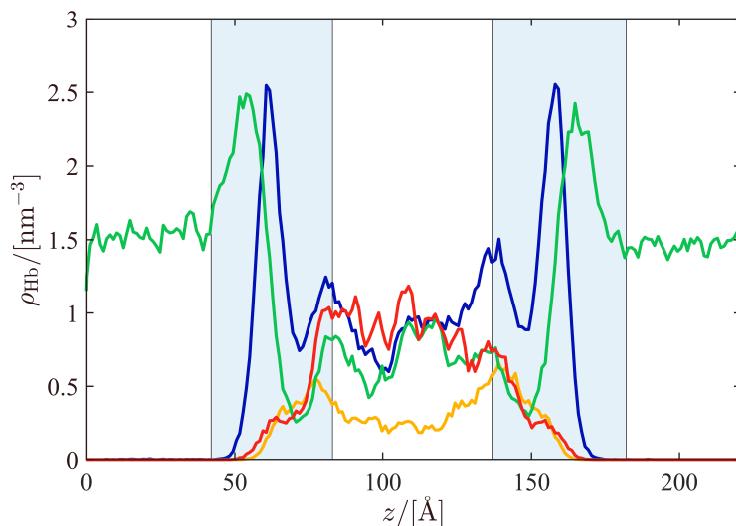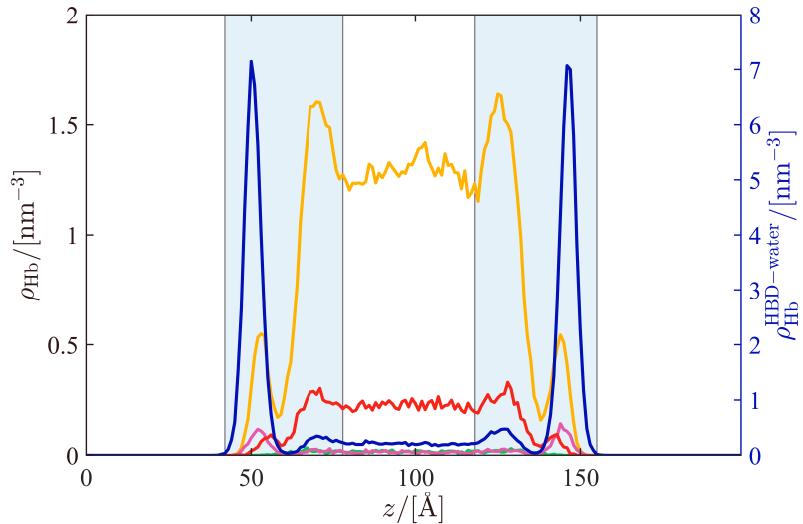
Figure S12: Computed hydrogen bond number densities (number of hydrogen bonds per nm^3) for the TBAC-dec/water system at 343 K and 1 atm, with charge scaling factors of (a) f_q=0.6, and (b) f_q=0.8. The blue, green, yellow, and red colors correspond to water-decanoic acid, water-chloride, decanoic acid-decanoic acid, and chloride-decanoic acid hydrogen bonds, respectively. The blue shaded areas indicate the interfaces.

(a)

(b)
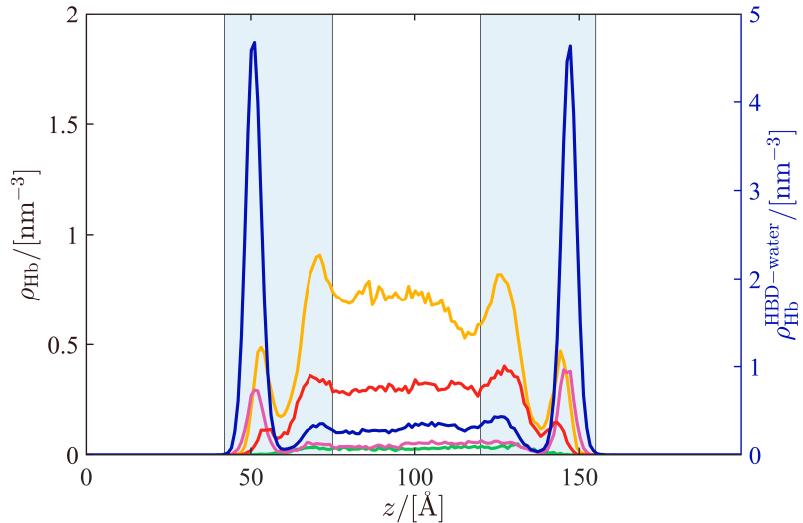
Figure S13: Computed hydrogen bond number densities (number of hydrogen bonds per nm³) for the Thy-dec/water system at $343\,\mathrm{K}$ and 1 atm, with charge scaling factors of (a) f_q=0.7/1, and (b) f_q=0.8/0.8. The blue, green, yellow, red, and pink colors correspond to water-decanoic acid (right vertical axis), thymol-thymol, decanoic acid-decanoic acid, thymol-decanoic acid, and water-thymol hydrogen bonds, respectively. The blue shaded areas indicate the interfaces.

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