

Supplementary Material for: “Thermodynamic, transport, and structural properties of hydrophobic deep eutectic solvents composed of tetraalkylammonium chloride and decanoic acid”

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In this supplementary material, molecular structures and force field parameters used for the Molecular Dynamic (MD) simulations of tetraalkylammonium-based hydrophobic deep eutectic solvents (DESs), as well as additional simulation results are presented. Tetraalkylammonium chloride (TRAC) was used as the hydrogen bond acceptor (HBA) (with tetraalkylammonium (TRA) cation and chloride anion), and decanoic acid was used as the hydrogen bond donor (HBD). 50 HBA and 100 HBD molecules were used in all simulations, corresponding to an HBA/HBD molar ratio of 1:2. Cation alkyl chain lengths of 4 (butyl), 7 (heptyl), and 8 (octyl) were used, for which the corresponding cations are denoted by TBA, THA, and TOA, respectively. The all-atom non-polarizable General AMBER force field (GAFF)¹ was used for all DES components. Bonded terms (bond-stretching, angle-bending, and torsion) as well as non-bonded terms, i.e, Lennard-Jones (LJ) and electrostatic interactions, were

considered for modeling atomic/molecular interactions. For chloride anion, the LJ parameters by Fox and Kollman² were used. All partial atomic charges were derived from quantum mechanical calculations at the HF/6-31G* level of theory and the restrained electrostatic potential (RESP)³ charge fitting procedure using the Gaussian 09 Rev.B.01 software⁴ and the R.E.D-III.52 tools.⁵ To obtain a better agreement between the simulation results and experimental data from literature, a charge scaling of 0.6 was used for all HBA molecules (cations and anions), while the LJ parameters were not scaled. The charge and LJ scaling factors of 0.6 and 1, respectively, were used for all DESs in all production runs. The ionic (partial) charges reported in this document are therefore the scaled values by 0.6, whereas the LJ parameters are unscaled values. The structure and atom labels for all molecules (except for chloride anion) are presented in Figures S1 to S4, and the force field parameters for all molecules are listed in Tables S1 to S11. Finally, additional MD simulation results for densities, viscosities, self-diffusion coefficients, ionic conductivities, radial distribution functions (RDFs), coordination numbers, and hydrogen bond numbers (as addressed in the manuscript) are presented in Tables S12 to S18 and Figures S5 to S14. It should be noted that kcal.mol⁻¹ is used as the energy unit, which can be converted to the kelvin unit (K) by dividing the energy values by the Boltzmann constant (ca. 0.001985875 kcal.mol⁻¹K⁻¹).

Molecular Structures

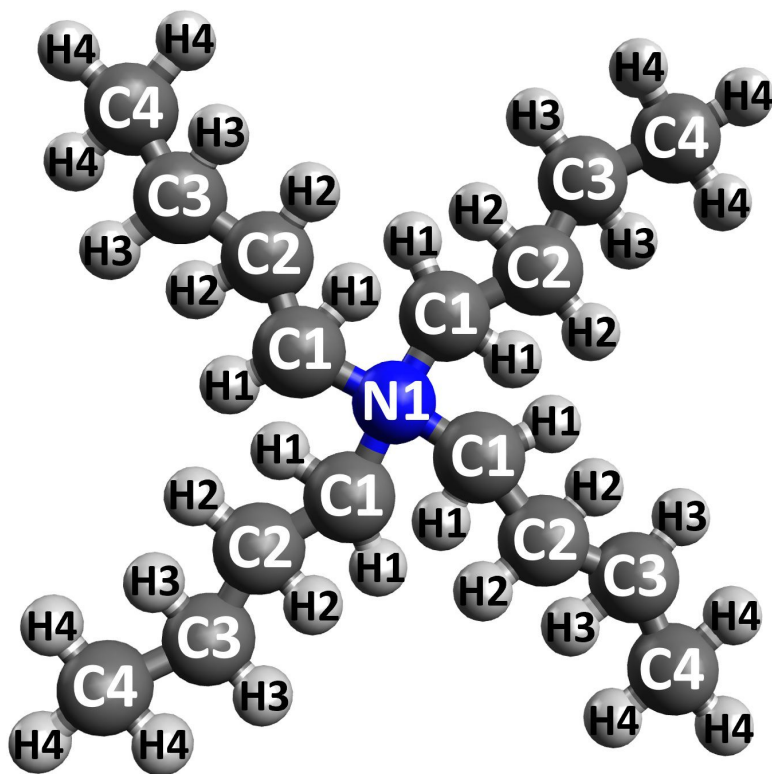


Figure S1: Structure and atom labels of the TBA cation.

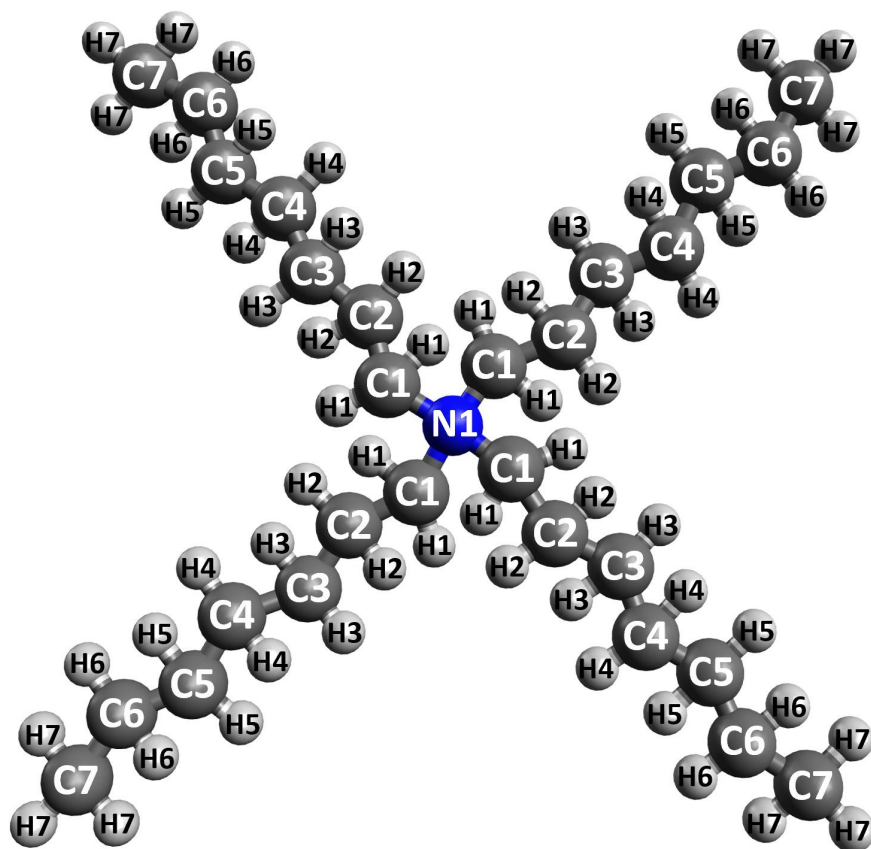


Figure S2: Structure and atom labels of the THA cation.

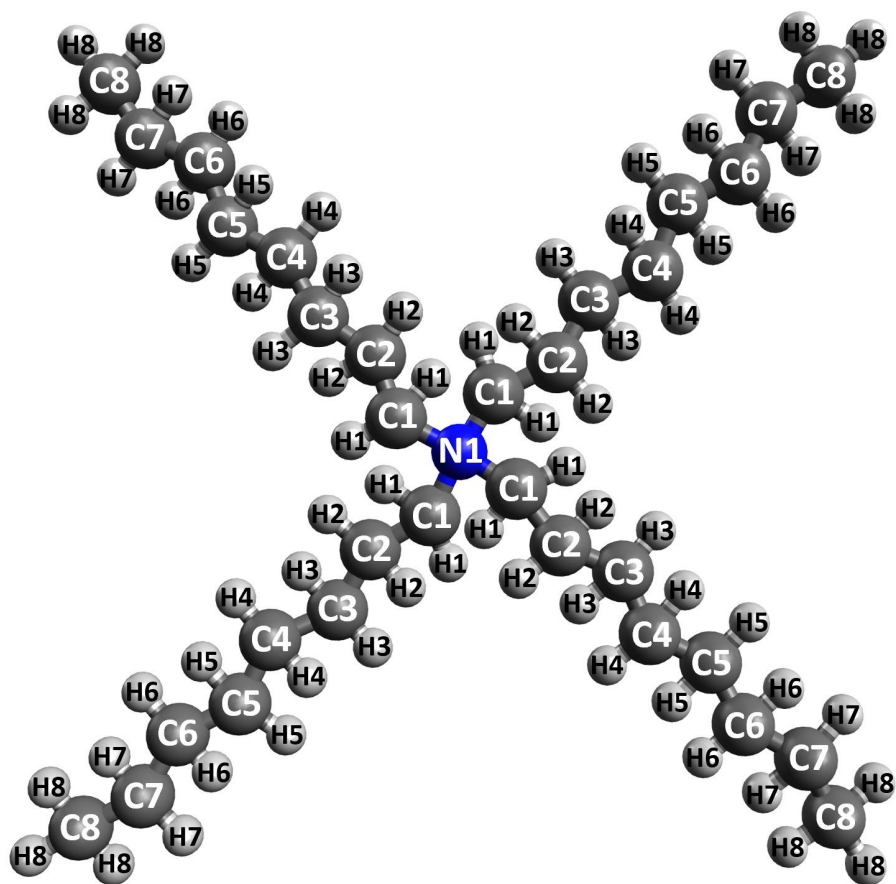


Figure S3: Structure and atom labels of the TOA cation.

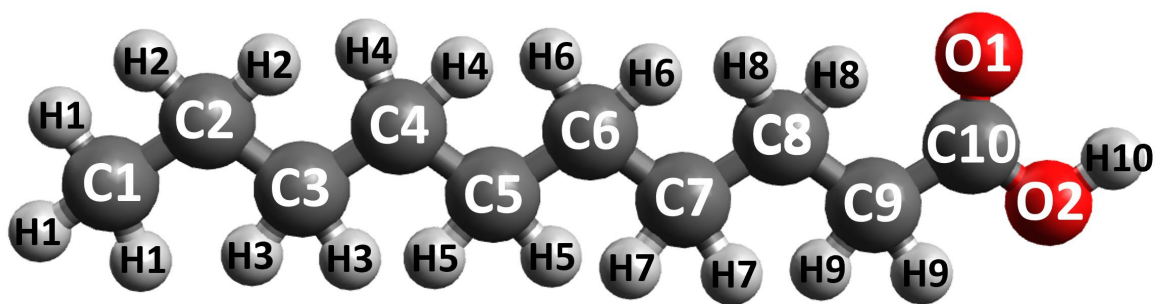


Figure S4: Structure and atom labels of decanoic acid.

Force Field Parameters for TRAC HBAs

Table S1: GAFF atom types and non-bonded parameters for TBA cation.¹ The listed partial charges (q) are the scaled charges (by 0.6) which were used in our MD simulations. 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 LJ interactions are truncated and shifted at 12 Å.

atom label	GAFF atom type	$q/[e^-]$	$\epsilon/[\text{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
C1	c3	-0.00288	0.1094	3.3997
C2	c3	-0.01068	0.1094	3.3997
C3	c3	-0.00576	0.1094	3.3997
C4	c3	-0.06414	0.1094	3.3997
H1	hx	0.03978	0.0157	1.9600
H2	hc	0.02208	0.0157	2.6495
H3	hc	0.01704	0.0157	2.6495
H4	hc	0.02514	0.0157	2.6495
N1	n4	0.00096	0.1700	3.2500

Table S2: GAFF atom types and non-bonded parameters for THA cation.¹ The listed partial charges (q) are the scaled charges (by 0.6) which were used in our MD simulations. 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 LJ interactions are truncated and shifted at 12 Å.

atom label	GAFF atom type	$q/[e^-]$	$\epsilon/[\text{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
C1	c3	-0.00108	0.1094	3.3997
C2	c3	0.00570	0.1094	3.3997
C3	c3	-0.01230	0.1094	3.3997
C4	c3	-0.00708	0.1094	3.3997
C5	c3	-0.00330	0.1094	3.3997
C6	c3	0.01350	0.1094	3.3997
C7	c3	-0.05934	0.1094	3.3997
H1	hx	0.03924	0.0157	1.9600
H2	hc	0.01752	0.0157	2.6495
H3	hc	0.00888	0.0157	2.6495
H4	hc	0.00300	0.0157	2.6495
H5	hc	0.00684	0.0157	2.6495
H6	hc	0.00636	0.0157	2.6495
H7	hc	0.01728	0.0157	2.6495
N1	n4	-0.00648	0.1700	3.2500

Table S3: GAFF atom types and non-bonded parameters for TOA cation.¹ The listed partial charges (q) are the scaled charges (by 0.6) which were used in our MD simulations. 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 LJ interactions are truncated and shifted at 12 Å.

atom label	GAFF atom type	$q/[e^-]$	$\epsilon/[\text{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
C1	c3	-0.00168	0.1094	3.3997
C2	c3	0.00426	0.1094	3.3997
C3	c3	-0.01356	0.1094	3.3997
C4	c3	-0.00042	0.1094	3.3997
C5	c3	0.00006	0.1094	3.3997
C6	c3	-0.00528	0.1094	3.3997
C7	c3	0.01272	0.1094	3.3997
C8	c3	-0.05346	0.1094	3.3997
H1	hx	0.03876	0.0157	1.9600
H2	hc	0.01722	0.0157	2.6495
H3	hc	0.00990	0.0157	2.6495
H4	hc	0.00240	0.0157	2.6495
H5	hc	0.00240	0.0157	2.6495
H6	hc	0.00606	0.0157	2.6495
H7	hc	0.00420	0.0157	2.6495
H8	hc	0.01512	0.0157	2.6495
N1	n4	0.00048	0.1700	3.2500

Table S4: GAFF atom type and non-bonded parameters for chloride anion.² The listed partial charge (q) is the scaled charge (by 0.6) which was used in our MD simulations. The LJ energy is calculated as: $E_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The LJ interactions are truncated and shifted at 12 Å.

atom label	GAFF atom type	partial charge	ϵ /[kcal.mol ⁻¹]	σ /[Å]
Cl	cl	-0.6	0.2650	3.4709

Table S5: Bond parameters for TBA, THA, and TOA cations¹. The bond energy is calculated according to: $E_{\text{bond}}(r) = k_r(r - r_0)^2$.

GAFF bond type	$k_r/[\text{kcal.mol}^{-1}.\text{\AA}^{-2}]$	$r_0/[\text{\AA}]$
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 S6: Angle parameters for TBA, THA, and TOA cations.¹ The angle energy is calculated according to: $E_{\text{angle}}(\theta) = k_{\theta}(\theta - \theta_0)^2$.

GAFF 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 S7: Dihedral parameters for TBA, THA, and TOA cations.¹ The dihedral energy is calculated according to: $E_{\text{dihedral}}(\phi) = A_0 + A_1 \cos(\phi) + A_2 \cos^2(\phi) + A_3 \cos^3(\phi)$.

GAFF 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-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 Decanoic Acid

Table S8: GAFF atom types and non-bonded parameters for decanoic acid.¹ The LJ energy is calculated as: $E_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where r is the site-site distance. The LJ interactions are truncated and shifted at 12 Å.

atom label	GAFF atom type	$q/[e^-]$	$\epsilon/[\text{kcal.mol}^{-1}]$	$\sigma/[\text{Å}]$
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 S9: Bond parameters for decanoic acid.¹ The bond energy is calculated according to: $E_{\text{bond}}(r) = k_r(r - r_0)^2$.

GAFF bond type	$k_r/[\text{kcal.mol}^{-1}.\text{\AA}^{-2}]$	$r_0/[\text{\AA}]$
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 S10: Angle parameters for decanoic acid.¹ The angle energy is calculated according to: $E_{\text{angle}}(\theta) = k_{\theta}(\theta - \theta_0)^2$.

GAFF 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 S11: Dihedral parameters for decanoic acid.¹ The dihedral energy is calculated according to: $E_{\text{dihedral}}(\phi) = A_0 + A_1 \cos(\phi) + A_2 \cos^2(\phi) + A_3 \cos^3(\phi)$.

GAFF 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
c3-o-c-oh ^a	2.2000	0.0000	2.2000	0.0000

^a Improper dihedral

Additional Simulation Results

Table S12: Computed average densities for TBAC-dec, THAC-dec, and TOAC-dec DESs, with HBA/HBD molar ratios of 1:2, at various temperatures and 1 atm. The values in parentheses are the uncertainties within a 95% confidence interval.

$T/[K]$	$\rho/[kg.m^{-3}]$		
	TBAC-dec	THAC-dec	TOAC-dec
298.15	901.8(0.8)	885.7(0.3)	883.0(1.0)
313.15	891.6(0.3)	875.6(0.6)	872.4(0.4)
323.15	884.2(0.3)	868.0(0.8)	865.1(0.7)
333.15	876.7(0.4)	861.1(0.3)	858.4(0.5)
343.15	869.4(0.3)	853.7(0.4)	850.8(0.8)
353.15	862.0(0.2)	846.7(0.5)	843.7(0.2)
363.15	854.8(0.2)	839.6(0.2)	836.9(0.2)

Table S13: Computed average viscosities for TBAC-dec, THAC-dec, and TOAC-dec DESs, with HBA/HBD molar ratios of 1:2, at various temperatures and 1 atm. The values in parentheses are the uncertainties within a 95% confidence interval.

T /[K]	η /[cP]		
	TBAC-dec	THAC-dec	TOAC-dec
323.15	75.8(6.8)	122.9(10.9)	188.2(55.1)
333.15	49.9(7.4)	91.0(13.0)	100.0(10.8)
343.15	28.8(4.2)	63.3(8.8)	69.3(3.8)
353.15	19.4(0.8)	38.8(2.8)	41.8(6.2)
363.15	13.0(1.5)	26.1(0.7)	31.1(4.0)

Table S14: Computed average finite size-corrected self-diffusion coefficients for cation, anion, and HBD in TBAC-dec DES, with a HBA/HBD molar ratio of 1:2, at various temperatures and 1 atm.

$T/[\text{K}]$	$D_{\text{self}}^{\infty}/[10^{-11}\text{m}^2.\text{s}^{-1}]$		
	anion	cation	HBD
323.15	1.22	0.93	1.44
333.15	2.20	1.67	2.53
343.15	3.53	2.77	3.89
353.15	5.59	4.20	6.37
363.15	8.58	6.47	9.24

Table S15: Computed average finite size-corrected self-diffusion coefficients for cation, anion, and HBD in THAC-dec DES, with a HBA/HBD molar ratio of 1:2, at various temperatures and 1 atm.

$T/[\text{K}]$	$D_{\text{self}}^{\infty}/[10^{-11}\text{m}^2.\text{s}^{-1}]$		
	anion	cation	HBD
323.15	0.55	0.39	0.90
333.15	0.93	0.69	1.55
343.15	1.42	1.03	2.44
353.15	2.33	1.72	3.73
363.15	3.46	2.51	5.67

Table S16: Computed average finite size-corrected self-diffusion coefficients for cation, anion, and HBD in TOAC-dec DES, with a HBA/HBD molar ratio of 1:2, at various temperatures and 1 atm.

$T/[\text{K}]$	$D_{\text{self}}^{\infty}/[10^{-11}\text{m}^2.\text{s}^{-1}]$		
	anion	cation	HBD
323.15	0.48	0.31	0.80
333.15	0.74	0.51	1.32
343.15	1.19	0.87	2.21
353.15	1.83	1.32	3.35
363.15	2.70	2.10	4.91

Table S17: Computed average ionic conductivities for TBAC-dec, THAC-dec, and TOAC-dec DESs, with HBA/HBD molar ratios of 1:2, at various temperatures and 1 atm.

T /[K]	κ /[$\mu\text{S}\cdot\text{cm}^{-1}$]		
	TBAC-dec	THAC-dec	TOAC-dec
323.15	380.5	129.3	101.0
333.15	658.4	212.8	153.6
343.15	1035.1	311.2	243.2
353.15	1546.6	496.0	358.0
363.15	2295.0	703.0	527.5

Table S18: Coordination numbers, CN_{ij} (of atom type j around atom type i), in TBAC-dec, THAC-dec DES, and TOAC-dec DESs at 343.15K and 1 atm. O, HO, N, and Cl denote the carbonyl oxygen and hydroxyl hydrogen of decanoic acid, nitrogen of cation, and chloride anion, respectively. If the numbers of atoms i and j are the same in the mixture, $CN_{ij} = CN_{ji}$. For the O-HO coordination number, only the intermolecular contributions are considered (Figure S7).

atom type i	atom type j	TBAC-dec		THAC-dec		TOAC-dec	
		CN_{ij}	CN_{ji}	CN_{ij}	CN_{ji}	CN_{ij}	CN_{ji}
N	Cl	2.43	2.43	2.03	2.03	2.02	2.02
O	HO	0.39	0.39	0.37	0.37	0.37	0.37
O	N	0.75	1.49	0.74	1.49	0.70	1.40
Cl	HO	1.20	0.60	1.24	0.62	1.18	0.59

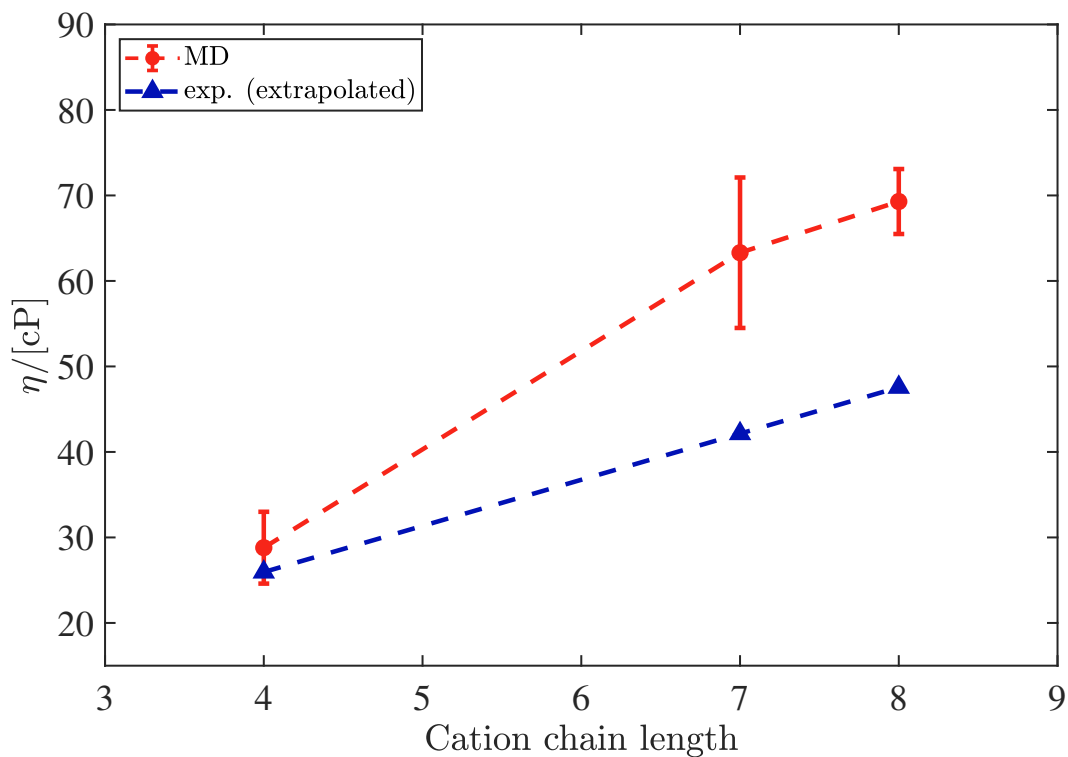


Figure S5: Viscosities of TRAC-dec DESs as a function of cation chain length at 343.15 K and 1 atm, compared with the extrapolated (to 343.15 K) values from experimental data by van Osch et al.⁶ The experimental viscosity data point of THAC-dec (chain length of 7), shown in this figure, was obtained by interpolating the experimental viscosities of TBAC-dec and TOAC-dec with respect to cation chain length, and is therefore not equal to the value reported by van Osch et al.⁶ The dashed lines are added to guide the eye.

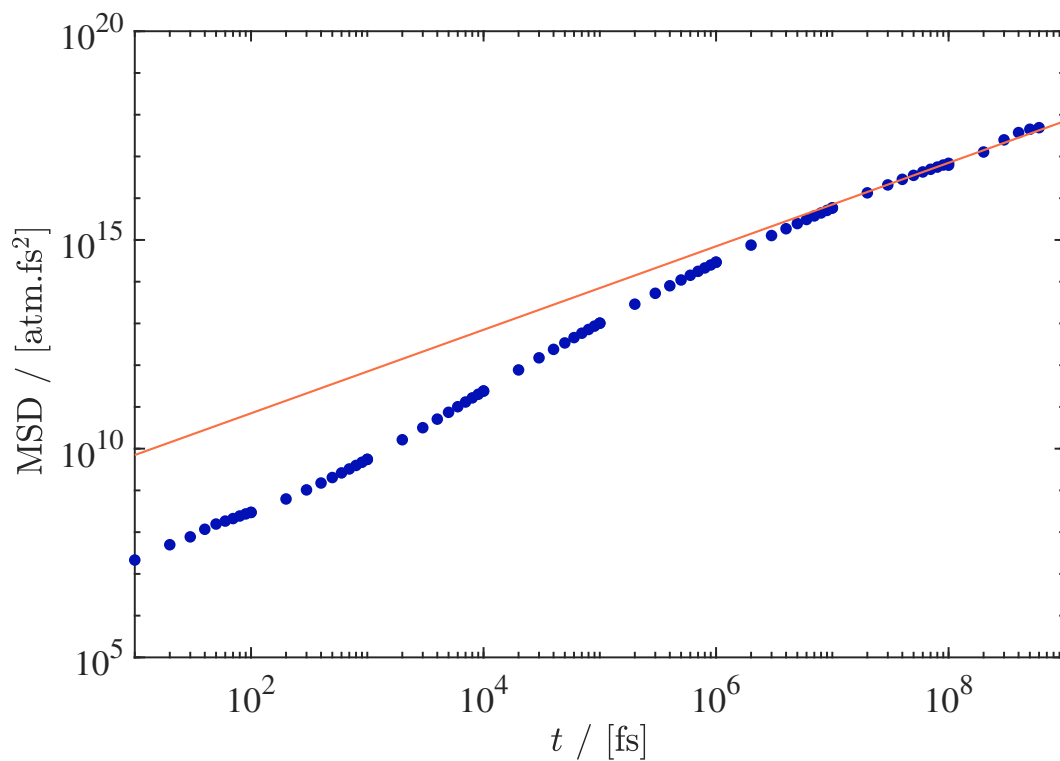


Figure S6: Log-log plot for the mean squared displacement (MSD) of the off-diagonal components of pressure tensor in TOAC-dec at 343.15 K as a function of correlation time (blue circles). The red solid line corresponds to the linear fit with a slope of 1 (diffusive regime), yielding a viscosity value of 69.3 cP.

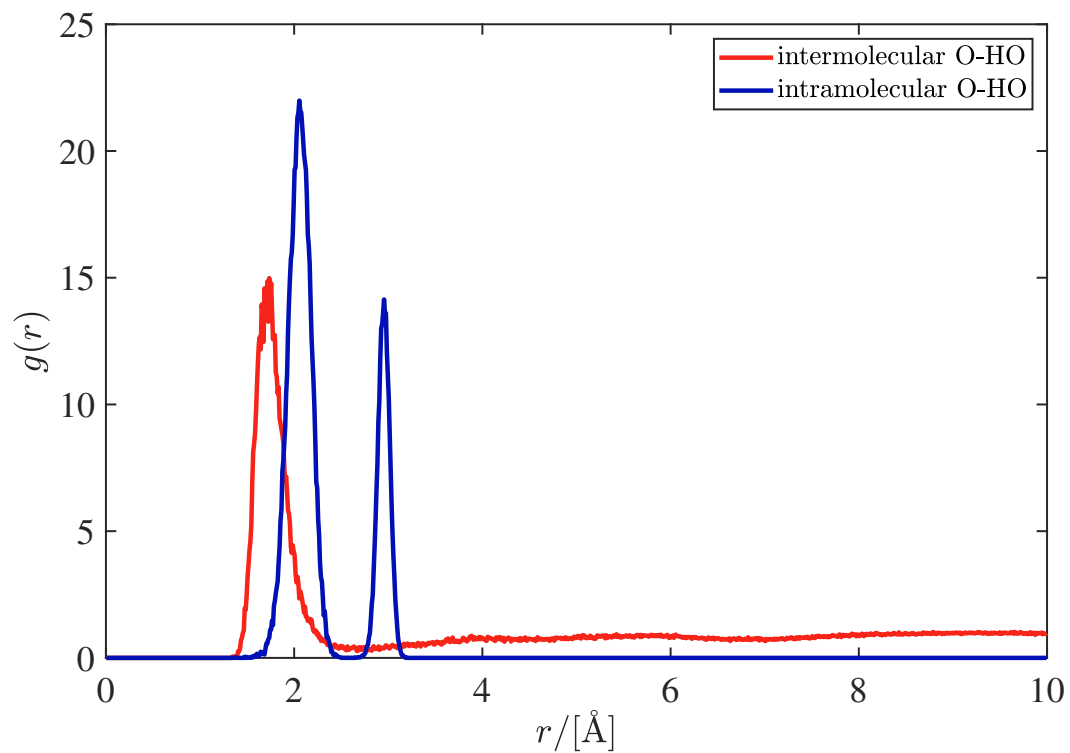


Figure S7: Inter- and intramolecular RDFs for the interaction between the hydroxyl hydrogen and carbonyl oxygen of decanoic acid in TBAC-dec at 343.15 K and 1 atm.

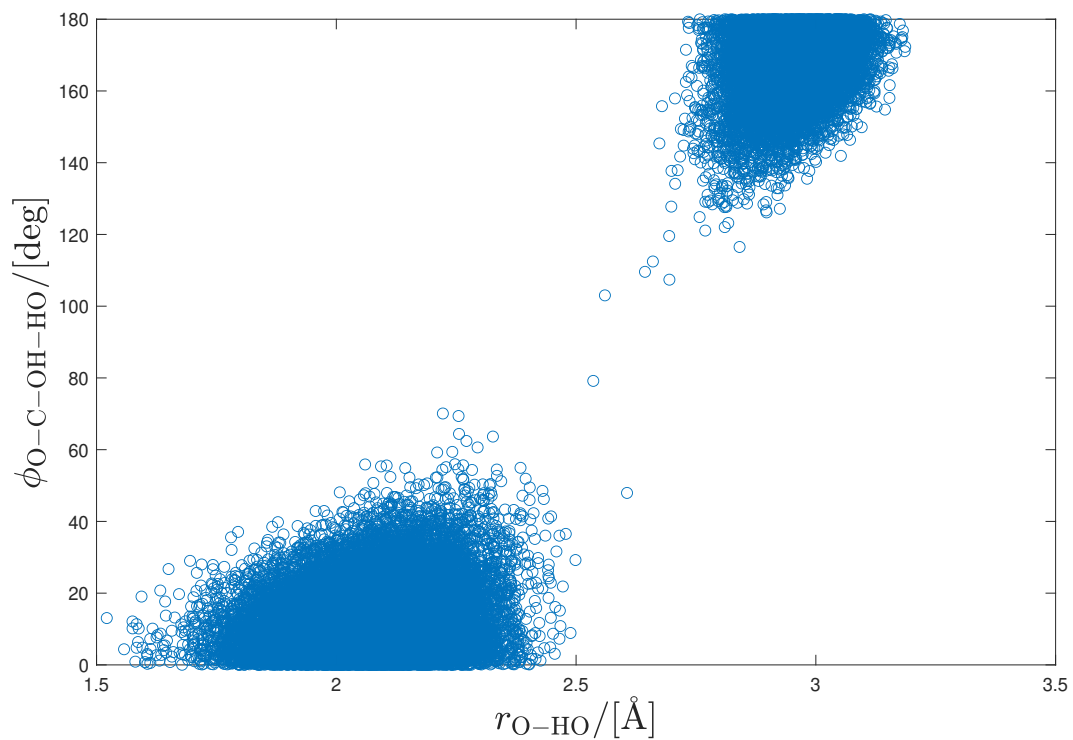


Figure S8: The O-C-OH-HO dihedral angle of decanoic acid at various intramolecular O-HO distances in TBAC-dec at 343.15 K and 1 atm. The depicted data points were obtained from snapshots of atomic coordinates from all 5 independent NVT runs (over the last 100 ns to 150 ns).

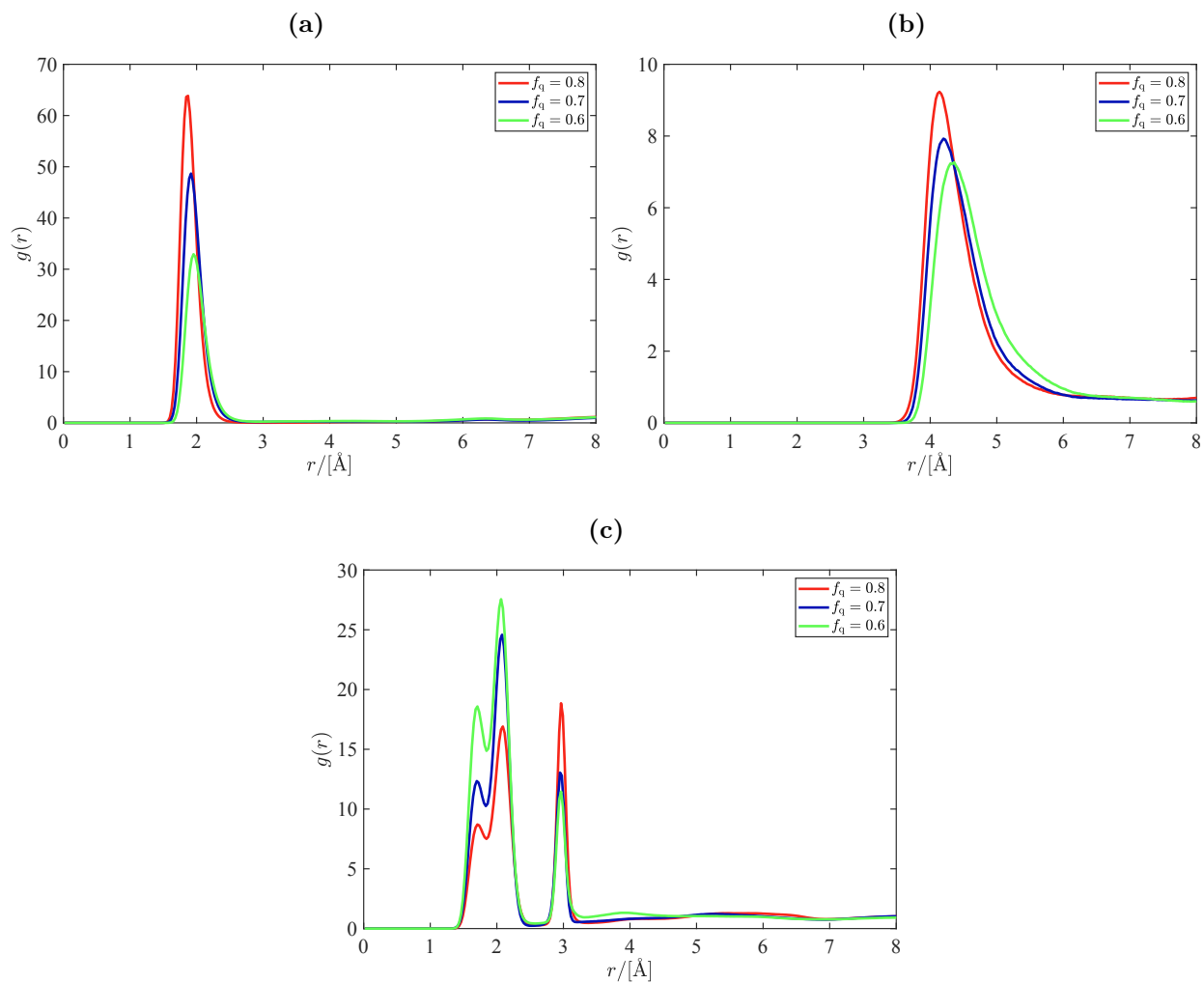


Figure S9: RDFs for the interactions between (a) chloride anion and hydroxyl hydrogen of decanoic acid (Cl-HO), (b) nitrogen atom of cation and chloride anion (N-Cl), and (c) carbonyl oxygen and hydroxyl hydrogen of decanoic acid (O-HO), from MD simulations of TBAC-dec at 298.15 K and 1 atm for various ionic charge scaling factors (f_q).

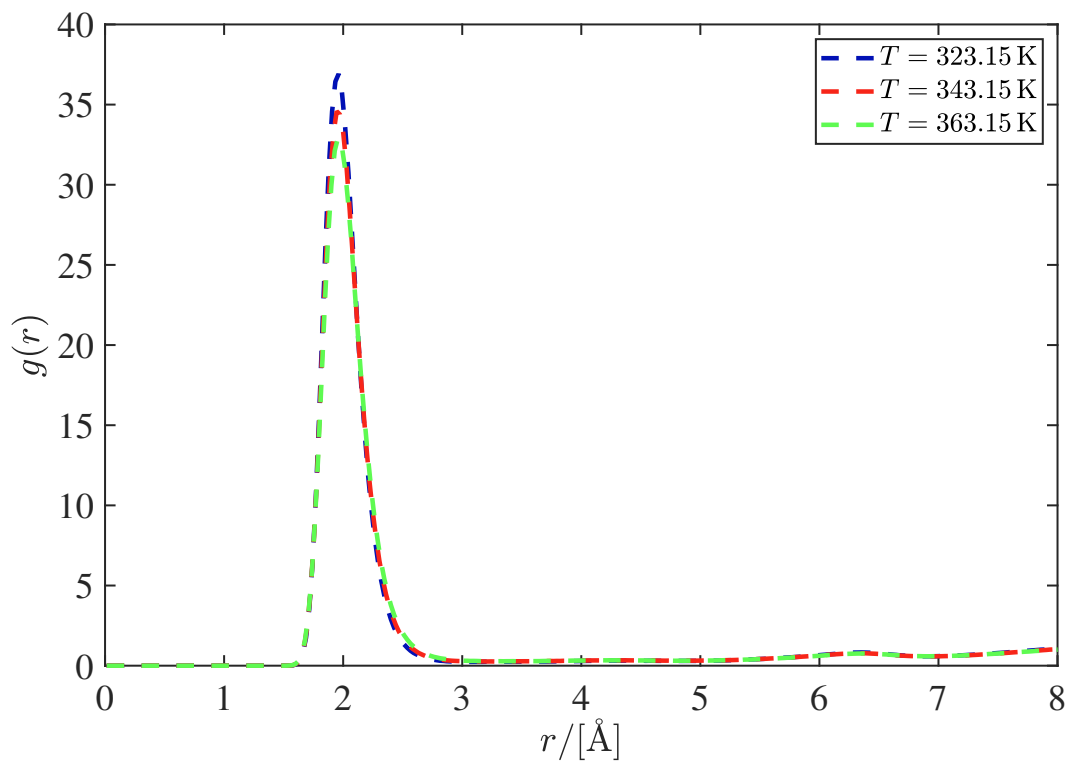


Figure S10: RDFs for the interaction between chloride anion and hydroxyl hydrogen of decanoic acid (Cl-HO) in TBAC-dec DES at various temperatures and 1 atm.

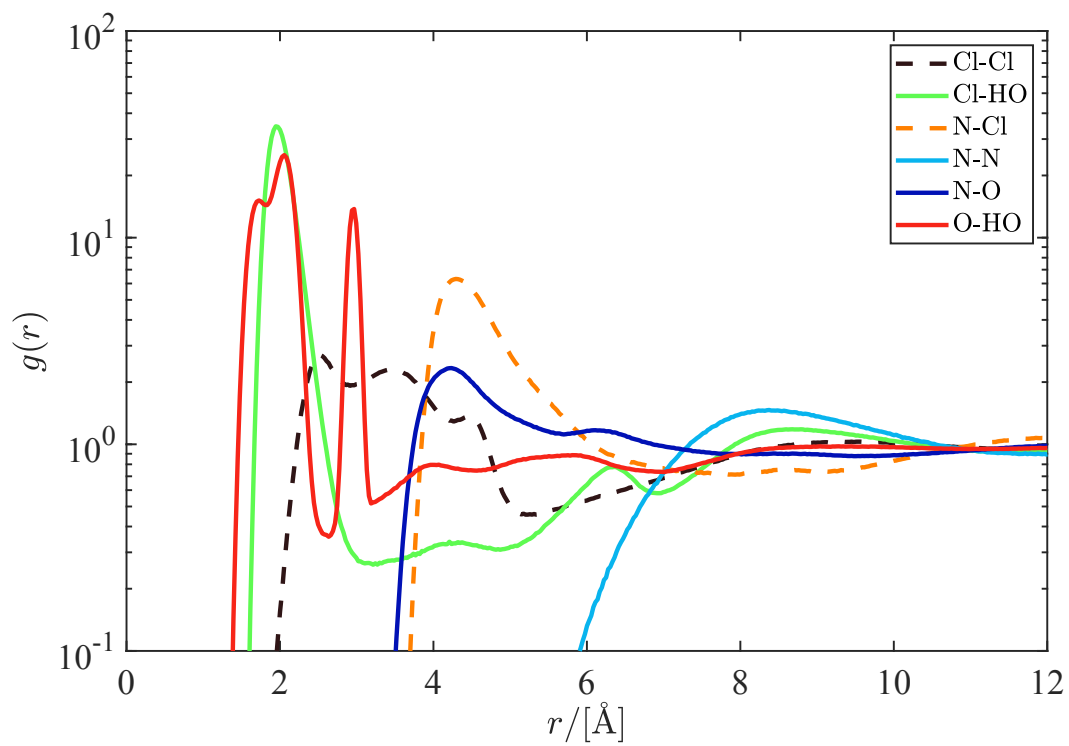


Figure S11: RDFs for various atom pairs in TBAC-dec DES at 343.15 K and 1 atm.

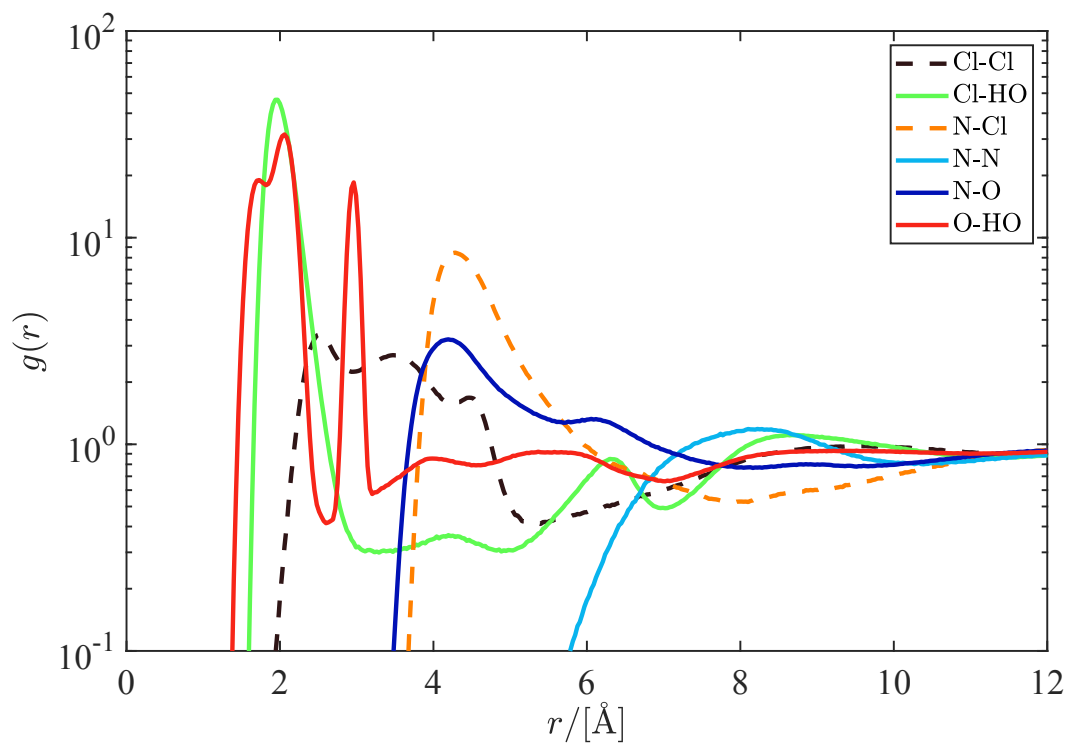


Figure S12: RDFs for various atom pairs in THAC-dec DES at 343.15 K and 1 atm.

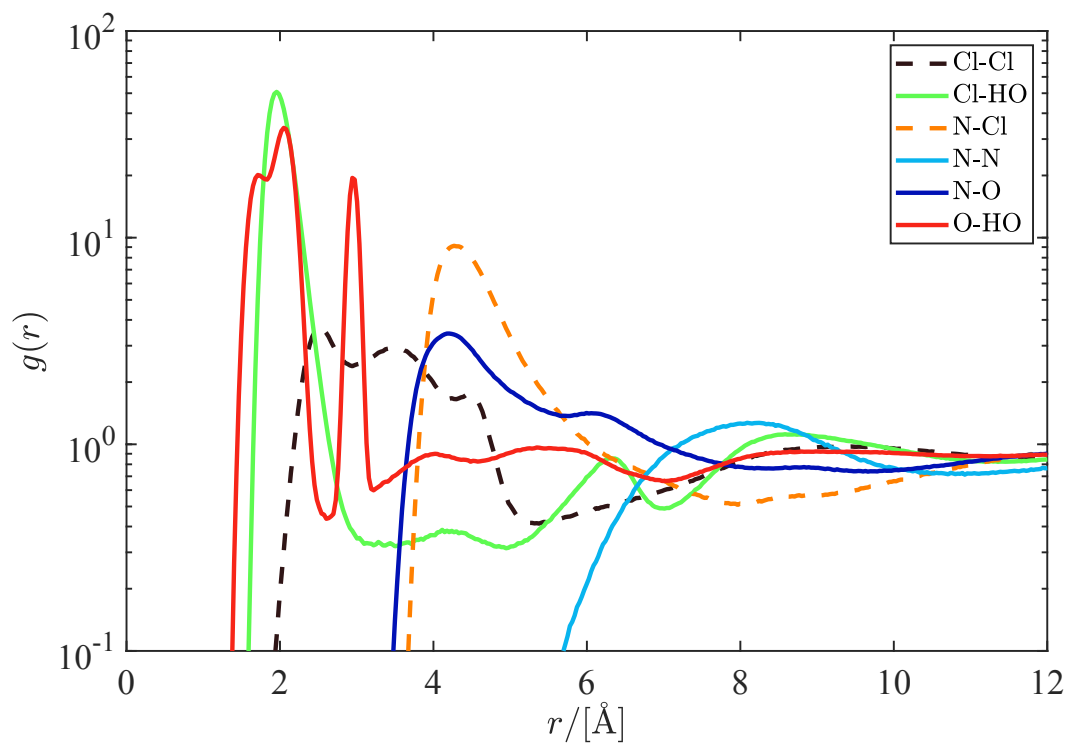


Figure S13: RDFs for various atom pairs in TOAC-dec DES at 343.15 K and 1 atm.

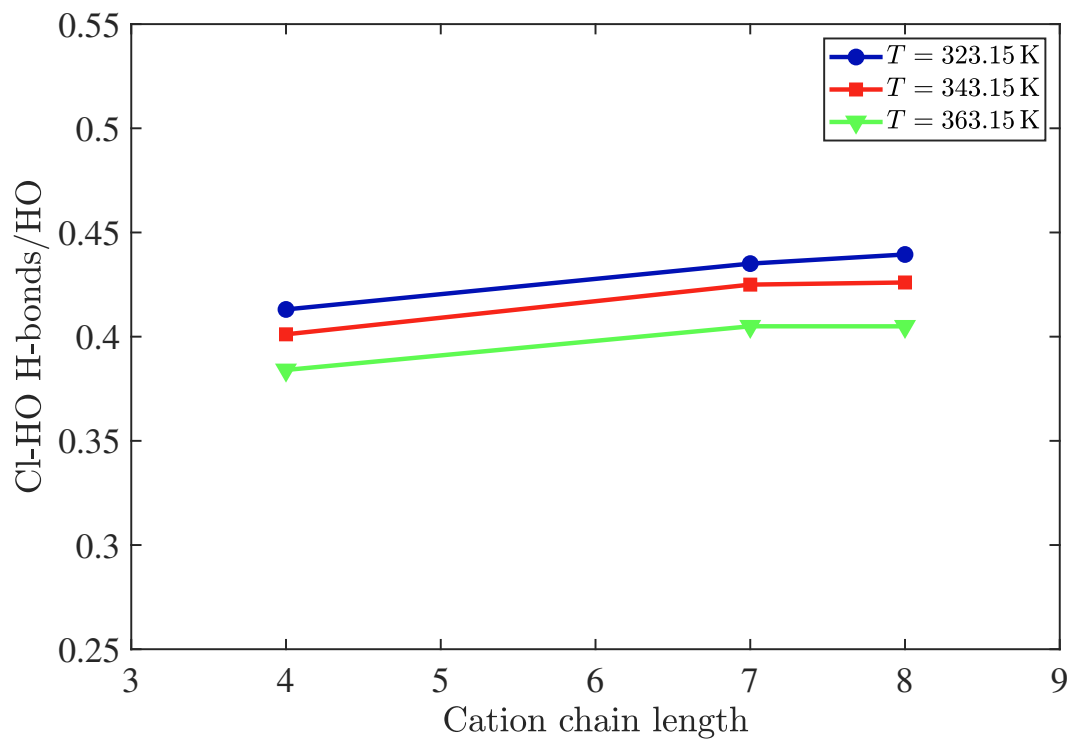


Figure S14: Number of Cl-HO hydrogen bonds (per number of HO atoms) at various temperatures and 1 atm, as a function of cation chain length for TRAC-dec DESs.

References

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