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

Thermophysical Properties of Glyceline-Water Mixtures Investigated by Molecular Modelling

Supplementary Information

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1. Force field parameters for the cholinium cation

Table S1: Partial charges and atomic masses.

no.	name	q /e	mass / a.u.
1	CA	-0.12078	12.011
2	HA	0.10737	1.008
3	HA	0.10737	1.008
4	HA	0.10737	1.008
5	NA	0.04518	14.0067
6	CS	-0.02898	12.011
7	CA	-0.12078	12.011
8	CA	-0.12078	12.011
9	HA	0.10737	1.008
10	HA	0.10737	1.008
11	HA	0.10737	1.008
12	HA	0.10737	1.008
13	HA	0.10737	1.008
14	HA	0.10737	1.008
15	HS	0.10044	1.008
16	HS	0.10044	1.008
17	CW	0.13509	12.011
18	OY	-0.55701	15.9994
19	HCW	0.0459	1.008
20	HCW	0.0459	1.008
21	HY	0.40905	1.008

Table S2: Lennard-Jones parameters.

name	σ / nm	ε / kJ mol^{-1}
CA	3.39967E-01	4.57730E-01
CS	3.39967E-01	4.57730E-01
CW	3.39967E-01	4.57730E-01
NA	3.25000E-01	7.11280E-01
OY	3.06647E-01	8.80314E-01
HA	1.95998E-01	6.56888E-02
HS	1.95998E-01	6.56888E-02
HCW	2.47135E-01	6.56888E-02
HY	1.99600E-02	4.18000E-03

Table S3: Equilibrium bond lengths.

atom i	atom j	bond length / nm
1	5	0.1499
2	1	0.1091
3	1	0.1091
4	1	0.1091
6	17	0.1535
7	5	0.1499
8	5	0.1499
9	7	0.1091
10	7	0.1091
11	7	0.1091
12	8	0.1091
13	8	0.1091
14	8	0.1091
15	6	0.1091
16	6	0.1091
17	18	0.1426
18	21	0.0974
19	17	0.1093
20	17	0.1093
5	6	0.1499

Table S4: Equilibrium bending angles and force constants.

atom i	atom j	atom k	θ_{eq} / °	K_θ / kJ mol^{-1} rad^{-2}
1	5	6	110.6400473	525.84512
1	5	7	110.6400473	525.84512
1	5	8	110.6400473	525.84512
2	1	3	110.7400473	326.68672
2	1	4	110.7400473	326.68672
2	1	5	107.9100461	410.19936
3	1	4	110.7400473	326.68672

3	1	5	107.9100461	410.19936
4	1	5	107.9100461	410.19936
5	6	15	107.9100461	410.19936
5	6	16	107.9100461	410.19936
5	6	17	114.3200492	539.3176
6	17	18	109.430047	566.68096
6	17	19	110.0700471	387.94048
6	17	20	110.0700471	387.94048
7	5	6	110.6400473	525.84512
7	5	8	110.6400473	525.84512
8	5	6	110.6400473	525.84512
9	7	5	107.9100461	410.19936
9	7	10	110.7400473	326.68672
9	7	11	110.7400473	326.68672
10	7	5	107.9100461	410.19936
10	7	11	110.7400473	326.68672
11	7	5	107.9100461	410.19936
12	8	5	107.9100461	410.19936
12	8	13	110.7400473	326.68672
12	8	14	110.7400473	326.68672
13	8	5	107.9100461	410.19936
13	8	14	110.7400473	326.68672
14	8	5	107.9100461	410.19936
15	6	16	109.5500472	327.85824
15	6	17	111.7400478	385.09536
16	6	17	111.7400478	385.09536
17	18	21	108.1600465	394.04912
19	17	18	109.8800469	426.51696
19	17	20	109.5500472	327.85824
20	17	18	109.8800469	426.51696

Table S5: Dihedral angles.

atom i	atom j	atom k	atom l	φ_s / °	K_φ / kJ mol^{-1}	n
1	5	6	15	0	0.652704	3
1	5	6	16	0	0.652704	3
1	5	6	17	0	0.652704	3
1	5	7	9	0	0.652704	3
1	5	7	10	0	0.652704	3
1	5	7	11	0	0.652704	3
1	5	8	12	0	0.652704	3
1	5	8	13	0	0.652704	3
1	5	8	14	0	0.652704	3
2	1	5	6	0	0.652704	3
2	1	5	7	0	0.652704	3
2	1	5	8	0	0.652704	3
3	1	5	6	0	0.652704	3
3	1	5	7	0	0.652704	3
3	1	5	8	0	0.652704	3
4	1	5	6	0	0.652704	3
4	1	5	7	0	0.652704	3
4	1	5	8	0	0.652704	3
5	6	17	18	0	0.652704	3
5	6	17	19	0	0.652704	3
5	6	17	20	0	0.652704	3
6	17	18	21	0	0.66944	3
6	17	18	21	0	1.046	1
7	5	6	15	0	0.652704	3
7	5	6	16	0	0.652704	3
7	5	6	17	0	0.652704	3
7	5	8	12	0	0.652704	3
7	5	8	13	0	0.652704	3
7	5	8	14	0	0.652704	3
8	5	6	15	0	0.652704	3
8	5	6	16	0	0.652704	3

8	5	6	17	0	0.652704	3
9	7	5	6	0	0.652704	3
9	7	5	8	0	0.652704	3
10	7	5	6	0	0.652704	3
10	7	5	8	0	0.652704	3
11	7	5	6	0	0.652704	3
11	7	5	8	0	0.652704	3
12	8	5	6	0	0.652704	3
13	8	5	6	0	0.652704	3
14	8	5	6	0	0.652704	3
15	6	17	18	0	0.652704	3
15	6	17	19	0	0.652704	3
15	6	17	20	0	0.652704	3
16	6	17	18	0	0.652704	3
16	6	17	19	0	0.652704	3
16	6	17	20	0	0.652704	3
19	17	18	21	0	0.698728	3
20	17	18	21	0	0.698728	3

2. Force field parameters for chloride anion

Table S6: Partial charges and atomic masses.

no.	name	q /e	mass / a.u.
1	Cl	-0.90	35.435

Table S7: Lennard-Jones parameters.

name	σ / nm	ε / kJ mol^{-1}
Cl	4.40100E-01	4.18480E-01

3. Force field parameters for glycerol

Table S8: Partial charges and atomic masses.

no.	name	q /e	mass / a.u.
1	C3	0.1197	12.010
2	C3	0.1521	12.010
3	C3	0.1197	12.010
4	OH	-0.6270	16.000
5	OH	-0.5848	16.000
6	OH	-0.6270	16.000
7	H1	0.0537	1.008
8	H1	0.0537	1.008
9	H1	0.0221	1.008
10	H1	0.0537	1.008
11	H1	0.0537	1.008
12	HO	0.4096	1.008
13	HO	0.3912	1.008
14	HO	0.4096	1.008

Table S9: Lennard-Jones parameters.

name	σ / nm	ε / kJ mol^{-1}
C3	3.40E-01	4.58E-01
H1	2.47E-01	6.57E-02
HO	2.00E-02	4.18E-03
OH	3.07E-01	8.80E-01

Table S10: Equilibrium bond lengths.

atom i	atom j	bond length / nm
1	2	1.54E-01
1	6	1.43E-01
1	7	1.09E-01
1	8	1.09E-01
2	3	1.54E-01

2	5	1.43E-01
2	9	1.09E-01
3	4	1.43E-01
3	10	1.09E-01
3	11	1.09E-01
4	12	9.74E-02
5	13	9.74E-02
6	14	9.74E-02

Table S11: Equilibrium bending angles and force constants.

atom i	atom j	atom k	θ_{eq} / °	K_θ / kJ mol^{-1} rad^{-2}
1	2	3	1.11E+02	5.29E+02
1	2	5	1.09E+02	5.67E+02
1	2	9	1.10E+02	3.88E+02
1	6	14	1.08E+02	3.94E+02
2	1	6	1.09E+02	5.67E+02
2	1	7	1.10E+02	3.88E+02
2	1	8	1.10E+02	3.88E+02
2	3	4	1.09E+02	5.67E+02
2	3	10	1.10E+02	3.88E+02
2	3	11	1.10E+02	3.88E+02
2	5	13	1.08E+02	3.94E+02
3	2	5	1.09E+02	5.67E+02
3	2	9	1.10E+02	3.88E+02
3	4	12	1.08E+02	3.94E+02
4	3	10	1.10E+02	4.27E+02
4	3	11	1.10E+02	4.27E+02
5	2	9	1.10E+02	4.27E+02
6	1	7	1.10E+02	4.27E+02
6	1	8	1.10E+02	4.27E+02
7	1	8	1.10E+02	3.28E+02
10	3	11	1.10E+02	3.28E+02

Table S12: Dihedral angles.

atom i	atom j	atom k	atom l	n	k1 / kJ mol^{-1}	k2 / kJ mol^{-1}	k3 / kJ mol^{-1}	k4 / kJ mol^{-1}
1	2	3	4	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
1	2	3	10	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
1	2	3	11	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
1	2	5	13	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
1	2	5	13	3	6.69E-01	2.01E+00	0.00E+00	-2.68E+00
2	1	6	14	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
2	1	6	14	3	6.69E-01	2.01E+00	0.00E+00	-2.68E+00
2	3	4	12	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
2	3	4	12	3	6.69E-01	2.01E+00	0.00E+00	-2.68E+00
3	2	5	13	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
3	2	5	13	3	6.69E-01	2.01E+00	0.00E+00	-2.68E+00
4	3	2	5	3	0.00E+00	0.00E+00	9.83E+00	0.00E+00
4	3	2	5	3	6.03E-01	1.81E+00	0.00E+00	-2.41E+00
4	3	2	9	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
5	2	3	10	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
5	2	3	11	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
6	1	2	3	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
6	1	2	5	3	0.00E+00	0.00E+00	9.83E+00	0.00E+00
6	1	2	5	3	6.03E-01	1.81E+00	0.00E+00	-2.41E+00
6	1	2	9	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
7	1	2	3	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
7	1	2	5	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
7	1	2	9	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
7	1	6	14	3	6.97E-01	2.09E+00	0.00E+00	-2.79E+00
8	1	2	3	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
8	1	2	5	3	1.05E+00	-1.05E+00	0.00E+00	0.00E+00
8	1	2	9	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
8	1	6	14	3	6.97E-01	2.09E+00	0.00E+00	-2.79E+00
9	2	3	10	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
9	2	3	11	3	6.51E-01	1.95E+00	0.00E+00	-2.60E+00
9	2	5	13	3	6.97E-01	2.09E+00	0.00E+00	-2.79E+00

10	3	4	12	3	6.97E-01	2.09E+00	0.00E+00	-2.79E+00
11	3	4	12	3	6.97E-01	2.09E+00	0.00E+00	-2.79E+00

4. Self-diffusion coefficients

Table S13: Uncorrected self-diffusion coefficients for different compositions and different temperatures. Errors listed equal one standard deviation.

System	x_w / mol/mol	D_{self} **(T = 280.15K) /** 10^{-5} cm²/s	D_{self} **(T = 320.15K) /** 10^{-5} cm²/s	D_{self} **(T = 360.15K) /** 10^{-5} cm²/s
C0	1.00	1.5236 ± 0.0282	3.8444 ± 0.0674	7.0428 ± 0.0799
C1	0.90	0.7245 ± 0.0121	1.9774 ± 0.0231	3.9689 ± 0.0297
C2	0.75	0.2287 ± 0.0073	0.8228 ± 0.0147	1.9504 ± 0.0217
C3	0.50	0.0410 ± 0.0133	0.2448 ± 0.0064	0.8053 ± 0.0251
C4	0.25	0.0135 ± 0.0124	0.8962 ± 0.0059	0.4087 ± 0.0242
C5	0.10	0.0121 ± 0.0206	0.0570 ± 0.0106	0.3008 ± 0.0253
TIP4P	1.00	-	0.3038	-

5. Finite size effects

Table S14: Composition and box lengths for different system sizes of composition C3.

L_{Box} / nm	N_{Ch} and N_{Cl}	N_{Gly}	N_{W}
4.94623	225	450	675
5.44400	300	600	900
5.86419	375	750	1125
6.85893	600	1200	1800

6. Binary mixture glycerol and water

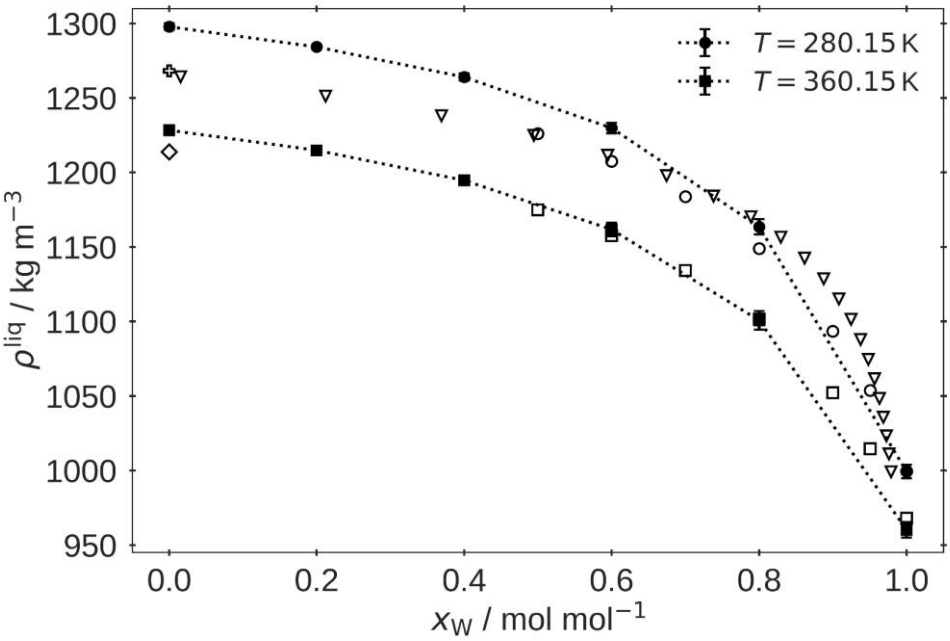

Figure S1: Liquid density of a binary mixture of glycerol and water for different water mole fractions at two different temperatures (280.15 K and 360.15 K). Experimental data are taken from Ref. [1] (open circles at 280.15 K and open squares at 360.15 K), from Ref. [2] (open plus at 283.15 K and open diamond at 368.15 K), from Ref. [3] (open triangles down at 288.15 K).

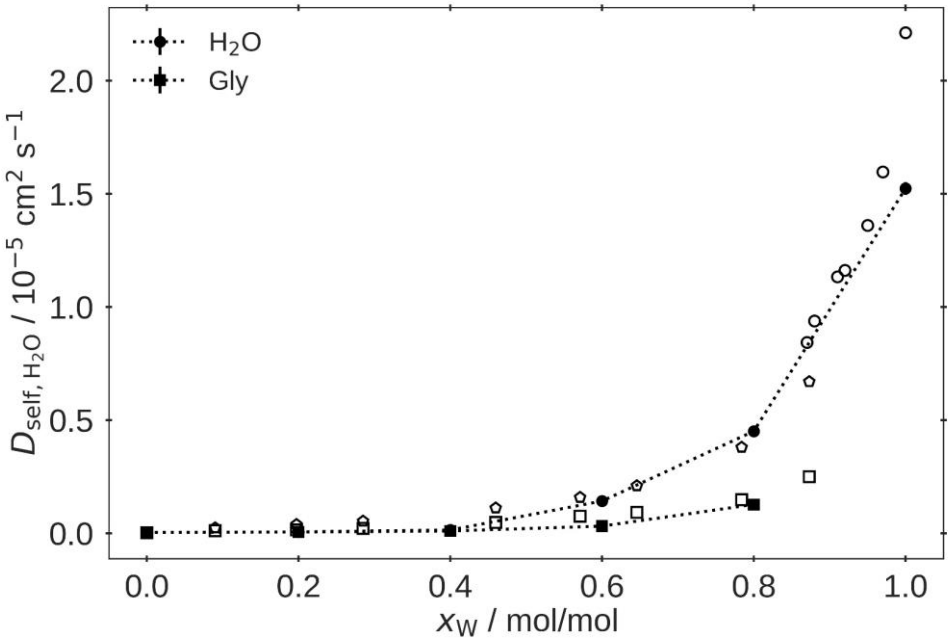

Figure S2: Self-diffusion coefficient of a binary mixture including glycerol and water for different water mole fractions at 280.15 K. Experimental data for water are taken from Ref. [4] (open triangles) and Ref. [5] (open circles) while experimental data for glycerol are taken from Ref. [4] (open squares). Note that all experimental data are measured at 298.15 K.

7. Binary mixture choline and water

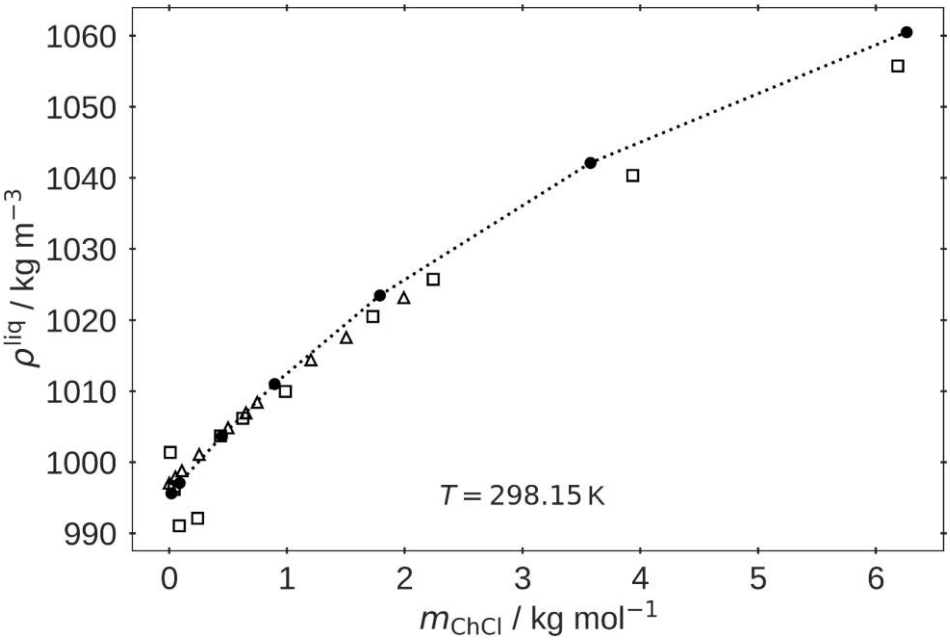

Figure S3: Liquid density of a binary mixture of choline chloride and water as function of ChCl molality at 298.15 K. Experimental data are taken from Refs [6, 7] and are represented by open symbols.

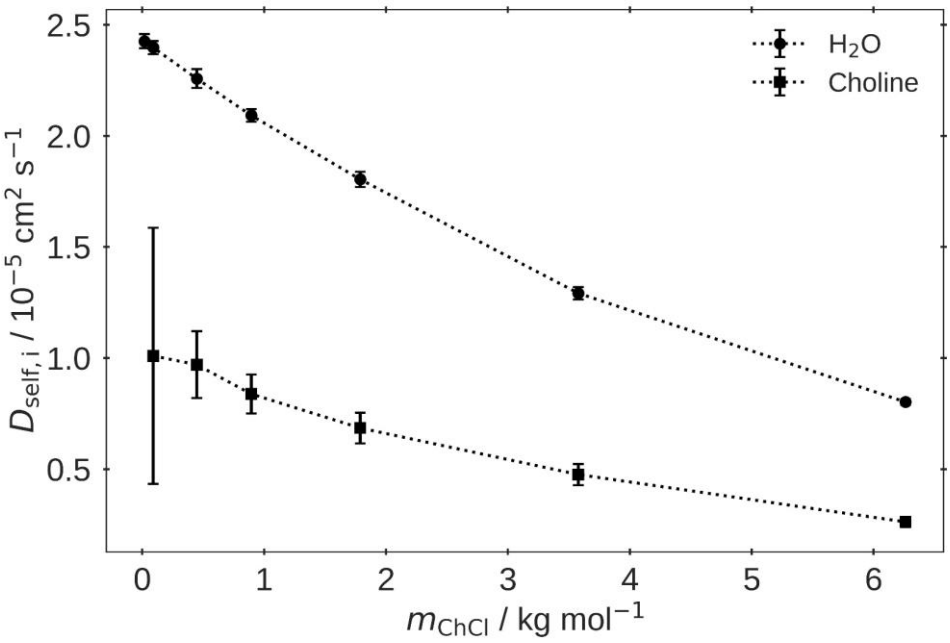

Figure S4: Self-diffusion coefficients in a binary mixture of choline chloride and water as function of ChCl molality at 298.15 K.

8. Radial distribution functions

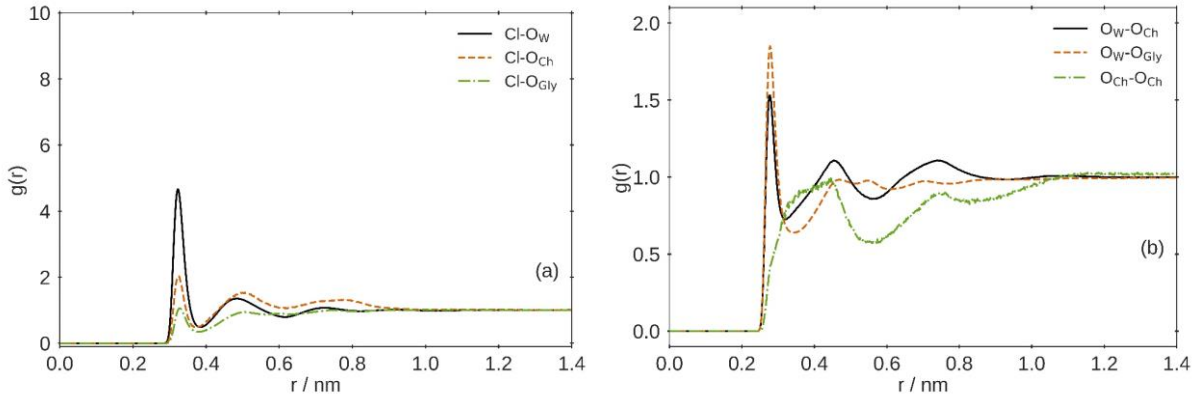

Figure S5: Radial distribution function for composition C1 at 280.15K.

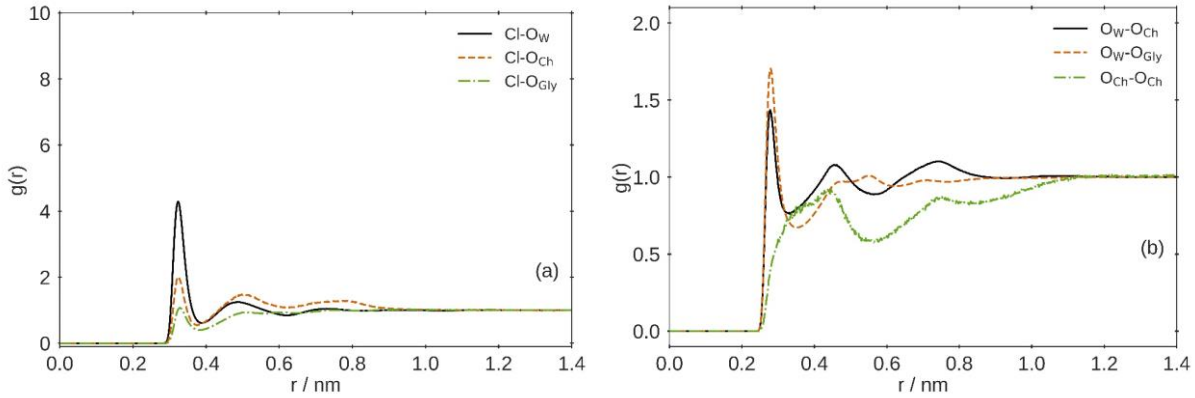

Figure S6: Radial distribution function for composition C1 at 320.15K.

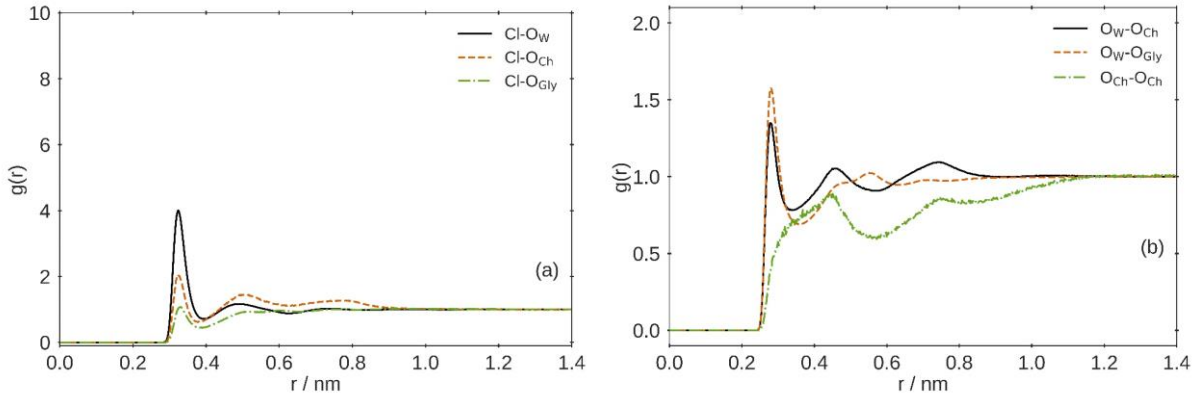

Figure S7: Radial distribution function for composition C1 at 360.15K.

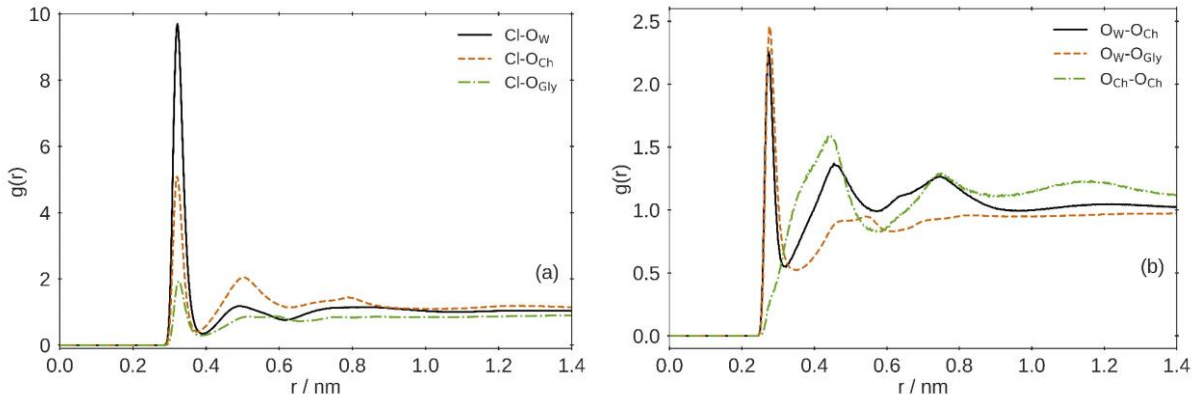

Figure S8: Radial distribution function for composition C3 at 280.15K.

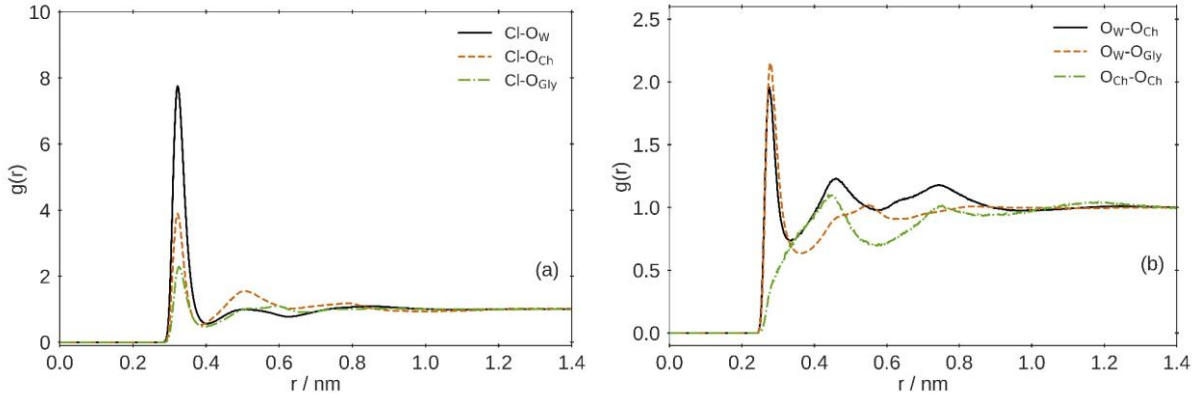

Figure S9: Radial distribution function for composition C3 at 360.15K.

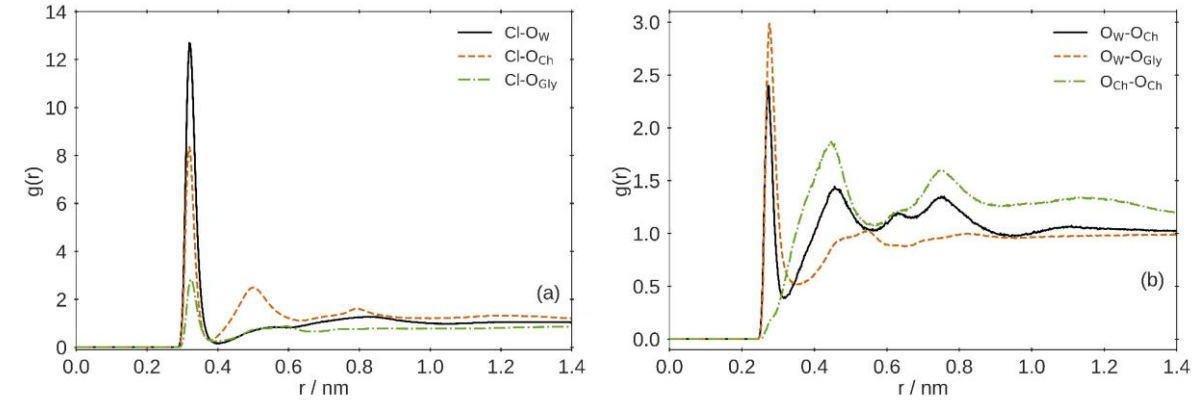

Figure S10: Radial distribution function for composition C5 at 280.15K.

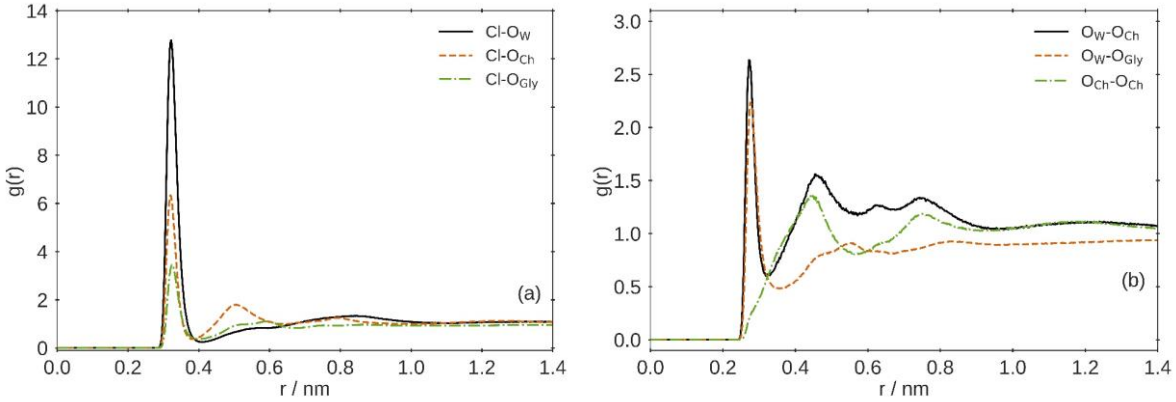

Figure S11: Radial distribution function for composition C5 at 320.15K.

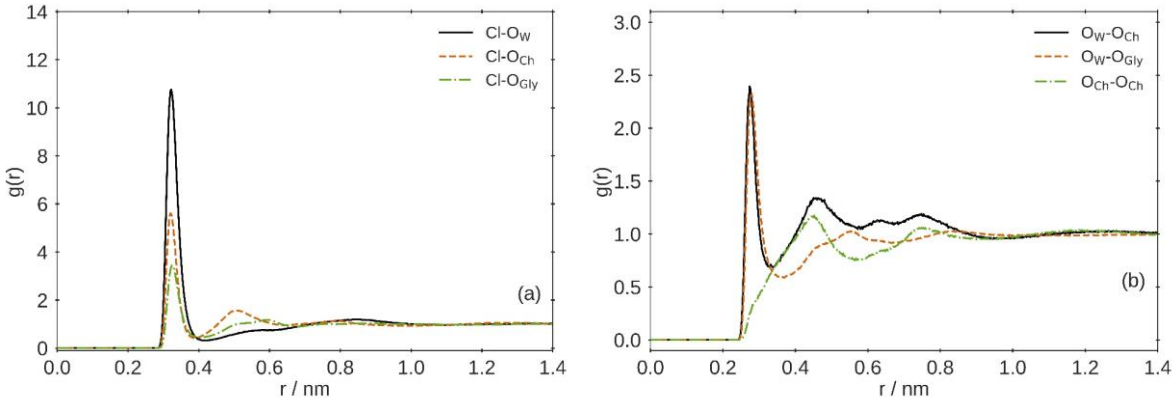

Figure S12: Radial distribution function for composition C5 at 360.15K.

9. Self-Diffusion coefficients of choline, chloride and glycerol

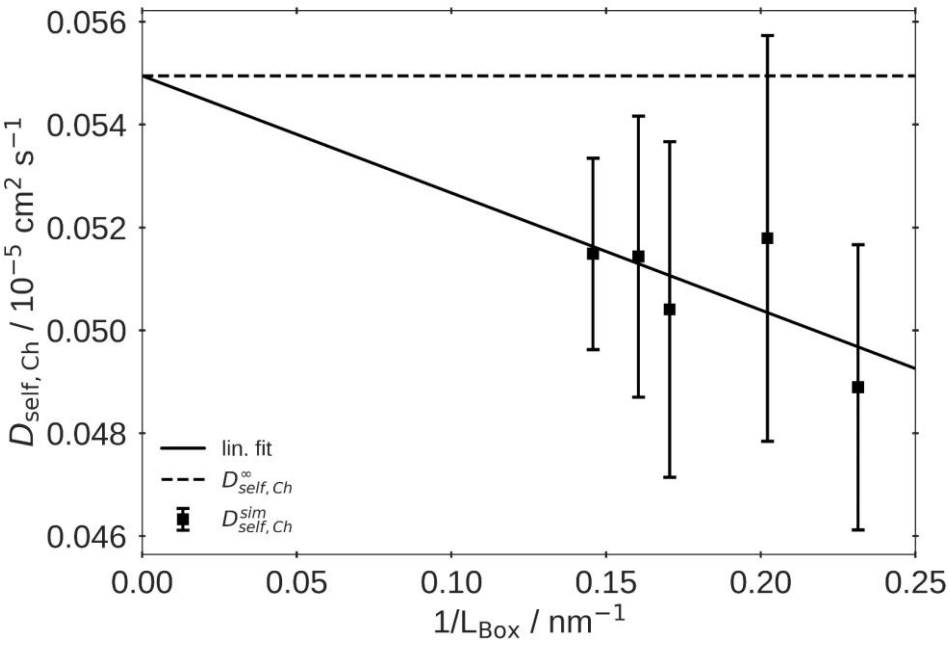

Figure S13: Self-diffusion coefficient of cholinium cation as function of the inverse box length for system C3.

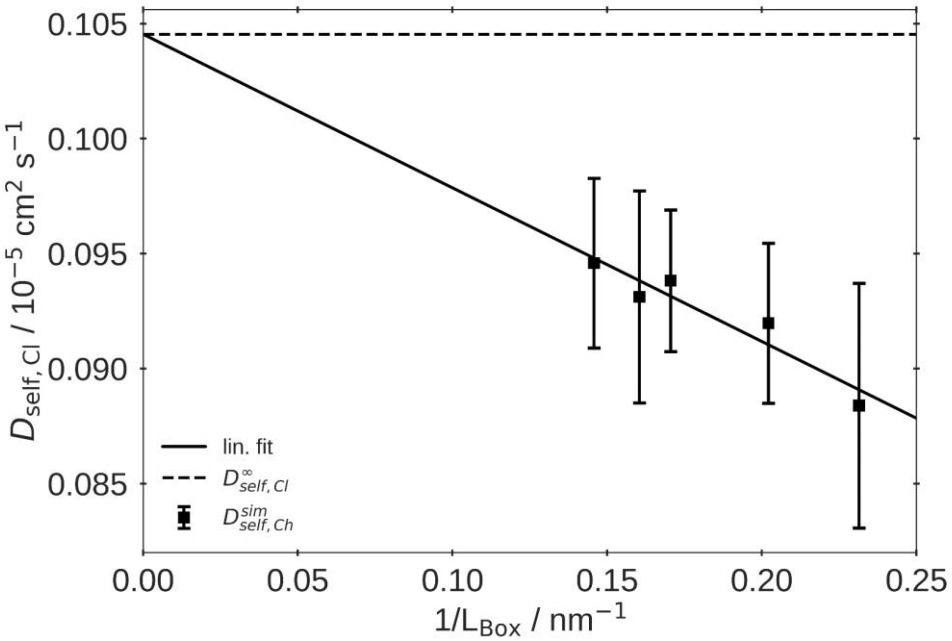

Figure S14: Self-diffusion coefficient of chloride as function of the inverse box length for system C3.

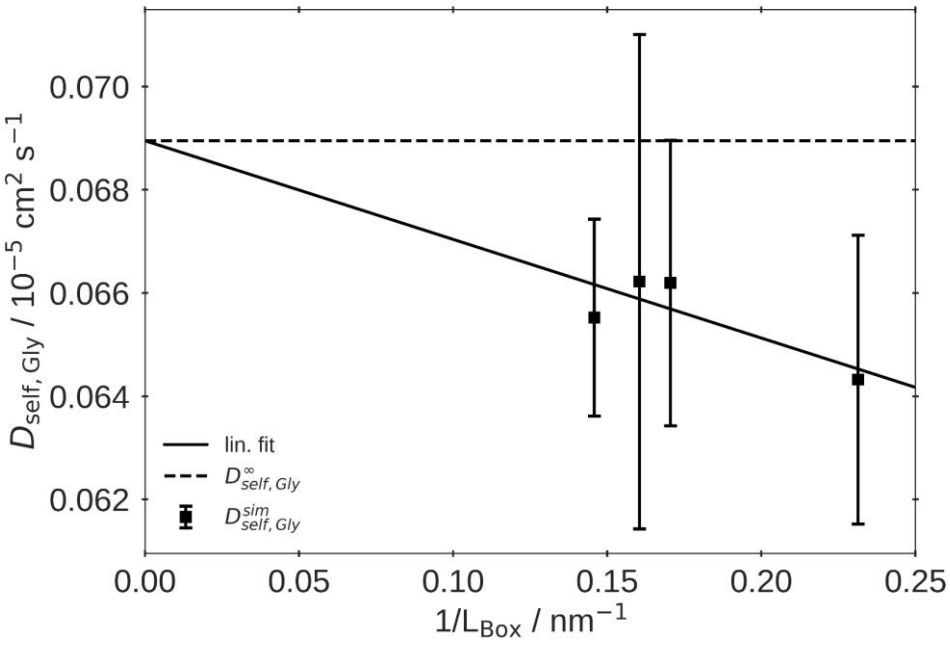

Figure 15: Self-diffusion coefficient of glycerol as function of the inverse box length for system C3.

10.References

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