Electronic Supplementary Information

Hydration and ion association of aqueous choline chloride and chlorocholine chloride

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Supplementary Tables

Table S1: Coordinates of the atoms of Ch^+ for its minimum-energy conformation in water at 298.15 K obtained by DFT calculations using the B3LYP density functional and a 6-31++G** basis set with the Poisson-Boltzmann finite element (PBF) method as implemented in Jaguar (Schrödinger Suite 2017-3) to account for solvation.[1–4] Also included are the associated GAFF Lennard-Jones parameters, σ and ε,[5] and partial charges, q, obtained with the ESP method.[6] For site designations see Fig. 1 of the Main Manuscript.

site	x / nm	y / nm	z / nm	σ / nm	ε / kcal mol^{-1}	q
N	0.164	0.137	0.190	0.325	0.170	0.1263
Cm1	0.254	0.235	0.118	0.340	0.109	–0.3722
Hm	0.331	0.178	0.066	0.196	0.016	0.1971
Hm	0.195	0.291	0.045	0.196	0.016	0.1831
Hm	0.299	0.302	0.191	0.196	0.016	0.1975
Cm2	0.250	0.051	0.281	0.340	0.109	–0.4768
Hm	0.324	–0.001	0.219	0.196	0.016	0.2294
Hm	0.300	0.116	0.353	0.196	0.016	0.2126
Hm	0.186	-0.021	0.332	0.196	0.016	0.2127
Cm3	0.096	0.046	0.089	0.340	0.109	–0.3743
Hm	0.174	–0.010	0.037	0.196	0.016	0.1979
Hm	0.029	–0.021	0.143	0.196	0.016	0.1979
Hm	0.041	0.107	0.018	0.196	0.016	0.1837
Cb1	–0.034	0.302	0.202	0.340	0.109	0.2615
Hb1	0.020	0.381	0.149	0.247	0.016	0.0290
Hb1	–0.093	0.247	0.128	0.247	0.016	0.0286
Cb2	0.062	0.209	0.277	0.340	0.109	–0.0725
Hb2	0.119	0.267	0.351	0.196	0.016	0.1395
Hb2	0.005	0.132	0.330	0.196	0.016	0.1401
O	–0.119	0.358	0.302	0.307	0.210	–0.7143
Ho	–0.181	0.418	0.258	0.117[a]	0.016[a]	0.4733

[a] Parameters of the mSPC/E model.[7]

Table S2: Coordinates of the atoms of $ClCh^+$ for its minimum-energy conformation in water at 298.15 K obtained by DFT calculations using the B3LYP density functional and a 6-31++G** basis set with the Poisson-Boltzmann finite element (PBF) method as implemented in Jaguar (Schrödinger Suite 2017-3) to account for solvation.[1–4] Also included are the associated GAFF Lennard-Jones parameters, σ and ε,[5] and partial charges, q, obtained with the ESP method.[6] For site designations see Fig. 1 of the Main Manuscript.

site	x / nm	y / nm	z / nm	σ / nm	ε / kcal mol^{-1}	q
N	0.170	0.156	0.175	0.325	0.170	0.3262
Cm1	0.209	0.064	0.289	0.340	0.109	–0.3757
Hm	0.121	0.008	0.322	0.196	0.016	0.1771
Hm	0.285	–0.005	0.253	0.196	0.016	0.1811
Hm	0.248	0.125	0.371	0.196	0.016	0.1919
Cm2	0.295	0.224	0.123	0.340	0.109	–0.4877
Hm	0.364	0.147	0.088	0.196	0.016	0.2183
Hm	0.266	0.289	0.040	0.196	0.016	0.2035
Hm	0.339	0.282	0.204	0.196	0.016	0.2035
Cm3	0.108	0.075	0.063	0.340	0.109	–0.3750
Hm	0.184	0.006	0.025	0.196	0.016	0.1808
Hm	0.023	0.018	0.101	0.196	0.016	0.1770
Hm	0.076	0.143	-0.016	0.196	0.016	0.1917
Cb1	–0.057	0.212	0.279	0.340	0.109	–0.2877
Hb1	–0.118	0.159	0.206	0.247	0.016	0.2000
Hb1	–0.044	0.151	0.369	0.247	0.016	0.1995
Cb2	0.075	0.265	0.223	0.340	0.109	–0.0042
Hb2	0.056	0.330	0.137	0.196	0.016	0.1191
Hb2	0.129	0.322	0.299	0.196	0.016	0.1188
Cl	–0.155	0.356	0.330	0.347	0.265	–0.1582

Table S3: Molar conductivities, Λ, of aqueous ChCl solutions (density gradient b = 0.0171 $kg^2L^{-1}mol^{-1}$) as a function of solute molality, m, and temperature, T.

T / K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$m \cdot 10^3$ / $mol\,kg^{-1}$	Λ / $S\,cm^2mol^{-1}$							
0.46147	71.918	82.451	93.375	104.848	116.746	129.014	141.437	153.717
0.70808	71.653	82.119	93.024	104.427	116.267	128.430	140.698	152.798
1.04728	71.253	81.595	92.438	103.757	115.486	127.572	139.770	151.834
1.36893	71.000	81.337	92.152	103.445	115.151	127.209	139.514	151.616
1.73443	70.770	81.090	91.880	103.130	114.794	126.815	139.144	151.427
2.10711	70.636	80.847	91.629	102.844	114.487	126.480	138.749	151.067
2.65698	70.312	80.563	91.298	102.461	114.061	126.020	138.223	150.471
3.39713	69.962	80.164	90.860	101.970	113.514	125.425	137.639	149.916
4.22962	69.696	79.783	90.439	101.515	113.025	124.915	137.105	149.473
5.19678	69.363	79.466	90.076	101.105	112.562	124.383	136.440	148.434
6.28621	69.029	79.094	89.651	100.650	112.085	123.883	135.979	148.188

Table S4: Molar conductivities, Λ, of aqueous ClChCl solutions (density gradient b = 0.0282 $kg^2L^{-1}mol^{-1}$) as a function of solute molality, m, and temperature, T.

T / K	278.15	283.15	288.15	293.15	298.15	303.15	308.15	313.15
$m \cdot 10^3$ / $mol\,kg^{-1}$	Λ / $S\,cm^2mol^{-1}$							
0.21332	69.522	79.754	90.489	101.692	113.136	124.986	137.297	150.030
0.43939	69.142	79.328	90.000	101.127	112.577	124.452	136.697	149.269
0.68723	68.898	79.055	89.669	100.738	112.161	124.031	136.241	148.452
0.98347	68.629	78.692	89.269	100.280	111.685	123.486	135.629	148.063
1.29141	68.357	78.413	88.920	99.911	111.279	123.026	135.066	147.276
1.65909	68.163	78.194	88.687	99.643	110.964	122.680	134.675	146.850
2.09974	67.899	77.894	88.355	99.270	110.540	122.192	134.098	146.210
2.69283	67.566	77.498	87.903	98.775	109.998	121.581	133.490	145.472
3.35468	67.238	77.132	87.479	98.282	109.432	120.981	132.841	144.845
4.17889	66.887	76.673	86.969	97.723	108.824	120.308	131.990	144.169
5.11903	66.521	76.297	86.523	97.202	108.250	119.656	131.281	143.041

Table S5: Static permittivity, ε, relaxation amplitudes, S_j ($j = 1 \ldots 3$), relaxation times, τ_j, shape parameter, α_3, and infinite frequency permittivity, ε_∞, of the D+D+CC model fitted to the DR spectra of aqueous choline chloride at 25 °C and molar concentration c.

c / M	ε	S_1	τ_1 / ps	S_2 [a]	τ_2 [a] / ps	S_3	τ_3 / ps	α_3	ε_∞
0.0270	77.94	0.33	600	0.045	14.0	71.69	8.29	0	5.87
0.0501	77.91	0.68	504	0.084	14.0	71.50	8.30	0.002	5.65
0.0993	77.72	1.15	371	0.167	14.0	70.85	8.40	0.004	5.55
0.2419	76.06	1.46	218	0.406	14.0	68.35	8.57	0.007	5.84
0.2699	75.84	1.22	260	0.450	14.0	68.77	8.55	0.018	5.40
0.3342	75.13	1.45	216	0.561	14.0	67.12	8.71	0.011	6.01
0.4696	73.72	1.57	221	0.788	14.0	65.33	8.93	0.015	6.03
0.5998	71.91	1.24	188	1.006	14.0	63.62	9.16	0.018	6.05
0.6843	71.13	1.26	233	1.148	14.0	62.70	9.29	0.021	6.02
0.8074	69.66	1.16	239	1.354	14.0	60.77	9.58	0.022	6.37
1.0457	66.57			1.752	14.0	59.41	9.76	0.047	5.41
1.2653	64.09			2.118	14.0	56.64	10.21	0.046	5.34
1.5957	60.51			2.668	14.0	52.10	10.85	0.040	5.74

[a] Parameter values fixed, see Main Manuscript for details.

Table S6: Static permittivity, ε, relaxation amplitudes, S_j ($j = 1 \ldots 3$), relaxation times, τ_j, shape parameter, α_3, and infinite frequency permittivity, ε_∞, of the D+D+CC model fitted to the DR spectra of aqueous chlorocholine chloride at 25 °C and molar concentration c.

c / M	ε	S_1	τ_1 / ps	S_2 [a]	τ_2 [a] / ps	S_3	τ_3 / ps	α_3	ε_∞
0.0275	78.43	0.60	774	0.236	18.5	72.15	8.33	0.004	5.44
0.0509	77.60			0.437	18.5	72.22	8.24	0.012	4.95
0.0987	77.62	0.60	570	0.848	18.5	71.23	8.24	0.016	4.94
0.2411	76.26	1.13	261	2.071	18.5	67.77	8.47	0.016	5.29
0.3339	75.21	1.01	228	2.868	18.5	66.26	8.56	0.021	5.08
0.4681	73.61	0.81	217	4.019	18.5	63.6	8.76	0.025	5.18
0.5982	72.19	0.95	233	5.135	18.5	60.68	8.97	0.023	5.43
0.6810	71.27	0.95	237	5.844	18.5	58.93	9.12	0.024	5.54
0.8030	69.87	0.68	312	6.888	18.5	57.14	9.21	0.035	5.16
0.8821	69.05	0.74	311	7.566	18.5	55.48	9.35	0.036	5.26
1.0438	67.20	0.64	362	8.948	18.5	52.31	9.56	0.040	5.3
1.2566	65.26	0.97	613	10.766	18.5	48.29	9.84	0.048	5.23
1.5825	61.00			13.545	18.5	42.22	10.53	0.064	5.23

[a] Parameter values fixed, see Main Manuscript for details.

Table S7: Static permittivity, ε, relaxation amplitudes, S_j ($j = 1 \ldots 3$), relaxation times, τ_j, shape parameter, α_3, and infinite frequency permittivity, ε_∞, of the D+D+CC model fitted to the DR spectra of aqueous choline chloride at temperature, T, and molar concentration c ($m = 0.2800\,\mathrm{mol\,kg^{-1}}$). Also given are the corresponding densities, ρ, and conductivities, κ.

T / K	c / M	ρ / kg·L^{-1}	κ / S·m^{-1}	ε	S_1	τ_1 / ps	S_2 [a]	τ_2 [a] / ps	S_3	τ_3 / ps	α_3	ε_∞
278.15	0.2709	1.00516	1.35	82.62	1.84	226	0.49	22.9	73.98	14.53	0.001	6.31
288.15	0.2705	1.00381	1.75	79.19	1.31	222	0.47	17.7	71.37	11.19	0.0082	6.04
298.15	0.2699	1.00154	2.22	75.84	1.22	262	0.45	14.0	68.78	8.55	0.0186	5.40
308.15	0.2690	0.99840	2.77	72.35	1.39	199	0.44	11.2	65.69	6.66	0.018	4.83
318.15	0.2687	0.99732	3.41	69.14	1.26	137	0.42	9.1	62.78	5.42	0.0087	4.69
328.15	0.2679	0.99420	4.14	64.78	1.24	158	0.41	7.5	58.55	4.32	0.005	4.58
338.15	0.2675	0.99280	4.98	61.65	0.93	229	0.40	6.2	55.09	3.69	0	5.23

[a] Parameter values fixed, see Main Manuscript for details.

Table S8: Structural parameters of Ch^+ and $ClCh^+$ hydration in aqueous solution at 25 °C and infinite dilution: Maximum values of radial distribution functions, $g_{ij}(r)$, at distance, $r_{ij,M1}$, and associated coordination numbers, n_{ij}. For the site labelling see Fig. 1 of the main manuscript.

	Ch^+	$ClCh^+$
	$-N^+[CH_3]_3$ moiety	
g_{NOw}	1.50	1.52
$r_{NOw,M1}$ / nm	0.432	0.430
$g_{Hmi Ow}$	0.95-1.07	0.99-1.09
$r_{Hmi Ow,M1}$ / nm	0.233-0.237	0.233-0.237
$g_{Cmi Ow}$	1.56-1.64	1.59-1.65
$r_{Cmi Ow,M1}$ / nm	0.312-0.315	0.310-0.312
$n_{Cmi Ow}$	5.88-6.58	5.93-6.48
	$-CH_2-$ groups	
g_{Cb1Ow}	1.43	1.25
$r_{Cb1Ow,M1}$ / nm	0.345	0.340
n_{Cb1Ow}	12.65	6.51
g_{Hb1Ow}	1.16	1.13
$r_{Hb1Ow,M1}$ / nm	0.253	0.247
g_{Cb2Ow}	0.94	0.99
$r_{Cb2Ow,M1}$ / nm	0.320	0.315
g_{Hb2Ow}	0.96	1.01
$r_{Hb2Ow,M1}$ / nm	0.233	0.233
	–OH group	Cl atom
g_{OOw}, g_{ClOw}	1.91	1.86
$r_{OOw,M1}$, $r_{ClOw,M1}$ / nm	0.297	0.325
n_{OOw}, n_{ClOw}	7.07	10.7
g_{OHw}	1.06	
$r_{OHw,M1}$ / nm	0.180	
n_{OHw}	1.36	
g_{HOw}	1.76	
$r_{HOw,M1}$ / nm	0.175	
n_{HOw}	0.95	
	total coordination number	
n	24.8	26.7

Supplementary Figures

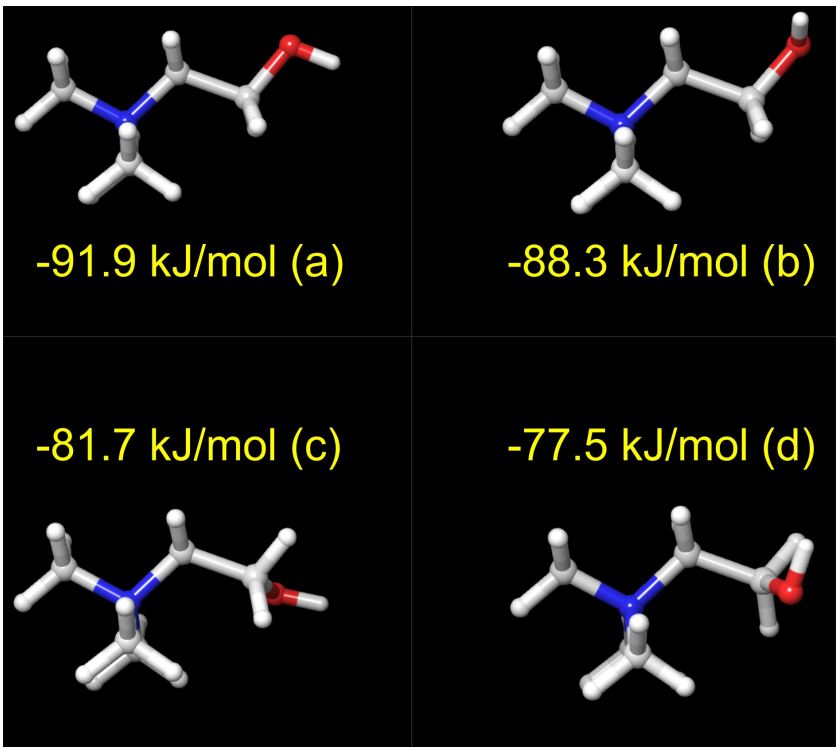

Figure S1: Minimum energy conformations of choline ion obtained with Monte Carlo/stochastic dynamics (MC/SD) using the OPLSA-2005 force field with implicit water model.[8] Note that only one of the two equivalent conformations (b) with −88.3 kJ/mol is shown.

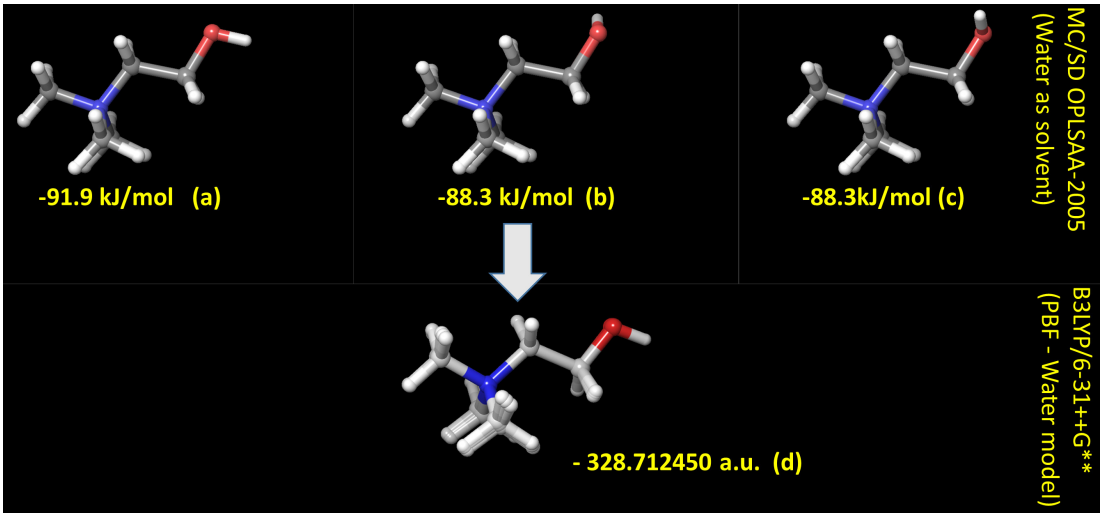

Figure S2: QM optimizations[1–4] of the three minimum energy conformations, (a) - (c), of Ch^+ from MC/SD (see Fig. S1) converge to a single structure (d).

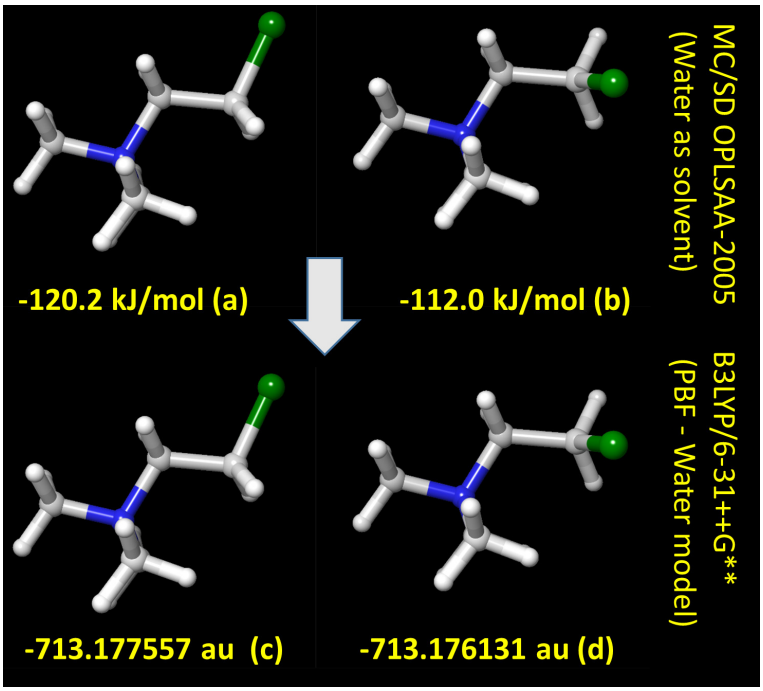

Figure S3: Minimum energy conformations, (a) and (b), of chlorocholine ion obtained with Monte Carlo/stochastic dynamics (MC/SD) using the OPLSA-2005 force field with implicit water model[8] and resulting conformations, (c) and (d), after subsequent QM optimization.[1–4] The energy difference between (c) and (d) is 3.74 kJ/mol.

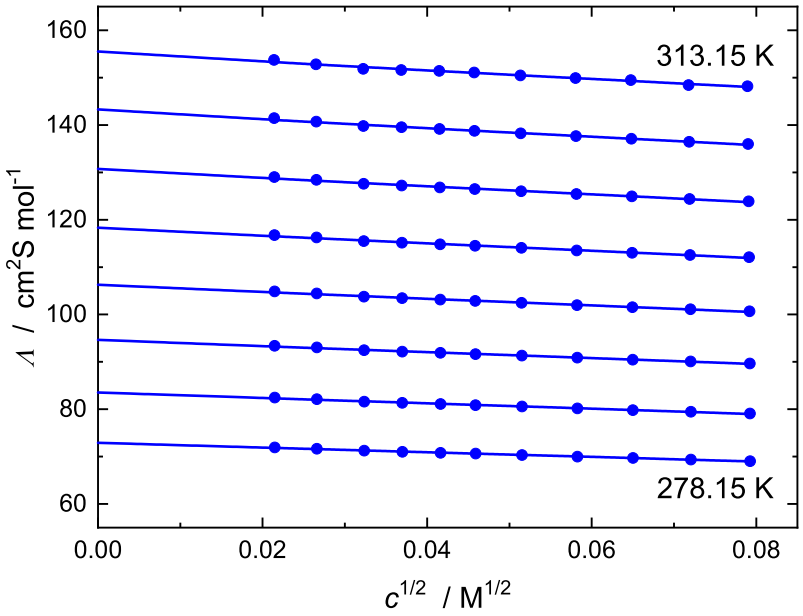

Figure S4: Molar conductivities, Λ, of aqueous ChCl solutions as a function of solute concentration, c, and temperature, T, between 278.15 K and 313.15 K in steps of 5 K.

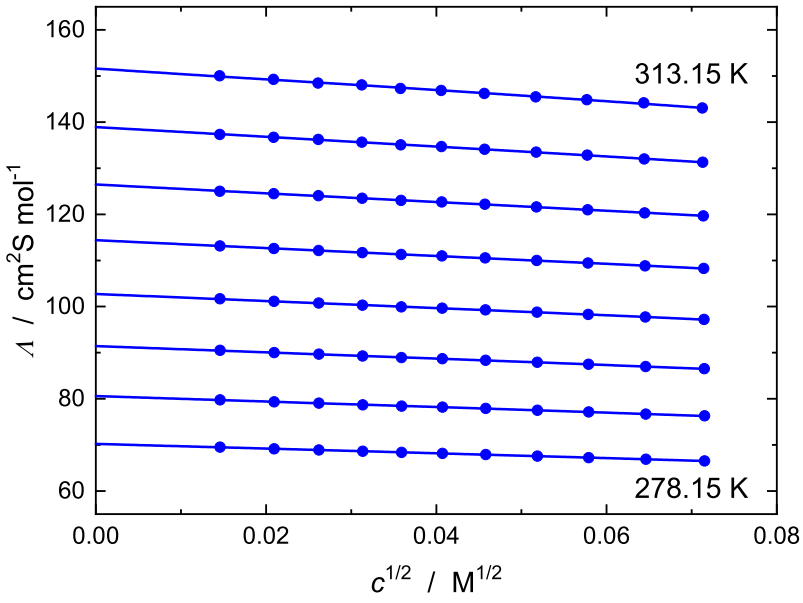

Figure S5: Molar conductivities, Λ, of aqueous ClChCl solutions as a function of solute concentration, c, and temperature, T, between 278.15 K and 313.15 K in steps of 5 K.

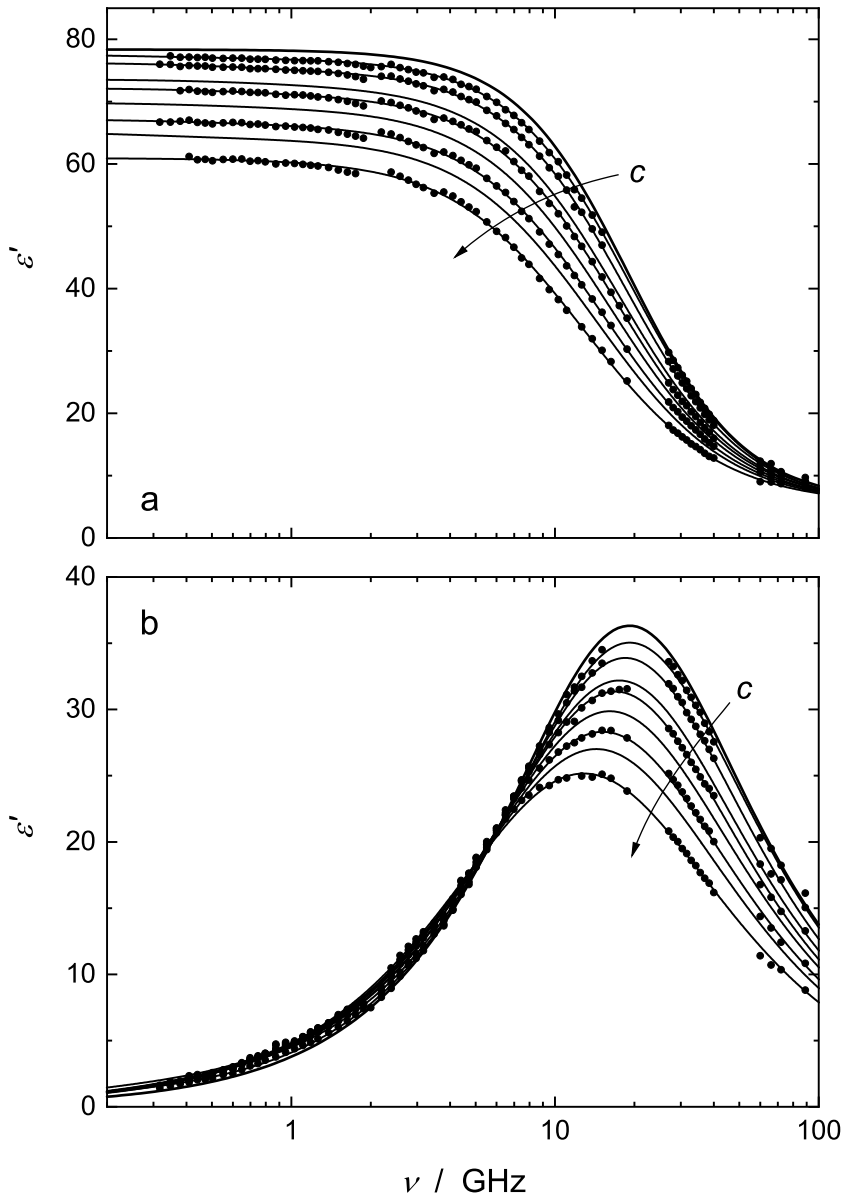

Figure S6: (a) Relative permittivity, $\varepsilon'(\nu)$, and (b) dielectric loss, $\varepsilon''(\nu)$, spectra of aqueous ChChCl at 298.15 K and c / M = 0, 0.0987, 0.2411, 0.4681, 0.5982, 0.8030, 1.0438, 1.2566, 1.5825. The symbols represent the experimental data (partly omitted for visual clarity) and the lines the fits of the D+D+CC model. The arrows indicate the data trend with increasing c.

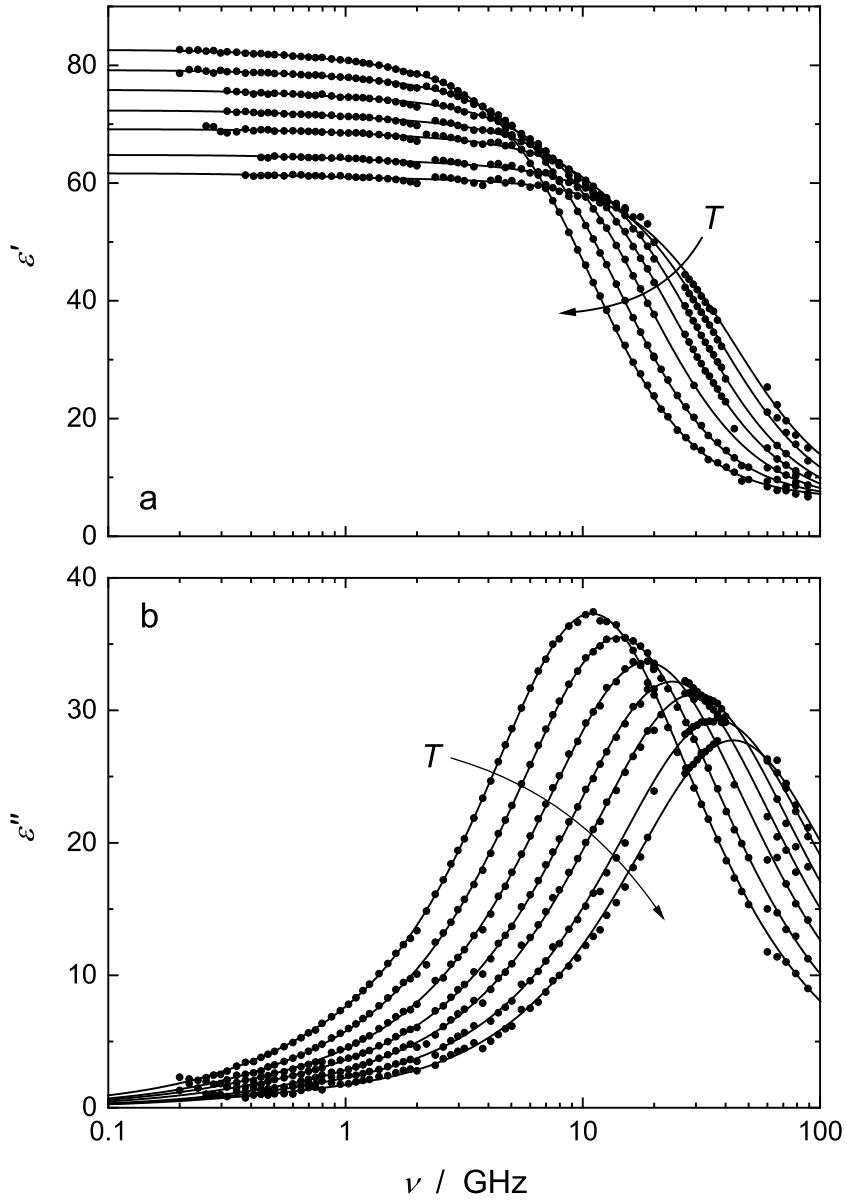

Figure S7: (a) Relative permittivity, $\varepsilon'(\nu)$, and (b) dielectric loss, $\varepsilon''(\nu)$, spectra of 0.27 M aqueous ChCl from 278.15 K to 338.15 K in steps of 10 K (increasing in arrow direction). The symbols represent the experimental data (partly omitted for visual clarity) and the lines the fits of the D+D+CC model.

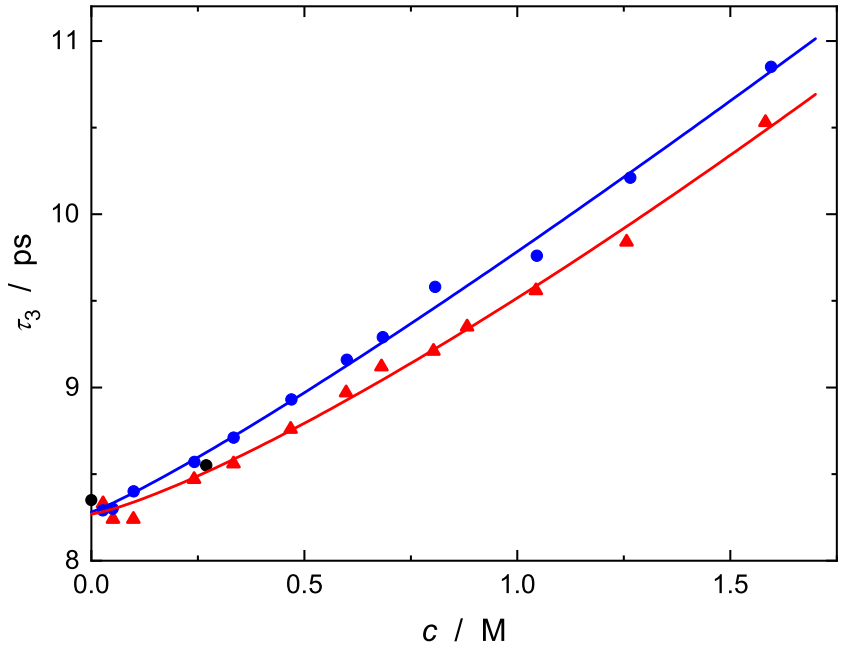

Figure S8: Relaxation time of bulk-like water, τ_3, of aqueous ChCl (●) and ClChCl (▲) as a function of concentration, c, at 298.15 K. Lines as a guide to the eye.

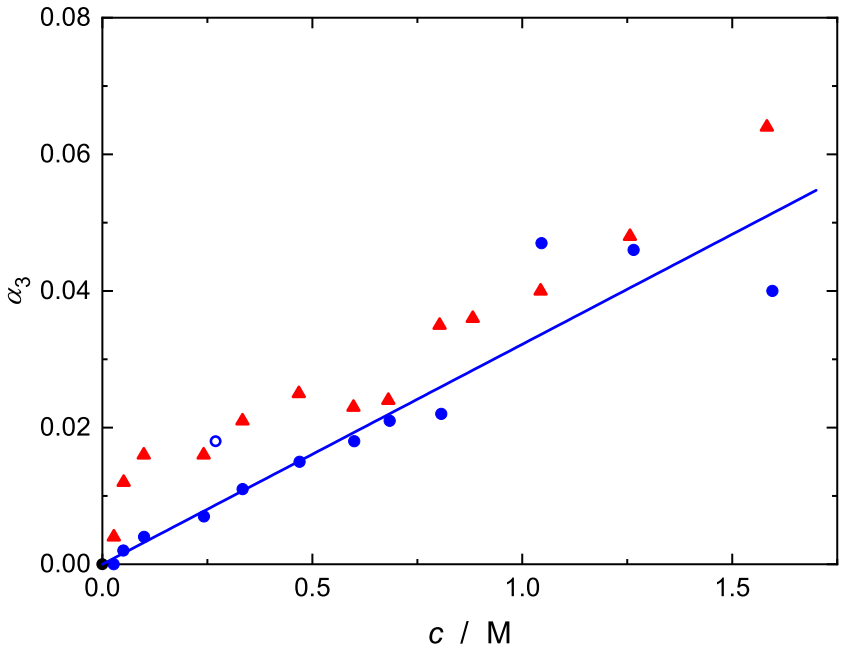

Figure S9: Cole-Cole width parameter of bulk-like water, α_3, of aqueous ChCl (●) and ClChCl (▲) as a function of concentration, c, at 298.15 K. The lines is a straight-line fit of the ChCl data forced through the origin (open symbol neglected).

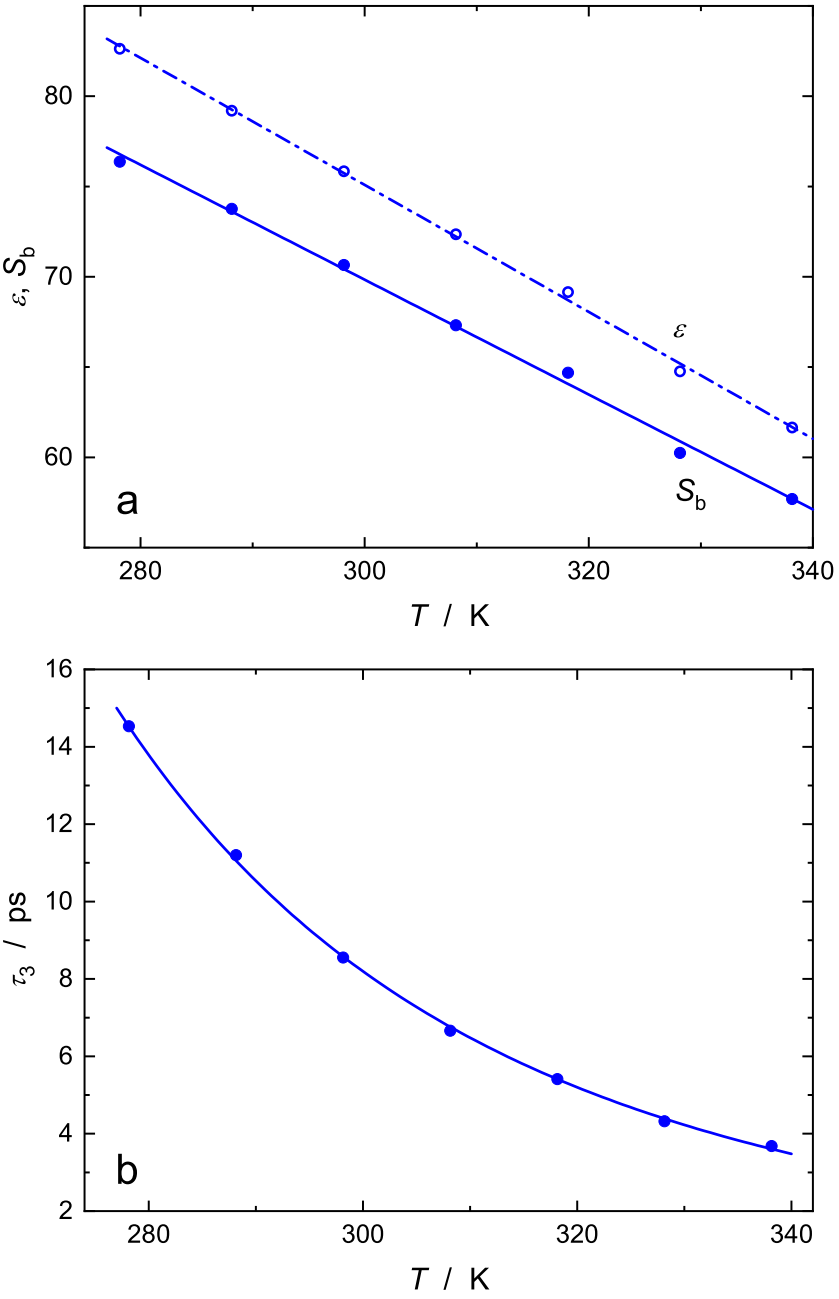

Figure S10: (a) Static relative permittivity, ε (○), and amplitude of bulk-like water, S_w (●); (b) bulk-water relaxation time, τ_3, of 0.2800 mol kg^{-1} aqueous ChCl as a function of temperature, T.

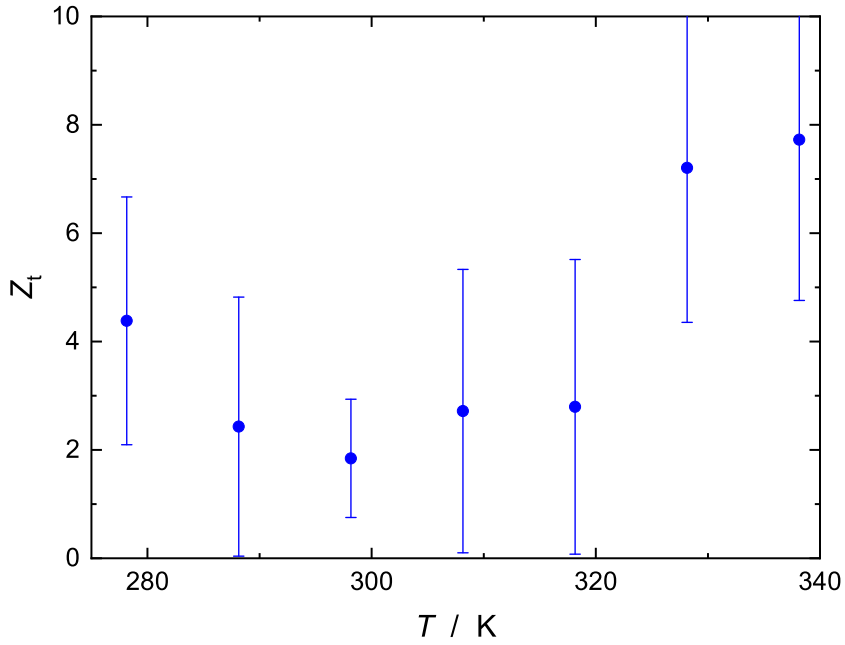

Figure S11: Total effective hydration number, Z_t, of 0.28 mol kg^{-1} aqueous ChCl (●) as a function of temperature, T. Lines as a guide to the eye; error bars estimated from $2 \times \sigma_{fit}$ of a straight-line fit to $S_w = f(T)$ (Fig. S10).

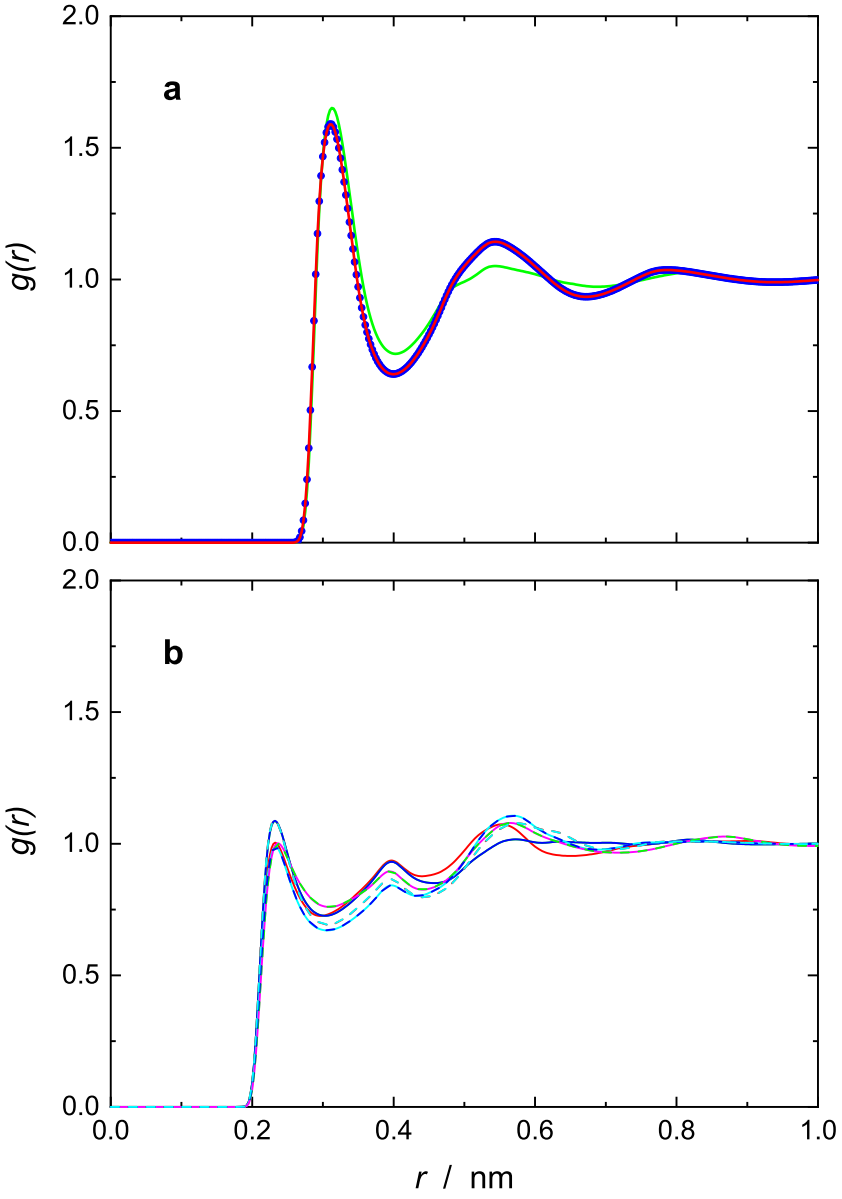

Figure S12: (a) Radial distribution functions $g_{\mathrm{Cm1Ow}}(r)$ (red line), $g_{\mathrm{Cm2Ow}}(r)$ (green line) and $g_{\mathrm{Cm3Ow}}(r)$ (blue symbols) for the trimethylammonium moiety of ClCh^{+} at infinite dilution in aqueous solution; (b) corresponding RDFs, $g_{\mathrm{Hm}i\mathrm{Ow}}(r)$, of methyl H atoms.

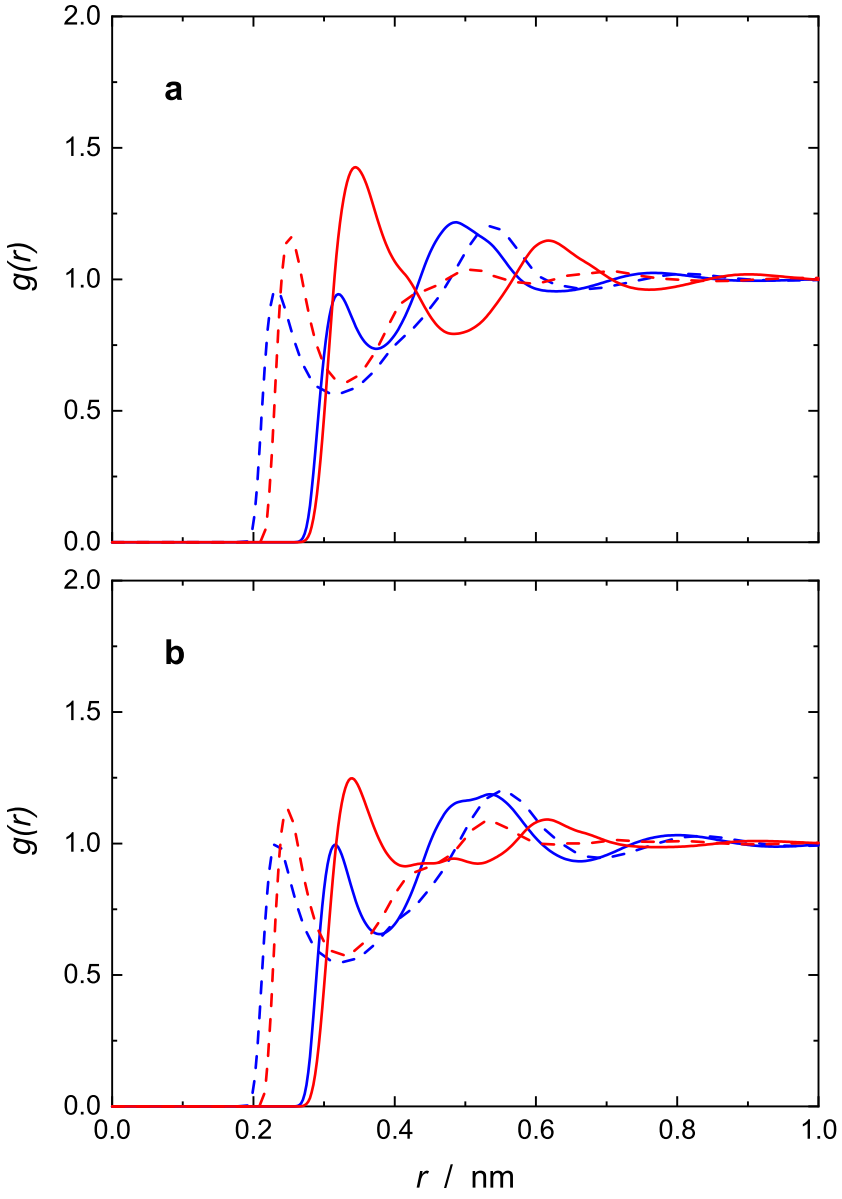

Figure S13: Radial distribution functions $g_{\mathrm{Cb1Ow}}(r)$ (solid red line), $g_{\mathrm{Cb1Hw}}(r)$ (broken red line), $g_{\mathrm{Cb2Ow}}(r)$ (solid blue line), and $g_{\mathrm{Cb2Hw}}(r)$ (broken blue line) for the carbon atoms of the ethyl moiety of (a) Ch^+ and (b) $ClCh^+$ at infinite dilution in aqueous solution.

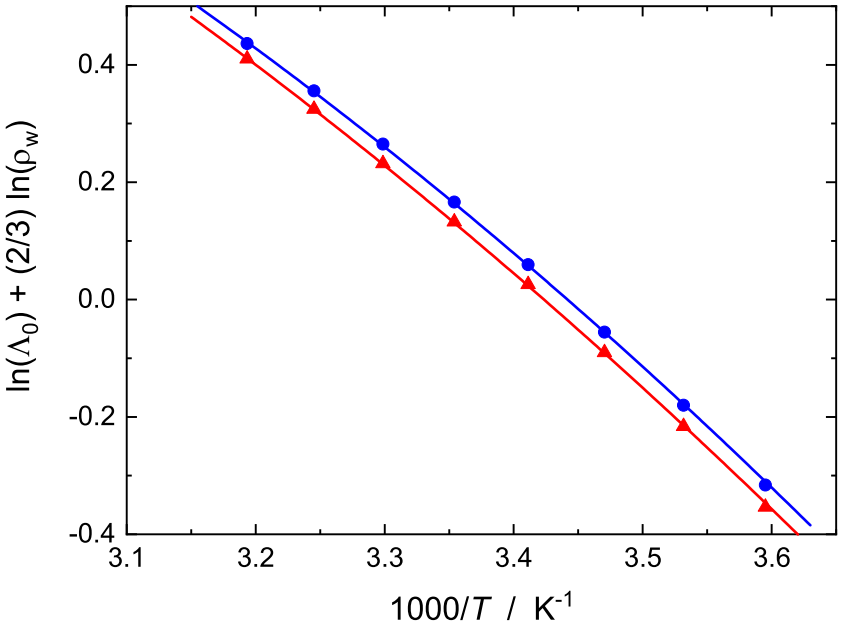

Figure S14: Brummer-Hill plot, $\ln[\Lambda_0/(\mathrm{S\,m^2mol^{-1}})] + (2/3) \times \ln[\rho_w/(\mathrm{kg\,m^3})]$, as a function of T^{-1} of aqueous ChCl (●) and ClChCl (▲).

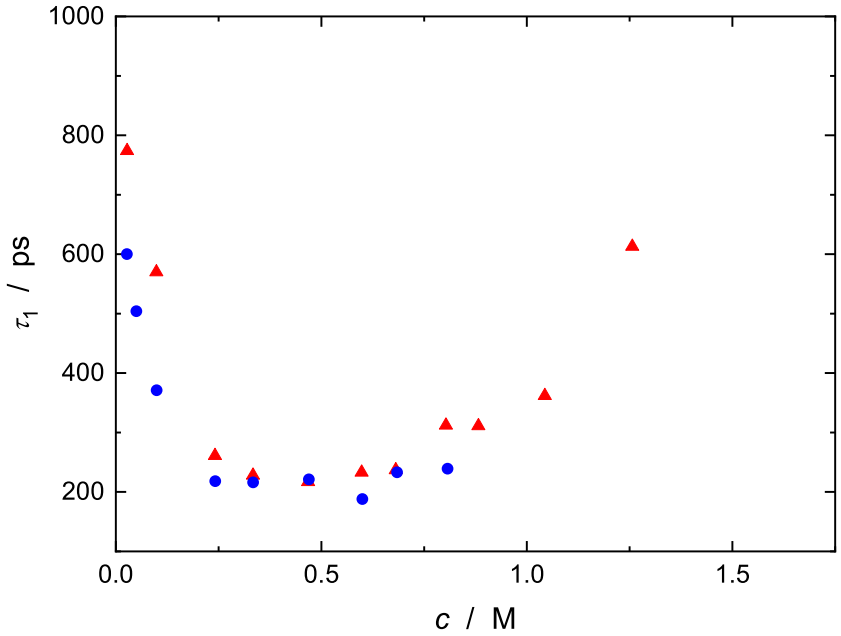

Figure S15: Relaxation time, τ_1, of the ion-pair/ion-cloud relaxation of aqueous ChCl (●) and ClChCl (▲) as a function of concentration, c, at 298.15 K.

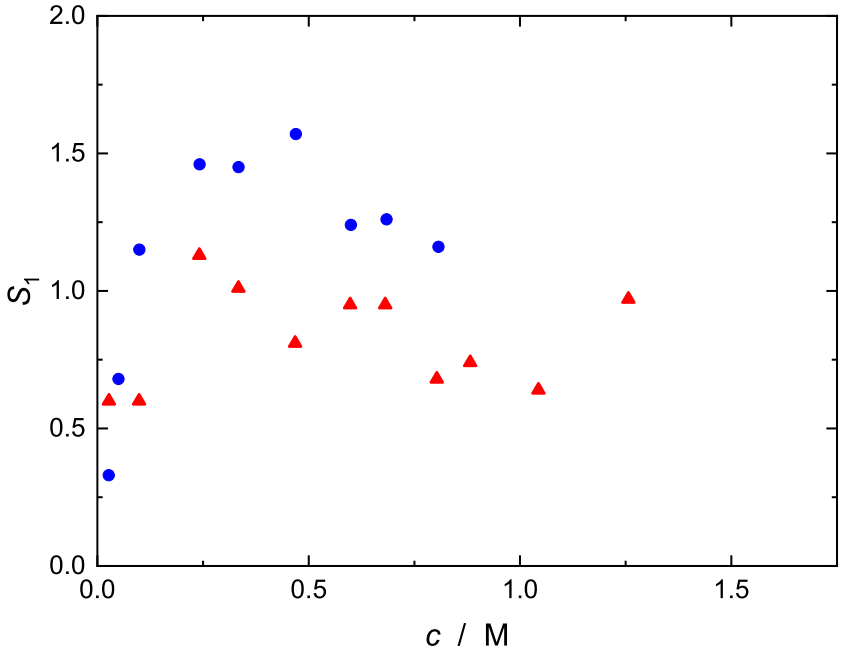

Figure S16: Amplitude, S_1, of the ion-pair/ion-cloud relaxation of aqueous ChCl (●) and ClChCl (▲) as a function of concentration, c, at 298.15 K.

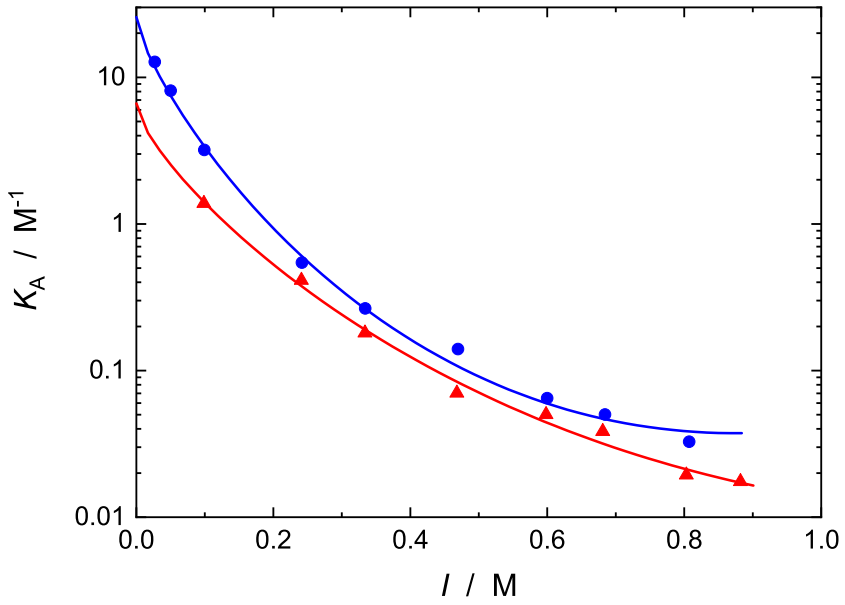

Figure S17: DRS association numbers, K_a, as a function of ionic strength, I, of aqueous ChCl (●) and ClChCl (▲) at 298.15 K assuming SIP formation.

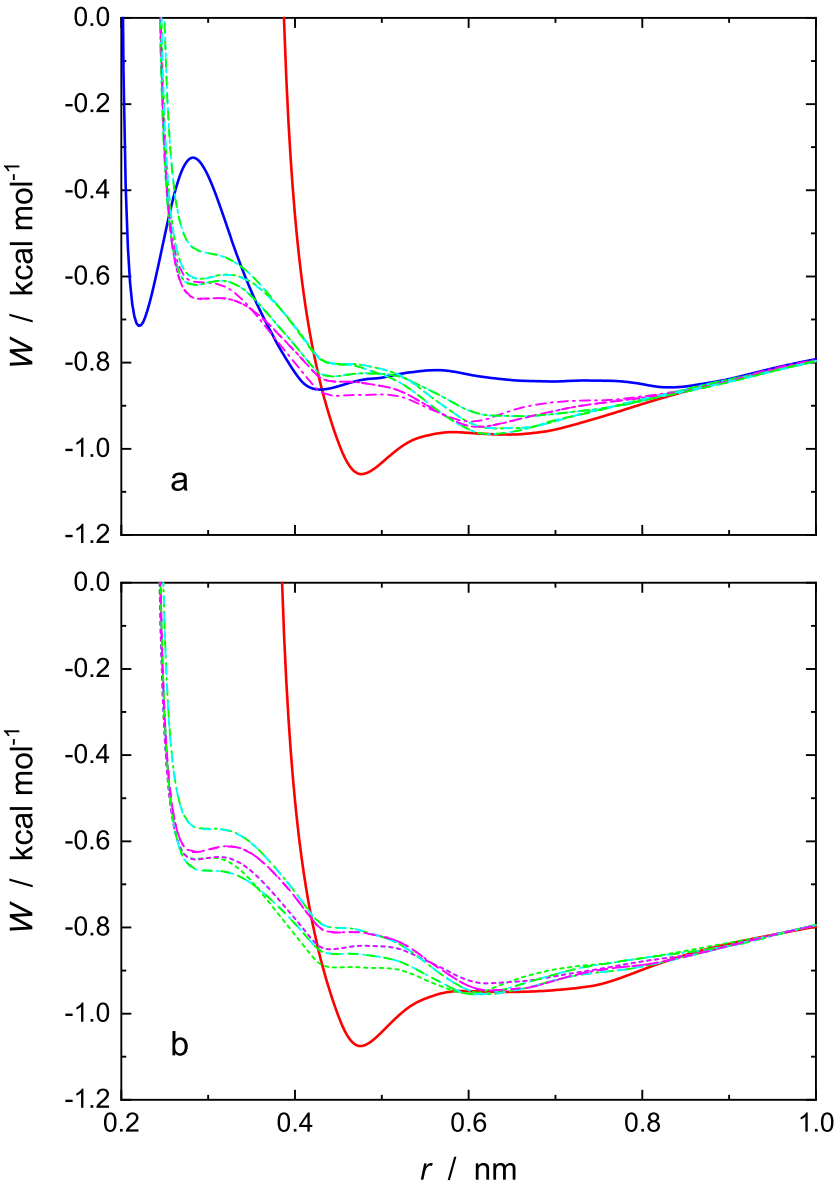

Figure S18: Potentials of mean force (PMFs), W, from 1D-RISM calculations between the anion and selected atoms of (a) ChCl and (b) ClChCl. The solid red line in panels (a) and (b) is the PMF between Cl^- and N; the blue line in (a) is between Cl^- and Ho; the dashed, dash-dotted and long-dashed curves in (a) and (b) are the PMFs between Cl^- and the nine Hm sites of the cations.

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