

**Supplementary Material for**  
**“Evidence for reduced hydrogen-bond cooperativity in ionic solvation shells from isotope-dependent dielectric relaxation”**

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**DIELECTRIC RELAXATION MEASUREMENTS OF ELECTROLYTE SOLUTIONS**

We have measured the complex permittivity for a series of NaCl and CsCl solutions in H<sub>2</sub>O and D<sub>2</sub>O in the frequency range of 1–50 GHz. The set-up was calibrated by measuring the permittivity of air (open circuit), deionized water (5.5 μS/m) at 23°C and silver paint (short circuit). The dielectric properties of pure water at the desired temperature were extracted from the results obtained previously by Buchner and co-workers [1].

In order to investigate the orientational dynamics of water molecules in solvation shells, we measured the amplitude of the Debye dipole relaxation process,  $A_D$ , in steps of 0.1 molal up to 1.0 molal. Upon preparation, the density of all samples was measured to calculate both the number of ions per volume unit,  $c$ , and the reduction of  $A_D$  due to dilution of the solvent, referred as  $A_{D,n}$ .

As shown in similar literature [1–3], the dielectric permittivity of aqueous electrolytes is well described using the Cole–Cole relaxation model and an additional contribution arising from the translational motion of ions, i.e. ionic conductivity. The total permittivity can be determined by performing a least-square fit of the following equation:

$$\hat{\epsilon}(\nu) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i2\pi\nu\tau_D)^{1-\alpha}} - \frac{i\kappa}{2\pi\nu\epsilon_0}, \quad (1)$$

with  $A_D(c) = \epsilon_s(c) - \epsilon_\infty$ . Based on earlier observations [4], we fixed  $\epsilon_\infty$  to the value of pure solvent during the fitting procedures to achieve better agreement in our values. In the case of D<sub>2</sub>O, however, experimental values for its dielectric properties are largely lacking. The dielectric properties of pure D<sub>2</sub>O at 23°C were determined first using equation (1) with  $\alpha = 0$  and  $\kappa = 0$ , and then obtaining  $\epsilon_\infty = 5.803$ ,  $A_D(0) = 72.783$  and  $\tau_D(0) = 11.07$  ps.

Apart from the dilution of the solvent, the dielectric response of the system is also reduced due to the strong orientational fields of ions, i.e. depolarization. In the main text we have defined depolarization as  $\Delta A_D(c) = A_{D,n}(c) - A_D(c)$ . Tables I–IV contain all the experimental values extracted for dielectric properties of the studied solutions.

TABLE I. Molality,  $m$ , density,  $\rho$ , ionic concentration,  $c$ , reduced dielectric response due to dilution of the solvent,  $A_{D,n}$ , depolarization,  $\Delta A_D$ , dielectric relaxation parameters  $\tau_D$ ,  $\alpha$  and specific conductivity,  $\kappa$ , of NaCl in H<sub>2</sub>O at 23°C.

$m$ [mol/kg]	$\rho$ [g/dm <sup>3</sup> ]	$c$ [mol/dm <sup>3</sup> ]	$A_{D,n}$	$\Delta A_D$	$\tau_D$ [ps]	$\alpha$	$\kappa$ [S/m]
0.1	1000.65	0.0996	73.043	1.452(33)	8.598	0.0006	1.025(4)
0.2	1004.75	0.1993	72.916	2.706(15)	8.538	0.0031	1.938(7)
0.3	1008.77	0.2984	72.786	3.870(20)	8.455	0.0050	2.806(9)
0.4	1012.70	0.3973	72.650	4.901(23)	8.398	0.0075	3.623(8)
0.5	1016.67	0.4954	72.521	5.904(20)	8.342	0.0098	4.410(5)
0.6	1020.57	0.5933	72.387	6.827(7)	8.299	0.0121	5.175(6)
0.7	1024.50	0.6913	72.255	7.761(33)	8.240	0.0142	5.914(5)
0.8	1028.40	0.7886	72.124	8.684(18)	8.190	0.0164	6.639(10)
0.9	1032.25	0.8854	71.991	9.565(17)	8.137	0.0186	7.338(6)
1.0	1036.00	0.9819	71.853	10.396(52)	8.099	0.0212	8.003(28)

TABLE II. Molality,  $m$ , density,  $\rho$ , ionic concentration,  $c$ , reduced dielectric response due to dilution of the solvent,  $A_{D,n}$ , depolarization,  $\Delta A_D$ , dielectric relaxation parameters  $\tau_D$ ,  $\alpha$  and specific conductivity,  $\kappa$ , of NaCl in  $D_2O$  at  $23^\circ C$ .

$m$ [mol/kg]	$\rho$ [g/dm <sup>3</sup> ]	$c$ [mol/dm <sup>3</sup> ]	$A_{D,n}$	$\Delta A_D$	$\tau_D$ [ps]	$\alpha$	$\kappa$ [S/m]
0.1	1108.00	0.0997	72.756	1.491(17)	10.931	0.0019	0.845(3)
0.2	1111.92	0.1992	72.631	2.749(32)	10.830	0.0006	1.592(6)
0.3	1115.93	0.2984	72.513	3.909(9)	10.732	0.0033	2.314(7)
0.4	1119.82	0.3971	72.389	4.969(13)	10.651	0.0055	2.991(6)
0.5	1123.63	0.4956	72.260	5.984(5)	10.575	0.0080	3.650(9)
0.6	1127.35	0.5935	72.129	6.933(12)	10.500	0.0103	4.273(9)
0.7	1131.10	0.6913	71.999	7.870(18)	10.432	0.0127	4.878(3)
0.8	1134.95	0.7886	71.877	8.813(31)	10.336	0.0148	5.491(17)
0.9	1138.57	0.8860	71.741	9.699(26)	10.258	0.0169	6.073(17)
1.0	1142.20	0.9825	71.608	10.545(26)	10.191	0.0190	6.631(16)

TABLE III. Molality,  $m$ , density,  $\rho$ , ionic concentration,  $c$ , reduced dielectric response due to dilution of the solvent,  $A_{D,n}$ , depolarization,  $\Delta A_D$ , dielectric relaxation parameters  $\tau_D$ ,  $\alpha$  and specific conductivity,  $\kappa$ , of CsCl in  $H_2O$  at  $23^\circ C$ .

$m$ [mol/kg]	$\rho$ [g/dm <sup>3</sup> ]	$c$ [mol/dm <sup>3</sup> ]	$A_{D,n}$	$\Delta A_D$	$\tau_D$ [ps]	$\alpha$	$\kappa$ [S/m]
0.1	1009.40	0.0996	72.881	0.975(21)	8.602	0.0016	1.241(7)
0.2	1022.00	0.1982	72.587	1.594(23)	8.534	0.0036	2.367(4)
0.3	1034.60	0.2967	72.295	2.104(32)	8.473	0.0059	3.448(5)
0.4	1047.00	0.3934	72.011	2.533(24)	8.428	0.0082	4.478(12)
0.5	1059.33	0.4902	71.719	2.912(40)	8.363	0.0102	5.490(20)
0.6	1071.55	0.5859	71.433	3.333(39)	8.338	0.0123	6.484(20)
0.7	1083.65	0.6806	71.151	3.720(39)	8.292	0.0140	7.460(8)
0.8	1095.75	0.7749	70.874	4.161(16)	8.246	0.0154	8.419(3)
0.9	1107.55	0.8685	70.583	4.498(47)	8.194	0.0169	9.369(4)
1.0	1119.15	0.9607	70.295	4.882(29)	8.152	0.0180	10.284(10)

TABLE IV. Molality,  $m$ , density,  $\rho$ , ionic concentration,  $c$ , reduced dielectric response due to dilution of the solvent,  $A_{D,n}$ , depolarization,  $\Delta A_D$ , dielectric relaxation parameters  $\tau_D$ ,  $\alpha$  and specific conductivity,  $\kappa$ , of CsCl in  $D_2O$  at  $23^\circ C$ .

$m$ [mol/kg]	$\rho$ [g/dm <sup>3</sup> ]	$c$ [mol/dm <sup>3</sup> ]	$A_{D,n}$	$\Delta A_D$	$\tau_D$ [ps]	$\alpha$	$\kappa$ [S/m]
0.1	1116.55	0.0996	72.618	1.009(11)	10.946	0.0013	1.030(2)
0.2	1128.80	0.1985	72.327	1.623(28)	10.848	0.0018	1.962(2)
0.3	1140.95	0.2967	72.038	2.119(17)	10.762	0.0045	2.856(1)
0.4	1153.10	0.3937	71.762	2.577(16)	10.695	0.0070	3.719(3)
0.5	1164.90	0.4903	71.468	2.982(10)	10.612	0.0090	4.554(7)
0.6	1176.90	0.5859	71.197	3.427(16)	10.548	0.0113	5.391(3)
0.7	1188.75	0.6809	70.923	3.827(19)	10.469	0.0127	6.213(13)
0.8	1200.25	0.7752	70.635	4.253(36)	10.369	0.0137	7.016(9)
0.9	1211.70	0.8686	70.352	4.647(30)	10.292	0.0150	7.802(9)
1.0	1222.92	0.9609	70.067	5.033(46)	10.232	0.0167	8.576(24)

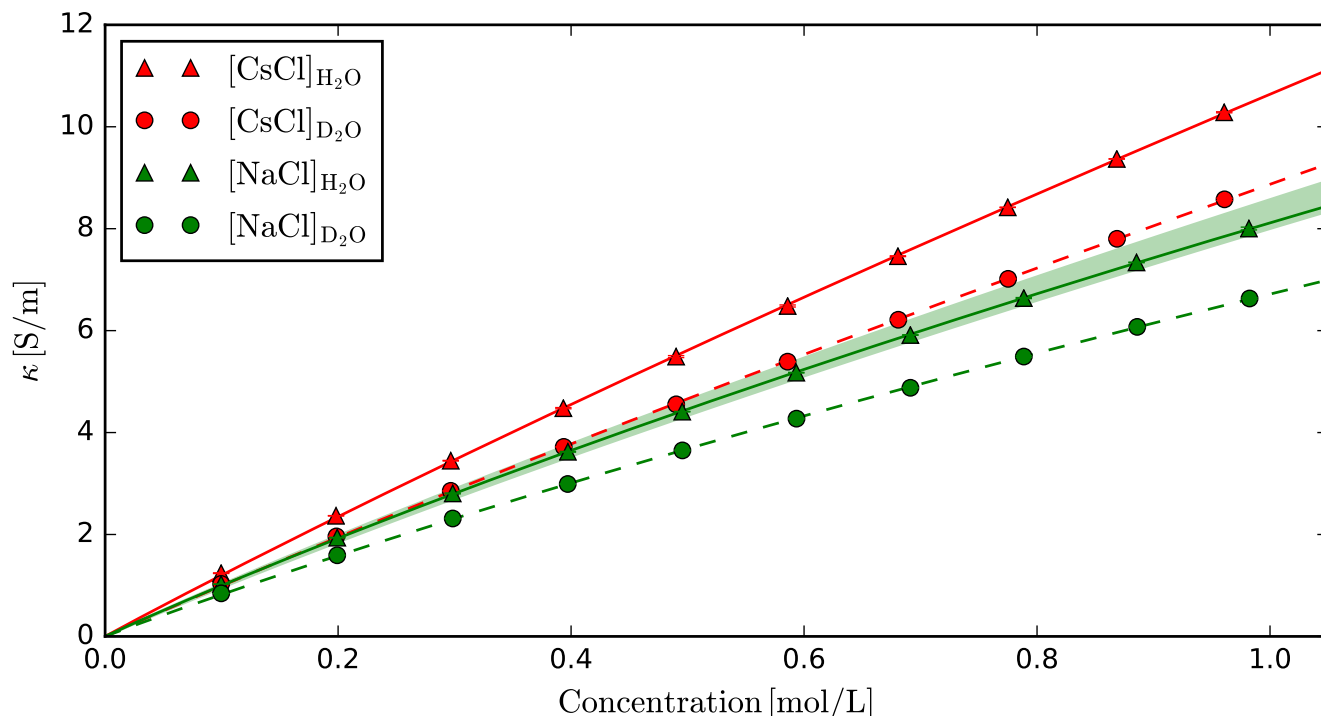


FIG. 1. Conductivity  $\kappa$  as a function of the salt concentration for the four salt solutions. The green area represents the interpolated confidence interval of  $\kappa([\text{NaCl}])$  in  $\text{H}_2\text{O}$  at  $23^\circ\text{C}$  reported in references [1] and [5].

#### CONDUCTIVITY DATA

Figure 1 displays conductivity data given in tables I–IV as a function of the ionic concentration. As is stated in the main text of the article, our experimental data are well described with the expression:

$$\kappa(c) = Ac - Bc^{3/2}, \quad (2)$$

which has the same functional form as the Kohlrausch’s law that applies only in dilute solutions. Despite the large literature on ionic conductivity, experimental data at high concentrations, and particularly in  $\text{D}_2\text{O}$ , are largely lacking. However,  $\text{NaCl}$  in  $\text{H}_2\text{O}$  has been studied previously at concentrations similar to ours [1, 5], and the interpolated confidence interval of  $\kappa([\text{NaCl}])$  in  $\text{H}_2\text{O}$  at  $23^\circ\text{C}$  obtained from this previous data (green area) agrees well with our experimental data.

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