# Supplementary Material for: A screening of results on the decay length in concentrated electrolytes<sup>†</sup>

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# S1 Simulation details

## S1.1 Simulations of aqueous electrolytes in realistic mica slabs

All simulations are performed using the GROMACS simulation package<sup>1,2</sup> version 2021 with a time step of  $\Delta t = 2$  fs. Centre-of-mass motion removal is performed by removing the translational velocity of the system every 100 time steps. A cut-off for the calculation of the Lennard-Jones interaction at  $r_{vdW} = 1.2$  nm is used, while the potential is shifted such that it is zero at the cut-off. Electrostatic forces are calculated via the smooth Particle-Mesh Ewald method with cubic interpolation. The relative strength of the shifted direct potential at the cut-off distance of  $r_{Coulomb} = 1.2$  nm is set to  $10^{-5}$ . Temperature coupling is implemented using the Bussi-Donadio-Parrinello thermostat at a temperature of 300 K and a coupling parameter  $\tau_T = 0.1$  ps. For pressure coupling we employ the Berendsen barostat with a target pressure of 1 bar and a coupling parameter of  $\tau_p = 1.0$  ps and the compressibility is set to  $4.5 \times 10^{-5}$  bar<sup>-1</sup>. For water the TIP4P/ $\varepsilon$  model<sup>3</sup> is employed and ions are treated as point charges with thermodynamically optimised Lennard-Jones parameters by Loche *et al.*<sup>4</sup>.

To mimic closely the experimental setup in a SFB apparatus, we employ a 2d-periodic simulation setup with cleaved mica sheets as boundaries. Mica are minerals that belong to the group of phyllosilicates, which are mainly composed of tetrahedral (T) and octahedral (O) layers. The tetrahedral layers consist of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra, with the oxygen atoms forming the corners and the connection between the individual tetrahedra. Parallel to the tetrahedral layers are the octahedral layers, formed of Al, Fe or Mg in the centre and oxygen or OH groups at the corners. The individual layers are connected exclusively by weak van-der-Waals interactions, resulting in perfect cleavage parallel to the layers. Depending on the combination of the tetrahedral and octahedral layers, two-, three- or four-layer minerals can be formed. The three-layer minerals are called the mica group. Thus, mica consists of one tetrahedral, one octahedral and a second tetrahedral layer (T-O-T). As a connection to the next T-O-T layer serve the so-called interlayer ions, *e.g.* K, Na or Ca. The mica surface considered in this work, muscovite (light mica), is dioctahedral and has the simplified structural formula KAl<sub>2</sub>[(OH)<sub>2</sub> AlSi<sub>3</sub>O<sub>10</sub>], which indicates that two of the octahedral sites are exclusively occupied by Al and the third octahedral site is not occupied, whereas the tetrahedral sites are occupied by both Si and Al atoms<sup>5,6</sup>. For the computational model, a muskovite unit cell from InterfaceFF<sup>7</sup> is used. The InterfaceFF force field package is a database consisting of atomistic nanostructures and corresponding force field parameters to allow for simulations with a high chemical accuracy. See S1(a) for a snapshot of the simulated muscovite double layer setup.

The system is prepared by cleaving the mica sheet to a structure-less wall mimicking a silica substrate, implemented via an integrated 9-3 Lennard-Jones potential corresponding to the integrated areal number density  $0.68 \text{ nm}^{-1}$  of atoms

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Fig. S1 Atomistic simulation system. (a) Snapshot of the mica double layer structure. Only the interlayer cations are shown here for clarity. (b) Solvated structure at distance D = 15 nm between the outermost mica atoms. Mica layers are non-covalently bound to silicon (indicated by shaded blue area) via van-der-Waals forces. Shown is the case without added salt, *i.e.* only the surface counter-ions are present.

of the same kind as the silicon atoms in the mica sheets. The mica sheets are separated from the walls by an interlayer of potassium cations. The system is simulated with 2D periodic boundary conditions for Lennard-Jones interactions and the Yeh-Berkowitz correction<sup>8</sup> for the Ewald sum with an effective vacuum layer between the periodic images of two times the simulation box volume. The initial structure is separated by a distance of D = 15 nm and filled with water, followed by steepest descent minimisations with a maximum of 10000 steps at a 0.01 nm step size and terminated at a maximum force of  $5 \text{ kJ mol}^{-1} \text{ nm}^{-1}$  and subsequent equilibration in the constant volume NVT ensemble, see Fig. S1(b). Then, a NPT run with anisotropic Berendsen pressure coupling was performed for 10 ns, yielding lateral dimensions ( $2.88 \times 3.00$ ) nm<sup>2</sup> and width in *z* direction 2.04 nm. In the production runs the distance *D* is varied and corresponding amounts of water and salt ion pairs are as described below. Note that in the aqueous phase the K surface counter-ions have been replaced by Na to avoid mixing effects of different salts in this study.

#### S1.2 Simulations at controlled water chemical potential

The computer simulation of interacting surfaces is still posing a challenging task, as the chemical potential of the confined species needs to be accounted for. We here follow the thermodynamic extrapolation method established for a single species (namely water)<sup>9</sup> but generalise this approach to the case of (binary) mixtures. In detail, we imply charge neutrality in the simulation box by treating separately the counter-ions that compensate for the surfaces' charge and the added salt. The number of water molecules,  $N_w$ , and salt ion pairs,  $N_{ion}$  is adjusted for a given, fixed, surface separation D in order to match the chemical potential in bulk at the desired concentration  $c_b$  in bulk. The latter is determined as described below in a cubic simulation box containing  $N_w = 2111$  water molecules, corresponding to a box length of ~ 4 nm. Using that the concentration of water at atmospheric conditions and T = 300 K is 55 mol/l, the number of salt molecules that need to be added then follows as  $N_w = c_{ion} \cdot N_w/(55 \text{ mol/l})$ , corresponding to  $N_{ion} = 4$  at the lowest concentration considered,  $c_b = 0.1 \text{ mol/l}$ , up to  $N_{ion} = 77$  at the highest concentration considered here,  $c_b = 2.0 \text{ mol/l}$ .

In order to measure the chemical potential of species  $\alpha$  with an accuracy as high as 0.01  $k_{\rm B}T$ , we split  $\mu$  into its contributions stemming from the ideal gas, from the Lennard-Jones interactions, and the Coulomb energy, respectively, according to

$$\mu_{\alpha}(z) = \mu_{\alpha}^{\text{id}}(z) + \mu_{\alpha}^{\text{LJ}}(z) + \mu_{\alpha}^{\text{Coul}}(z).$$
(S1)

Note that at interfaces or in confinement, the terms appearing in S1 in general depend on the position *z* normal to the interface. The first term is the ideal gas contribution  $k_{\rm B}T \log \left(\rho_{\alpha}(z)\Lambda_{\alpha}^3\right)$ , where  $\rho_{\alpha}(z)$  is the local number density and

 $\Lambda_{\alpha} = \sqrt{h^2/(2\pi m_{\alpha}k_{\rm B}T)}$  is the thermal de Broglie wavelength and  $m_{\alpha}$  the mass of particles of species  $\alpha$ . In thermodynamic equilibrium, the total chemical potential  $\mu_{\alpha}$  is independent of the position *z*, therefore it can be evaluated at an arbitrary position, which we choose for convenience in the centre of the water slab between the surfaces.

To obtain the excess chemical potentials it has proven convenient to employ a modified Hamiltonian approach<sup>9,10</sup> evaluating the free energy difference between a non-interacting molecule/salt ion pair and a fully coupled one, where the coupling is characterized by a parameter  $\lambda \in [0, 1]$  scaling the vdW/electrostatic interactions. The free energy difference between distinct  $\lambda$  states is then evaluated by the MBAR method, minimising the statistical uncertainty.<sup>11</sup>. In our simulations, we employ 38  $\lambda$  states, *cf*. Table S1 and evaluate the corresponding free energy changes using PyMBAR<sup>12</sup>. However, a significant reduction of the computation time can be achieved by realising that a TIP4P/ $\varepsilon$  water molecule consists of a single LJ interaction site only, therefore it is convenient to evaluate  $\mu_w^{LJ}$  via the Widom Test Particle Insertion method (TPI)<sup>13</sup>, rendering the first 20  $\lambda$  states obsolete for water.

state	0	1	2	3	4	5	6	7	8	9	10	11	12
λ <sub>coul</sub>	0	0	0	0	0	0	0	0	0	0	0	0	0
λ <sub>VdW</sub>	0.0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6
state	13	14	15	16	17	18	19	20	21	22	23	24	25
λ <sub>coul</sub>	0	0	0	0	0	0	0	0	0.075	0.15	0.225	0.30	0.375
λ <sub>VdW</sub>	0.65	0.7	0.75	0.8	0.85	0.9	0.95	1.0	1.0	1.0	1.0	1.0	1.0
state	26	27	28	29	30	31	32	33	34	35	36	37	-
λ <sub>coul</sub>	0.45	0.5	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.0	
λ <sub>VdW</sub>	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	

Table S1 Overview over the  $\lambda$ -states employed for the modified Hamiltonian simulations with the corresponding scaling factors.

## S2 Dielectric constant of the explicit solvent dumbbell model

### S2.1 Apparent dielectric constant from DFT calculations of a plate capacitor

To estimate the dielectric constant of the dumbbell solvent model presented in detail in the main text, we here follow an approach based on a plate capacitor setup, depicted in the inset of Fig. S2. The capacitor consists of two plates with opposite charge density  $\pm Q$  and is filled with the solvent model at the bulk concentration  $\rho_s = 55.6 \text{ mol/l}$ . A potential difference  $\Delta \Psi = 2\Psi_0 = 2k_BT \approx 0.05 \text{ V}$  is applied over a slit with D = 4 nm.

We then determined the *apparent* dielectric constant of the capacitor, *i.e.* assuming that it can be described in terms of a *homogeneous* dielectric background of the same width *D* based on the surface charge density: for a plate capacitor filled with a homogeneous dielectric, latter is given by

$$Q = C\Delta \Psi = \frac{\varepsilon_0 \varepsilon_r}{D} \Delta \Psi = \varepsilon_0 \varepsilon_r E.$$
(S2)

Note that the actual dielectric constant in bulk might be underestimated using this approach since interfacial effects (observed in Fig. S2 as deviations from the linear behaviour) need to be taken into account properly, which is typically done either by assuming a serial setup of capacitors<sup>14</sup> or through effective medium theory<sup>15,16</sup>. As observed in the aformentioned studies, the apparent dielectric constant can – depending on the interfacial properties – converge slowly to the bulk dielectric constant with increasing slit width *D*.

Solving Eq. (S2) for  $\varepsilon_r$  and employing the electrostatic potential profile obtained in our DFT formulation explained in detail in the main text, yields  $\varepsilon_r/\varepsilon_b \approx 2.4$ . Since we want to compare solvent-implicit calculations to the explicit solvent



Fig. S2 Capacitor setup for the solvent dielectric constant calculation Electrical potential along the *z*-axis perpendicular to the two plates with separation D = 4 nm for bulk solvent concentration  $\rho_{s,b} = 55.6 \text{ mol}/l$ . The diameter of the solvent beads is  $\sigma_s = 0.2 \text{ nm}$  and the dipole moment 1.85 D, the surface potential  $\psi_0 = 1 k_B T/e$ , and temperature T = 293 K. The inset shows the schematic model of the capacitor consisting of two infinite plates with surface charge density Q and pure dumbbell solvent inside.

case, where all electrostatic interactions are scaled by  $\varepsilon_b = 4.1$ , the corresponding value in the solvent-implicit calculations  $\varepsilon_r \approx 2.4 \cdot 4.1 = 9.8$ , which is the value given in the main text.

### S2.2 Dielectric constant of the dumbbell model from explicit molecular dynamics simulations

In order to validate the estimation of the solvent dielectric constant from the capacitor setup, we additionally performed MD simulations of a pure bulk system of dumbbell molecules using the GROMACS simulation package<sup>1</sup>. Note that we explicitly checked that simulations using ESPResSo<sup>17</sup> and LAMMPS<sup>18</sup> converge to the same value  $\varepsilon_r$ . In detail, we set up a cubic box of 2 nm sidelength containing 268 dumbbell molecules in all simulation packages, corre-

sponding to a density of 55.6 mol/l. We explicitly checked for the absence of finite size effects by performing simulations using the same density in cubic boxes of sidelengths 1.5 - 4 nm using GROMACS, yielding numerically identical results within the statistical uncertainty. The dumbbell charges are scaled by a factor  $1/\sqrt{\varepsilon_b}$  to account for the dielectric background  $\varepsilon_b = 4.1$  and the hard-sphere interaction is replaced by a Weeks-Chandler-Andersen potential,

$$u(r) = \begin{cases} 4u_0 \left[ \left(\frac{\sigma_s}{r}\right)^{12} - \left(\frac{\sigma_s}{r}\right)^6 \right] + u_0, & r < \sigma_s \\ 0, & r > \sigma_s \end{cases},$$
(S3)

where  $u_0 = 12k_BT$  ensures a strong repulsive interaction between the solvent sites of diameter  $\sigma_s$ . The bead-bead distance of the solvent model is fixed to 0.2 nm using the LINCS algorithm<sup>19</sup> with 4th order expansion and 1 iteration step. Temperature is controlled using the Bussi-Donadio-Parrinello thermostat<sup>20</sup> with a characteristic timescale of 0.1 ps and electrostatic interactions are treated using the Particle-Mesh Ewald method with the relative strength of the shifted direct potential at the cut-off distance of  $r_{\text{Coulomb}} = 0.4 \text{ nm}$  set to  $10^{-5}$ . We chose to set the mass of each bead to 9 atomic mass units and a integration timestep of 0.5 fs was employed with positions recorded every 1 ps for a simulation time of 5 ns. After neglecting an initial equilibration time of 100 ps, the dielectric constant is then evaluated from the total dipole moment fluctuations, calculated as  $\mathbf{M} = \sum_i q_i \mathbf{r}_i$ , where  $q_i$  is the charge and  $\mathbf{r}_i$  the position of bead *i*, according to<sup>21</sup>

$$\varepsilon_{\rm r} = 1 + \frac{\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}{3\varepsilon_0 V k_{\rm B} T}.$$
(S4)

The obtained value  $\varepsilon_r \approx 4.4$  is in fairly good agreement with the DFT result ( $\varepsilon_r \approx 2.4$ ) considering that the latter neglects the interfacial effects <sup>14–16</sup>.

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