Supplementary Material for "Constant Chemical Potential-Quantum Mechanical-Molecular Dynamics simulations of the Graphene-electrolyte double layer"

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S.1 Numerical Integration of the Equations

The integration of the Equation 3 and Equation 5 of the main text is performed numerically. Data are first smoothed by applying the Savitzky-Golay [1] finite impulse response smoothing filter of order 3 with a window width of 5 points, implemented in Matlab. The smoothed curves obtained are then integrated using the trapezoidal rule. Error bars are computed by error propagation through the integration procedure.

	KCl	LiCl	NaCl
concentration	$\Delta\psi^0$	$\Delta\psi^0$	$\Delta\psi^0$
0.5	0.359	0.385	0.383
2.0	0.341	0.399	0.402
3.0	0.312	0.418	0.404
4.0	0.286	0.436	0.416
4.4	0.267	0.428	0.406
6.0	–	0.471	0.420

Table S.1: Electrostatic potential drop ($\Delta\psi^0$) across the interface (in V) for the neutral electrode at each ionic system and concentration considered (in M).

	KCl	LiCl	NaCl
concentration	$\Delta\psi^-$	$\Delta\psi^-$	$\Delta\psi^-$
0.5	-0.672	-0.661	-0.664
2.0	-0.668	-0.607	-0.613
3.0	-0.688	-0.584	-0.593
4.0	-0.698	-0.565	-0.580
4.4	-0.721	-0.664	-0.580
6.0	–	-0.548	-0.583

Table S.2: Electrostatic potential drop ($\Delta\psi^-$) across the interface (in V) for the charges electrode at each ionic system and concentration considered (in M).

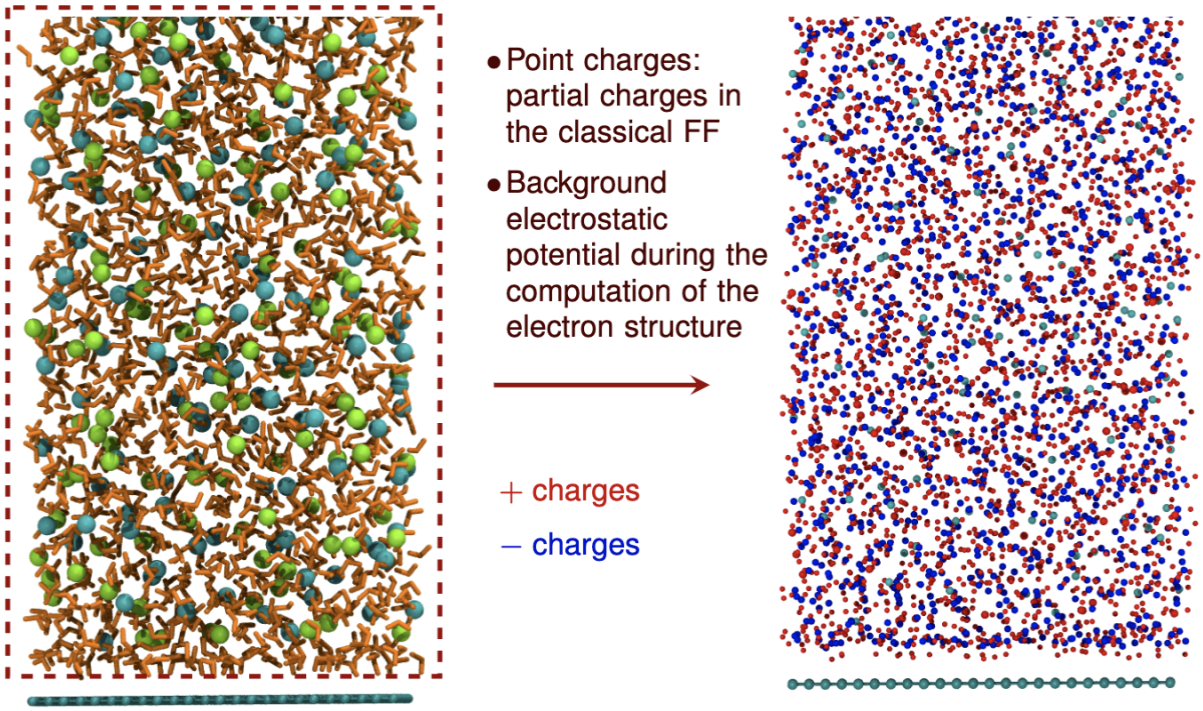

Figure S.1: Schematic of the QMMD part of the loop (represented in Figure 1 of the main paper) described in Section 2.2 of the main paper.

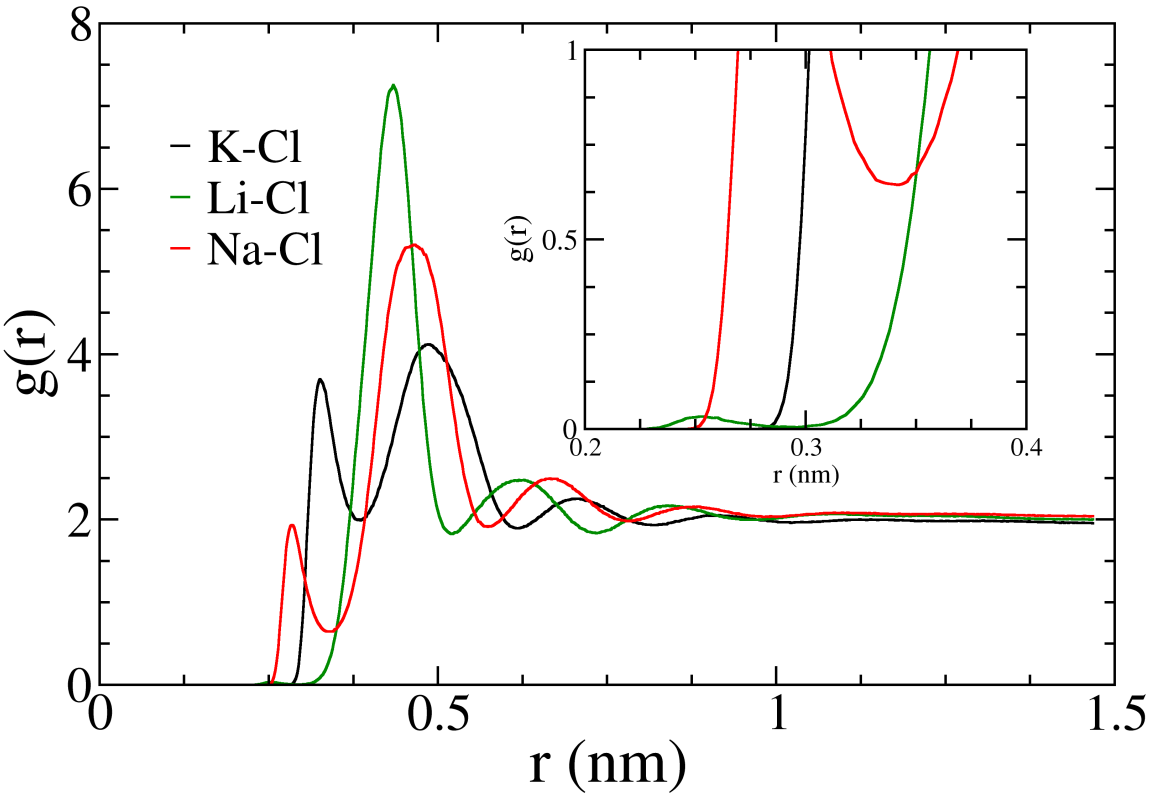

Figure S.2: Radial Distribution Function for the three systems considered. In the inset, particular of the initial region of the RDF.

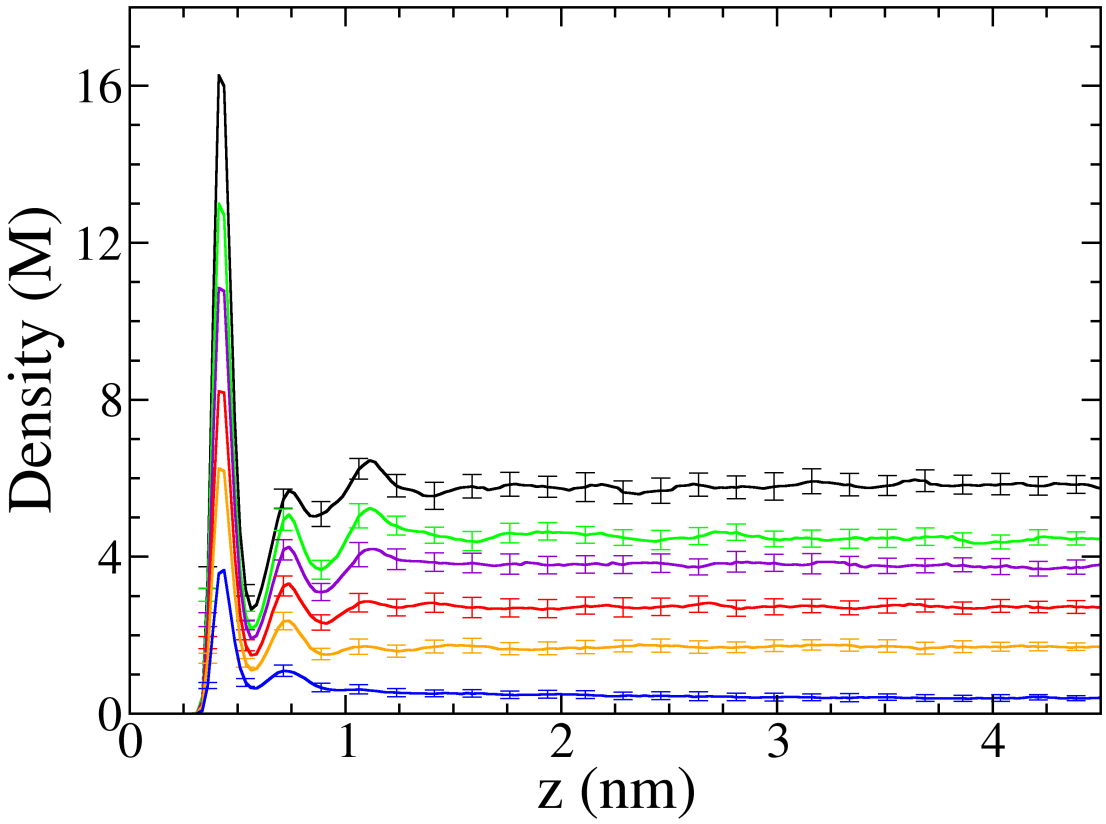

Figure S.3: Molar (M) density of Li^+ in the LiCl(aq) system for all the concentrations considered in this work. Blue, orange, red, magenta, green, black, curves correspond to bulk solution concentrations 0.5, 2, 3, 4, 4.4 and 6 M, respectively.

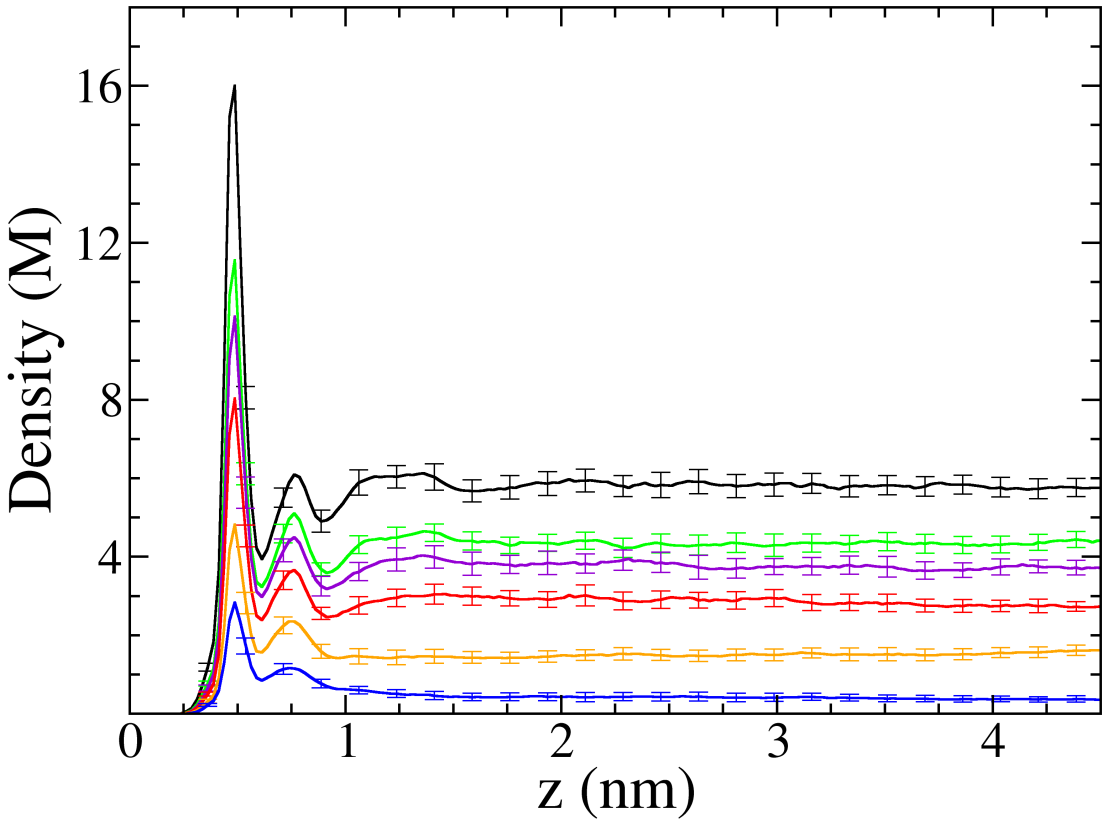

Figure S.4: Molar (M) density of the Na^+ in the NaCl(aq) system for all the concentrations considered in this work. Blue, orange, red, magenta, green, black, curves correspond to bulk solution concentrations 0.5, 2, 3, 4, 4.4 and 6 M, respectively.

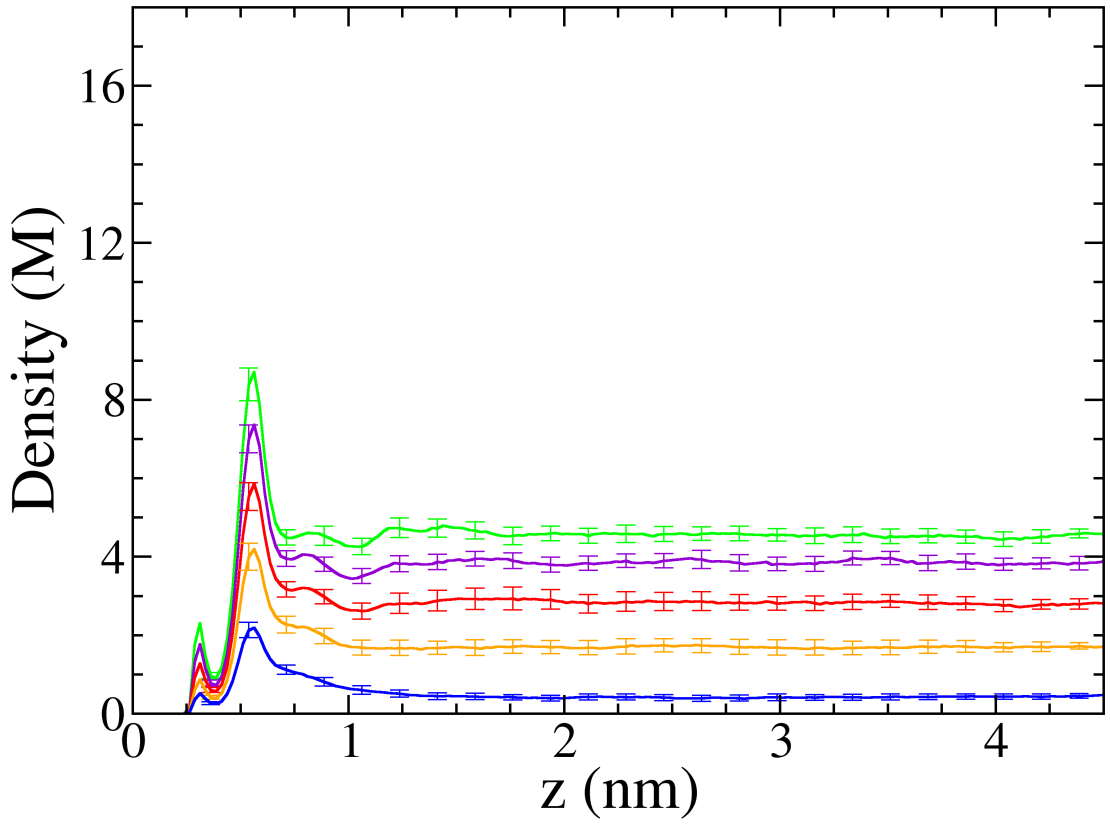

Figure S.5: Molar (M) density of K^+ in the KCl(aq) system for all the concentrations considered in this work. Blue, orange, red, magenta, green, black, curves correspond to bulk solution concentrations 0.5, 2, 3, 4, 4.4 and 6 M, respectively.

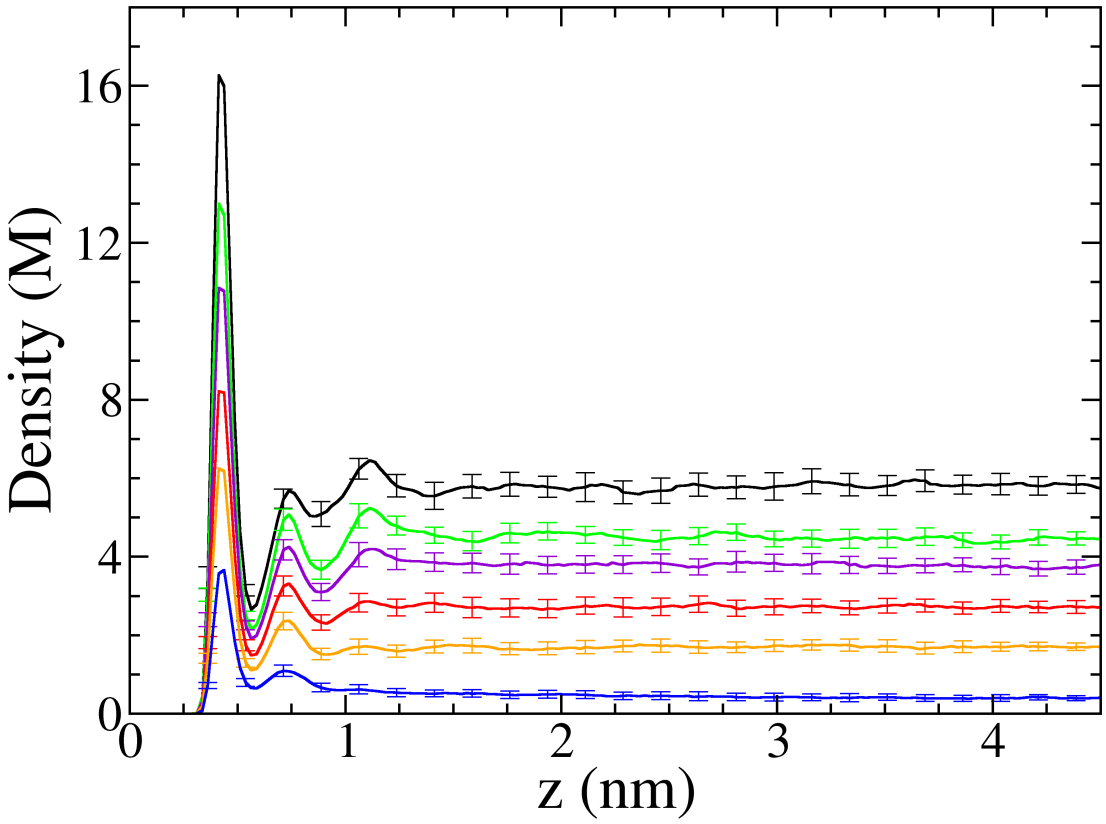

Figure S.6: Molar (M) density of the Cl^- ion in the LiCl(aq) system for all the concentrations considered in this work. Blue, orange, red, magenta, green, black, curves correspond to bulk solution concentrations 0.5, 2, 3, 4, 4.4 and 6 M, respectively.

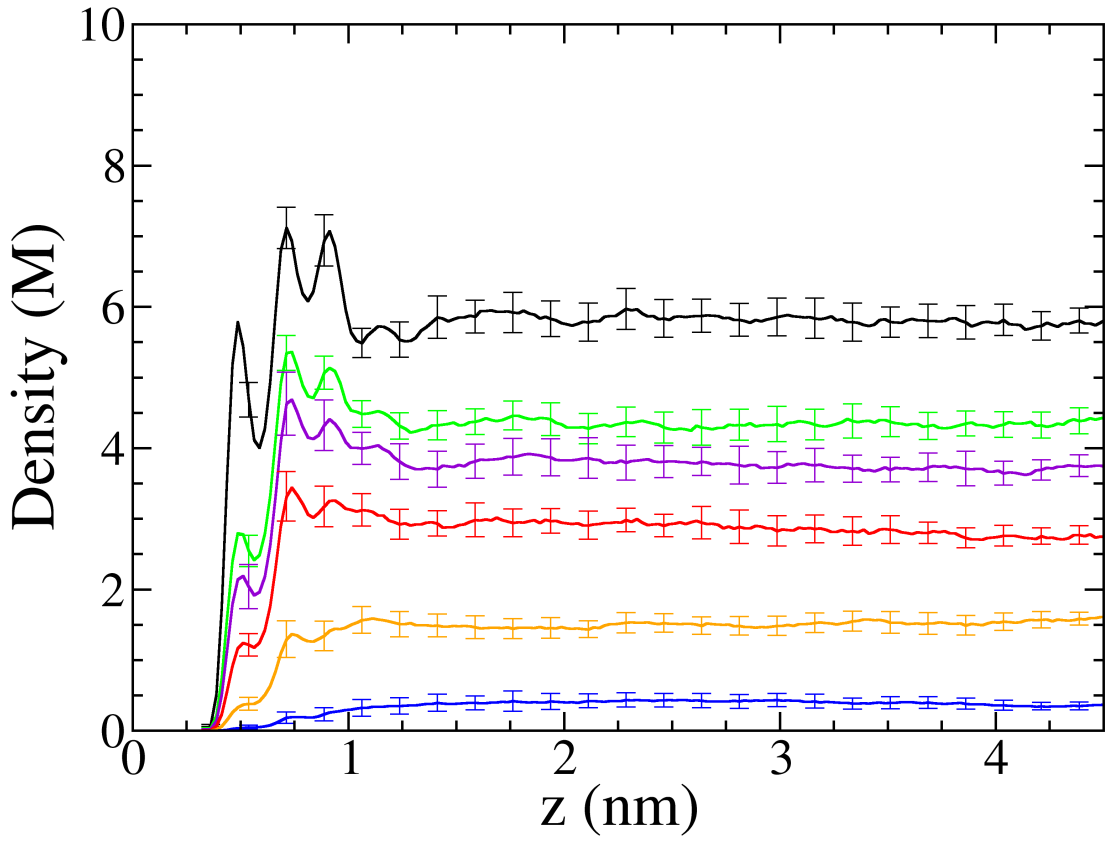

Figure S.7: Molar (M) density of the Cl^- ion in the NaCl(aq) system for all the concentrations considered in this work. Blue, orange, red, magenta, green, black, curves correspond to bulk solution concentrations 0.5, 2, 3, 4, 4.4 and 6 M, respectively.

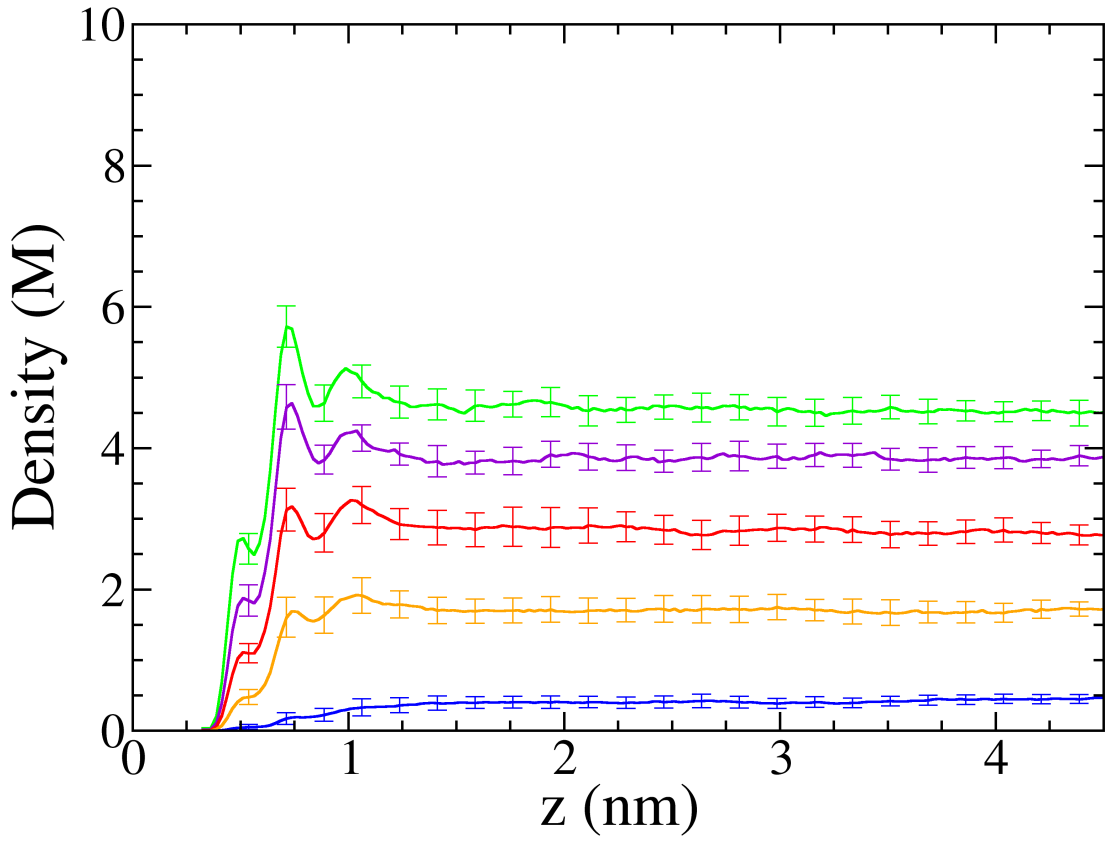

Figure S.8: Molar (M) density of the Cl^- ion in the KCl(aq) system for all the concentrations considered in this work. Blue, orange, red, magenta, green, black, curves correspond to bulk solution concentrations 0.5, 2, 3, 4, 4.4 and 6 M, respectively.

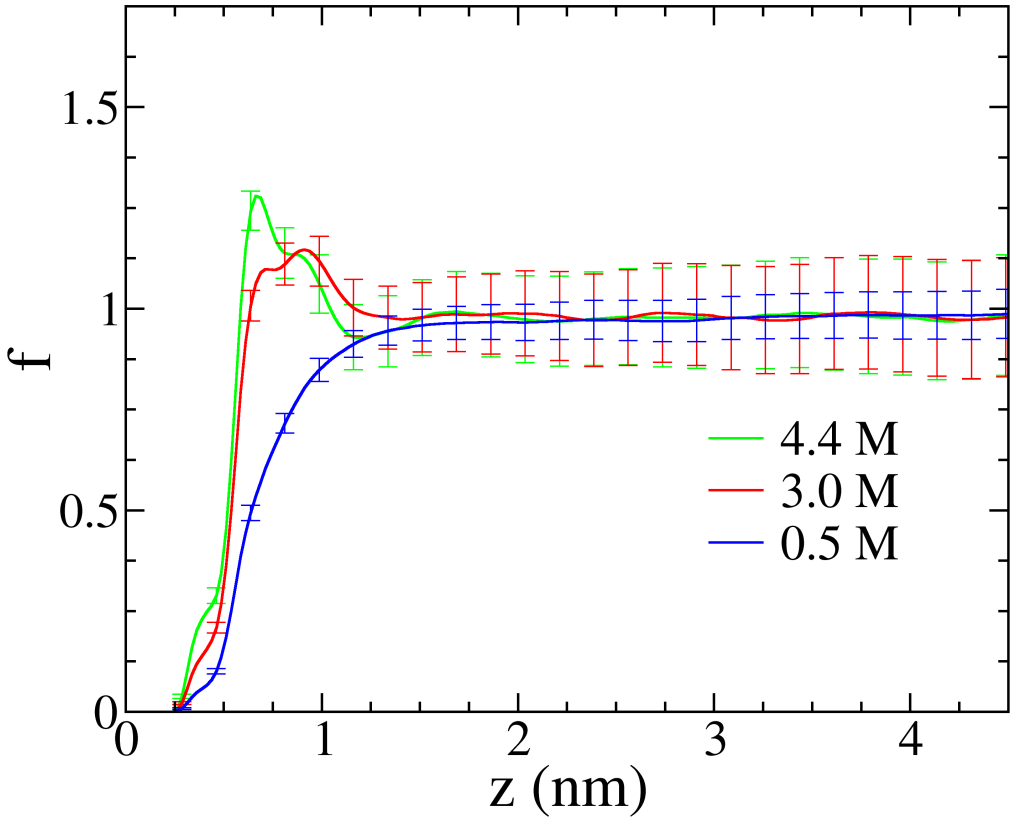

Figure S.9: Screening factor as defined in Equation 5 of the main text for the KCl(aq) system and all concentrations considered.

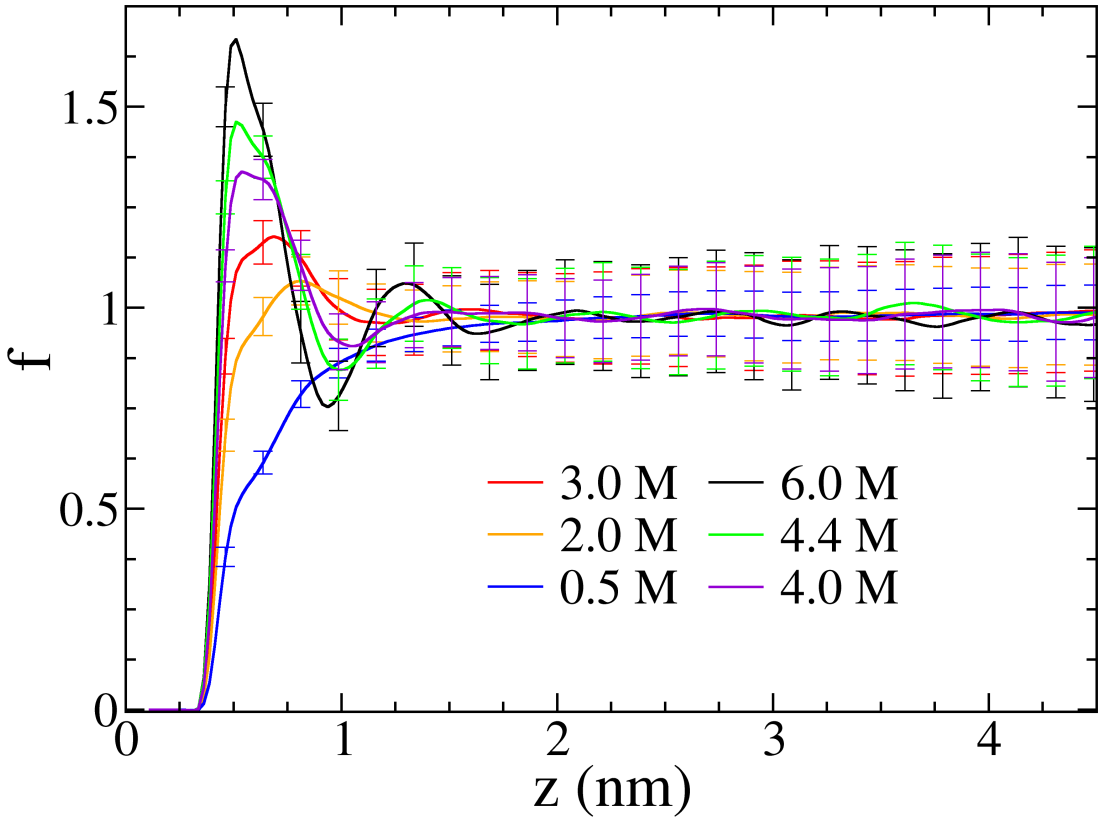

Figure S.10: Screening factor as defined in Equation 5 of the main text for the LiCl(aq) system and all concentrations considered.

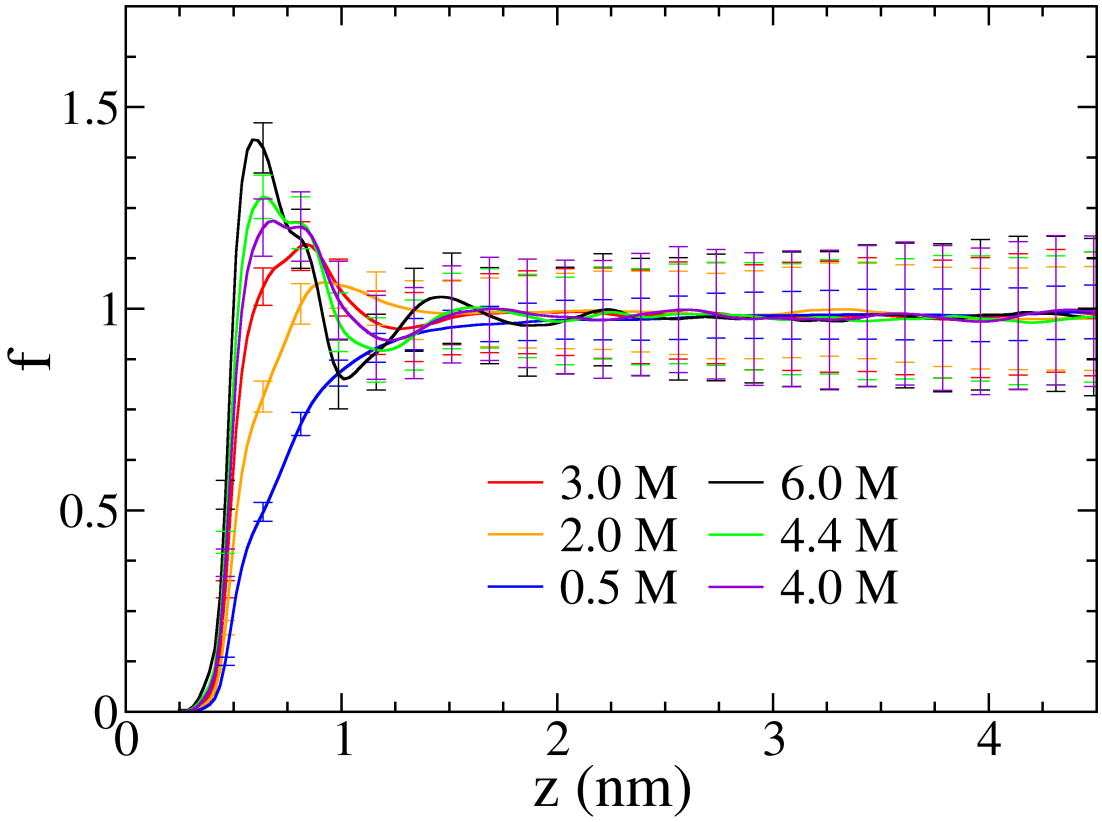

Figure S.11: Screening factor as defined in Equation 5 of the main text for the NaCl(aq) system and all concentrations considered.

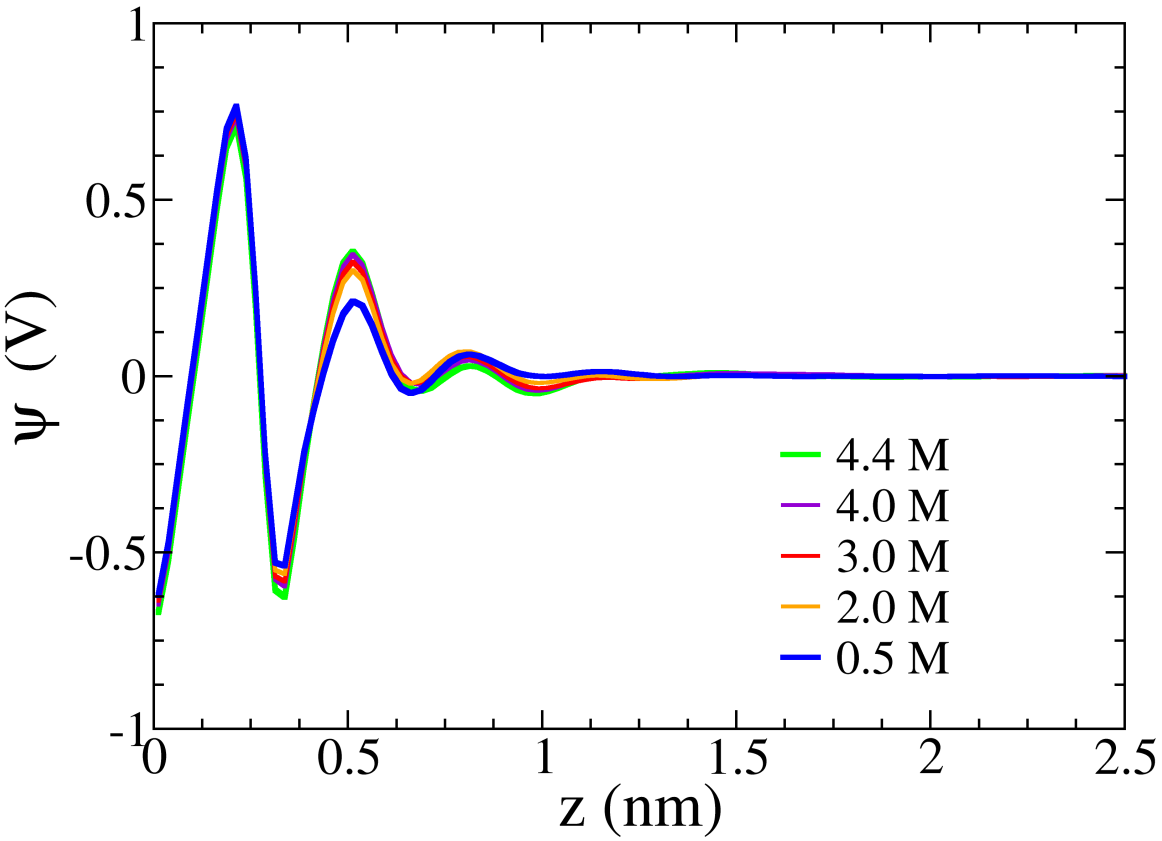

Figure S.12: Electrostatic potential as defined in Equation 4 of the main paper for the charged electrode, for the KCl(aq) system and all the concentrations considered.

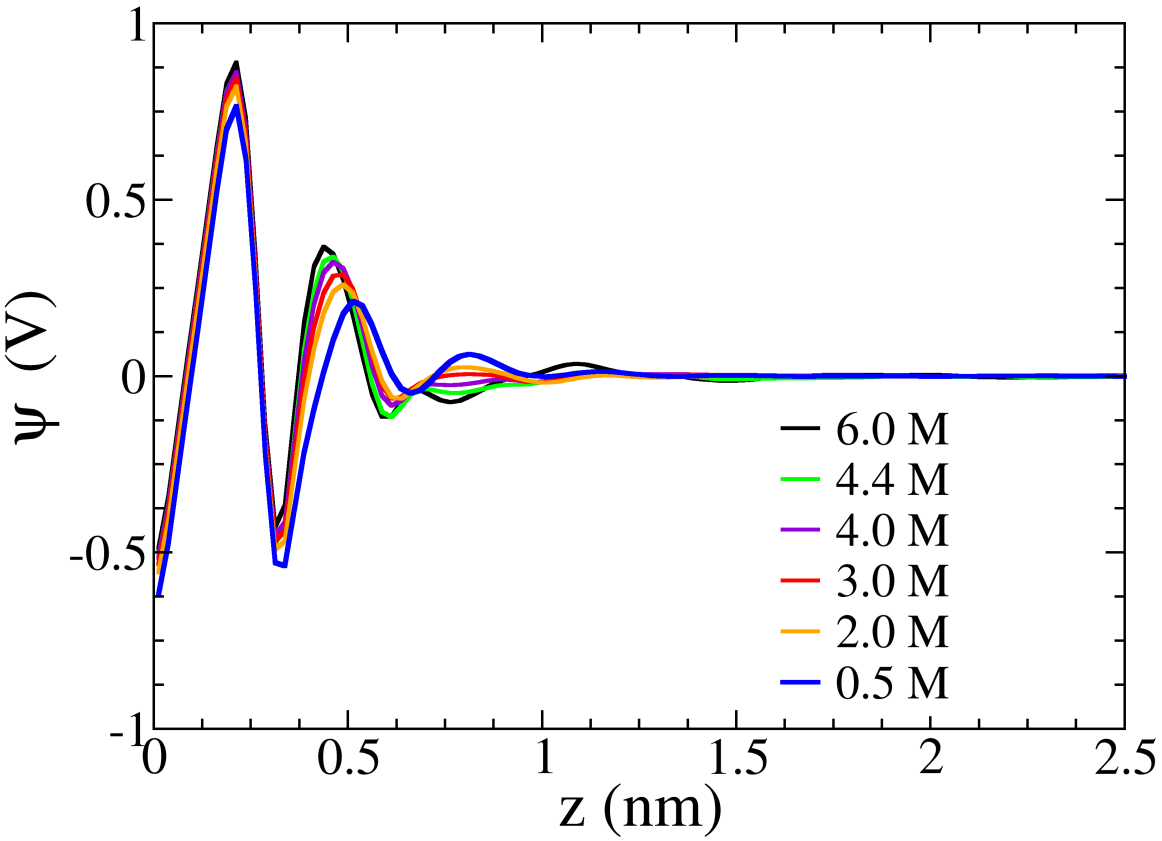

Figure S.13: Electrostatic potential as defined in Equation 4 of the main paper for the charged electrode, for the LiCl(aq) system and all the concentrations considered.

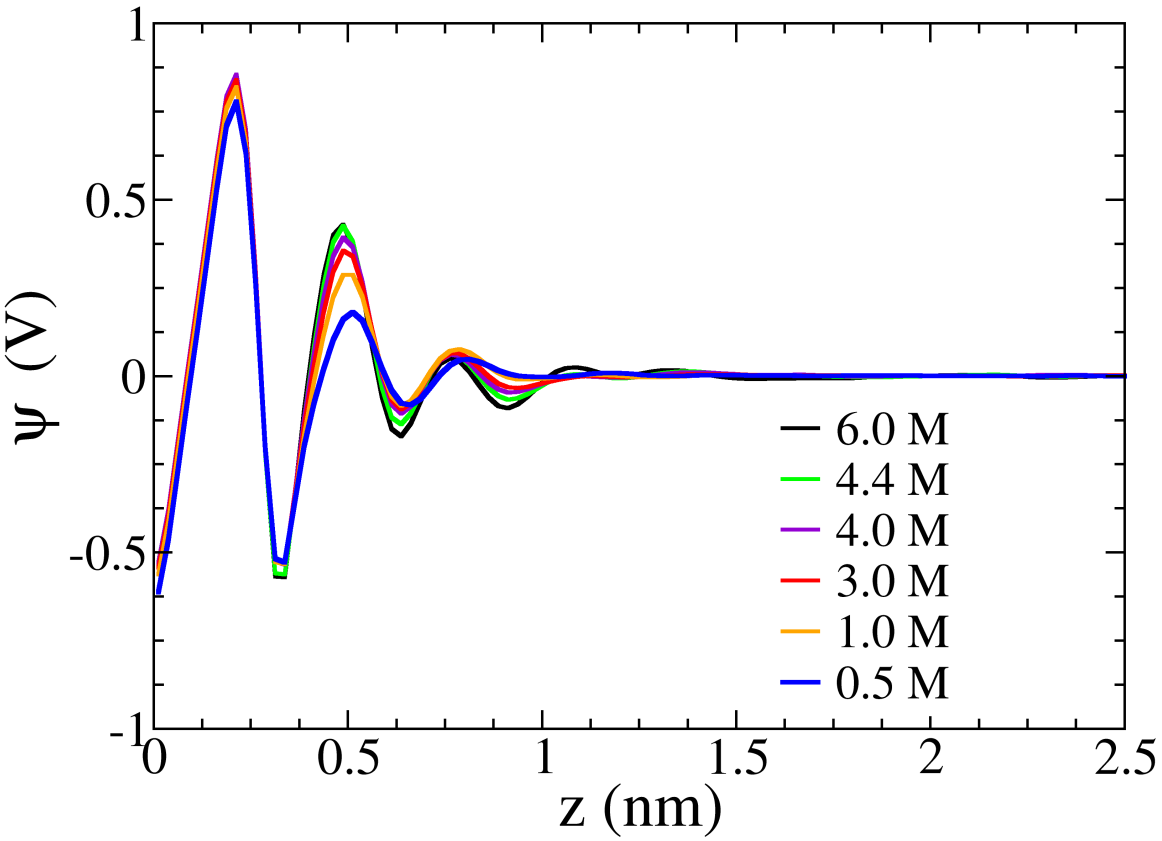

Figure S.14: Electrostatic potential as defined in Equation 4 of the main paper for the charged electrode, for the NaCl(aq) system and all the concentrations considered.

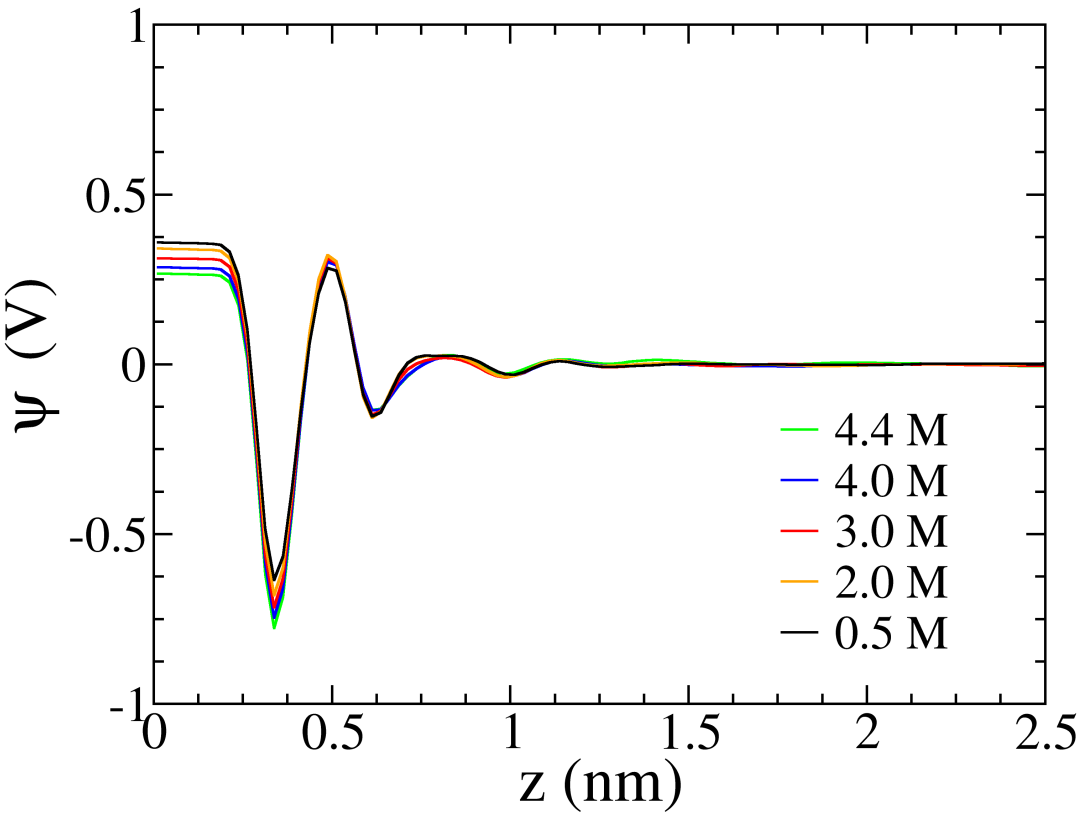

Figure S.15: Electrostatic potential as defined in Equation 4 in the main paper for the neutral electrode in the KCl(aq) system and all concentrations considered.

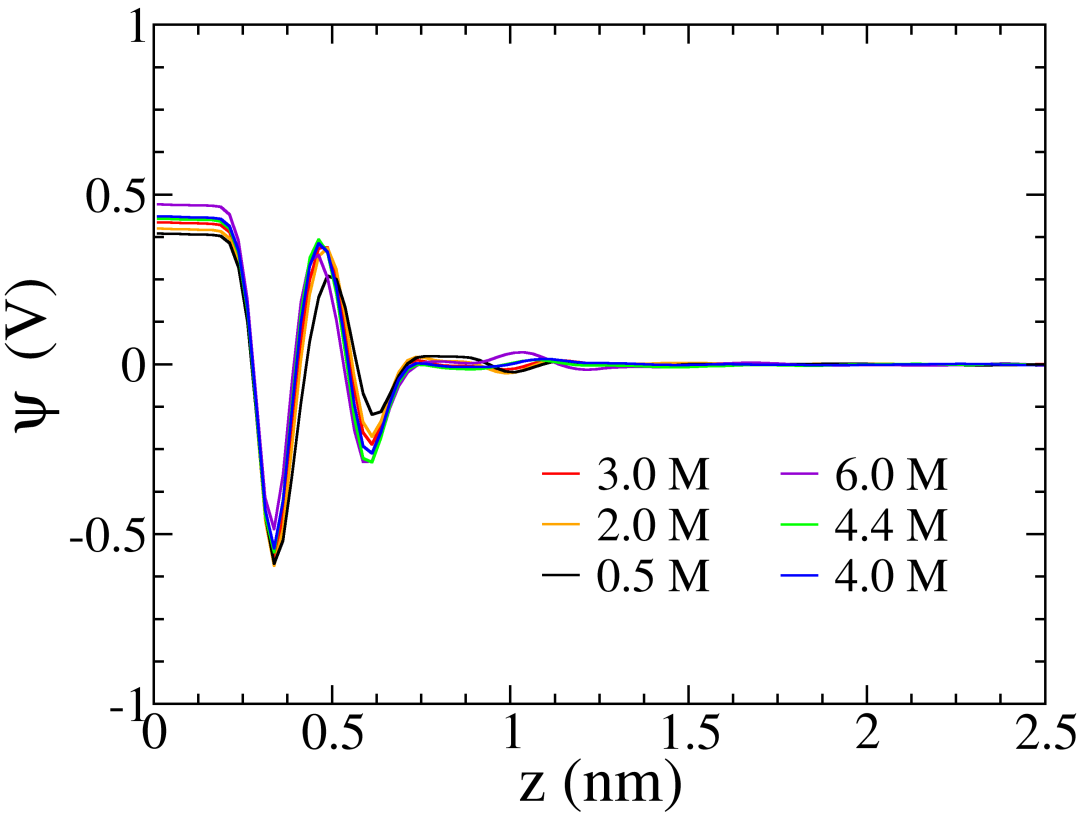

Figure S.16: Electrostatic potential as defined in Equation 4 in the main paper for the neutral electrode in the LiCl(aq) system and all concentrations considered.

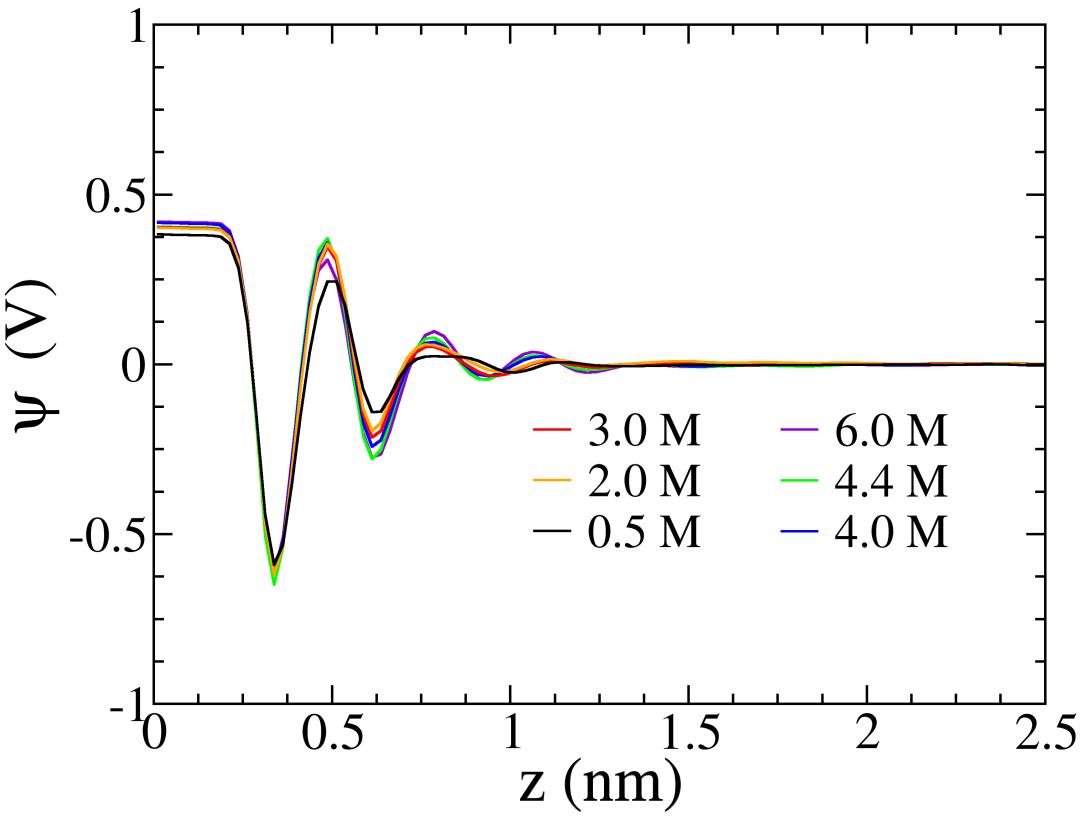

Figure S.17: Electrostatic potential as defined in Equation 4 in the main paper for the neutral electrode in the NaCl(aq) system and all concentrations considered.

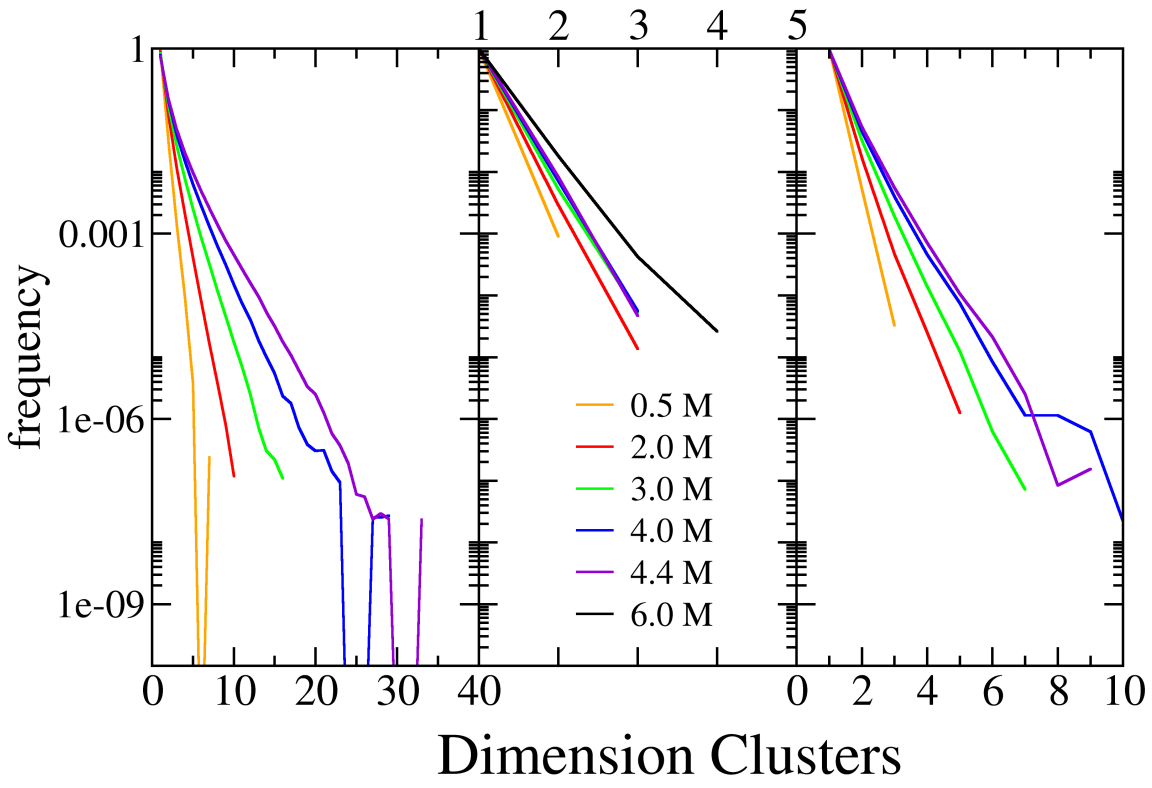

Figure S.18: Histogram of the relative frequency of the cluster of different sizes for all the systems: (from left to right) KCl, LiCl, NaCl and all the concentrations considered.

S.2 Electrode Charge Screeninig

We report here the screening factor f calculated using the total charge of all the atoms in the electrolyte $\rho_{el}(z')$, defines as [2]:

$$f(z) = -\int_0^z \frac{\rho_{el}(z')}{\sigma} \mathrm{d}z' \tag{S.1}$$

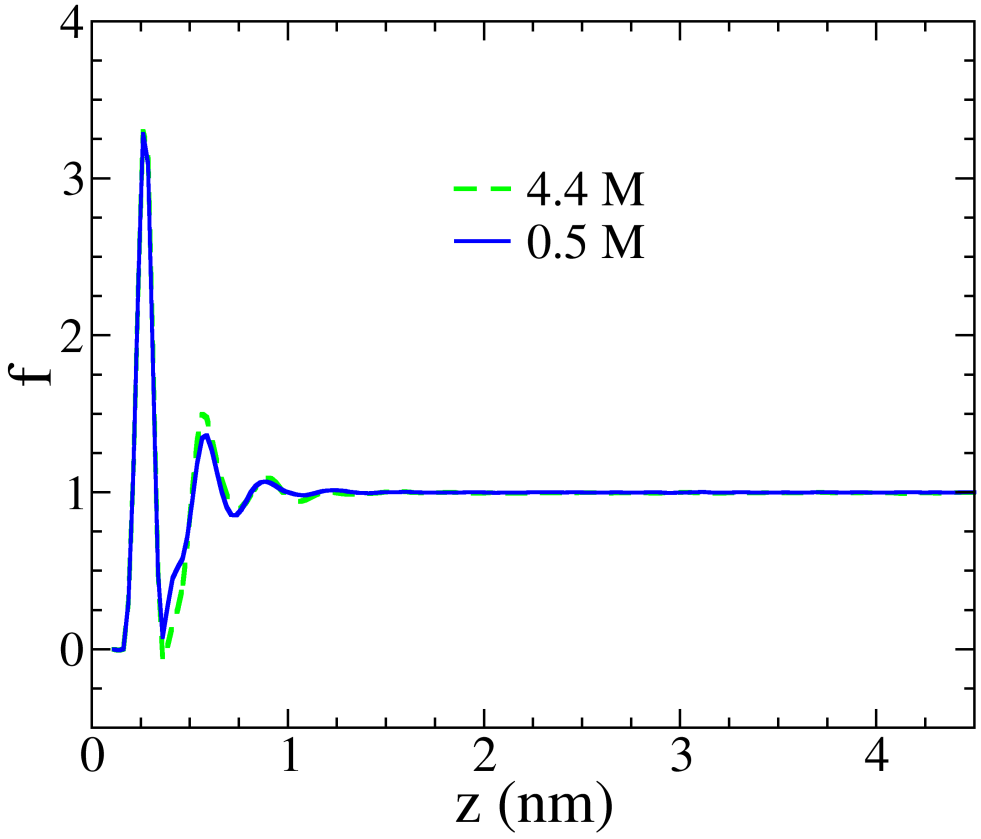

Figure S.19: Screening factor as defined in eq. (S.1) for the KCl(aq) system using total charge of the electrolyte atoms (ions plus water molecules) We included only a subset of the concentrations without error bars for clarity.

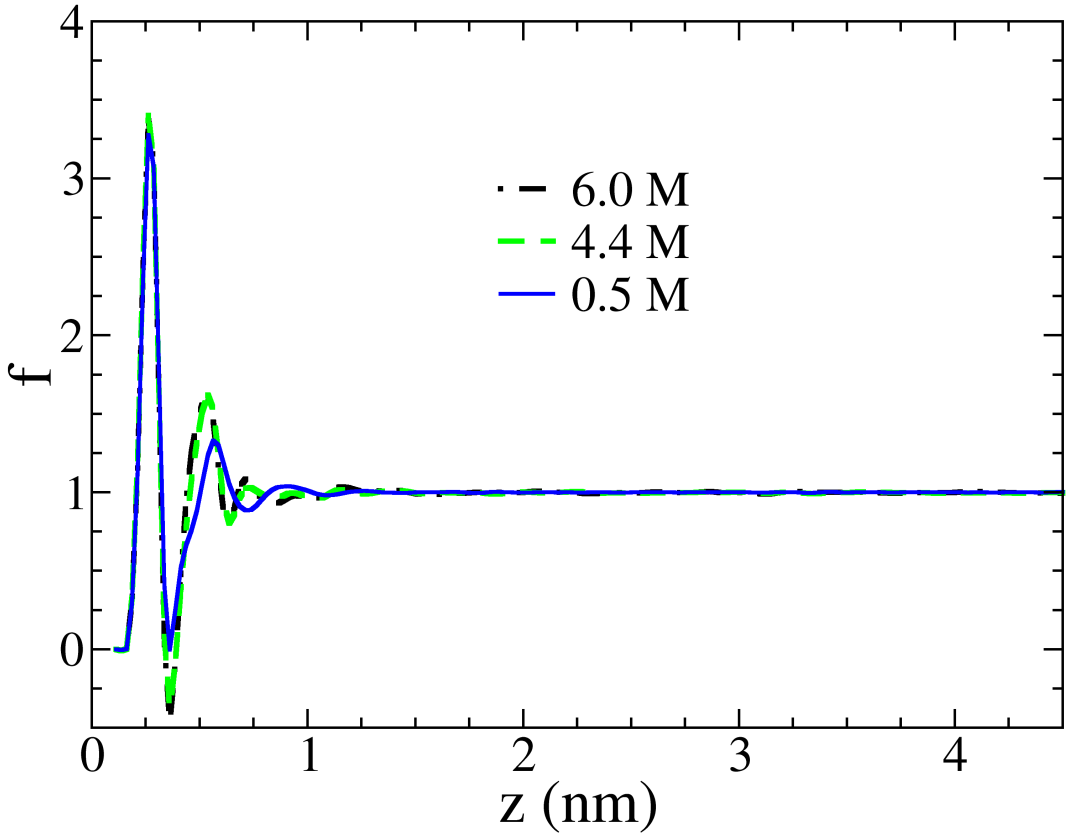

Figure S.20: Screening factor as defined in eq. (S.1) for the LiCl(aq) system using total charge of the electrolyte atoms (ions plus water molecules) We included only a subset of the concentrations without error bars for clarity.

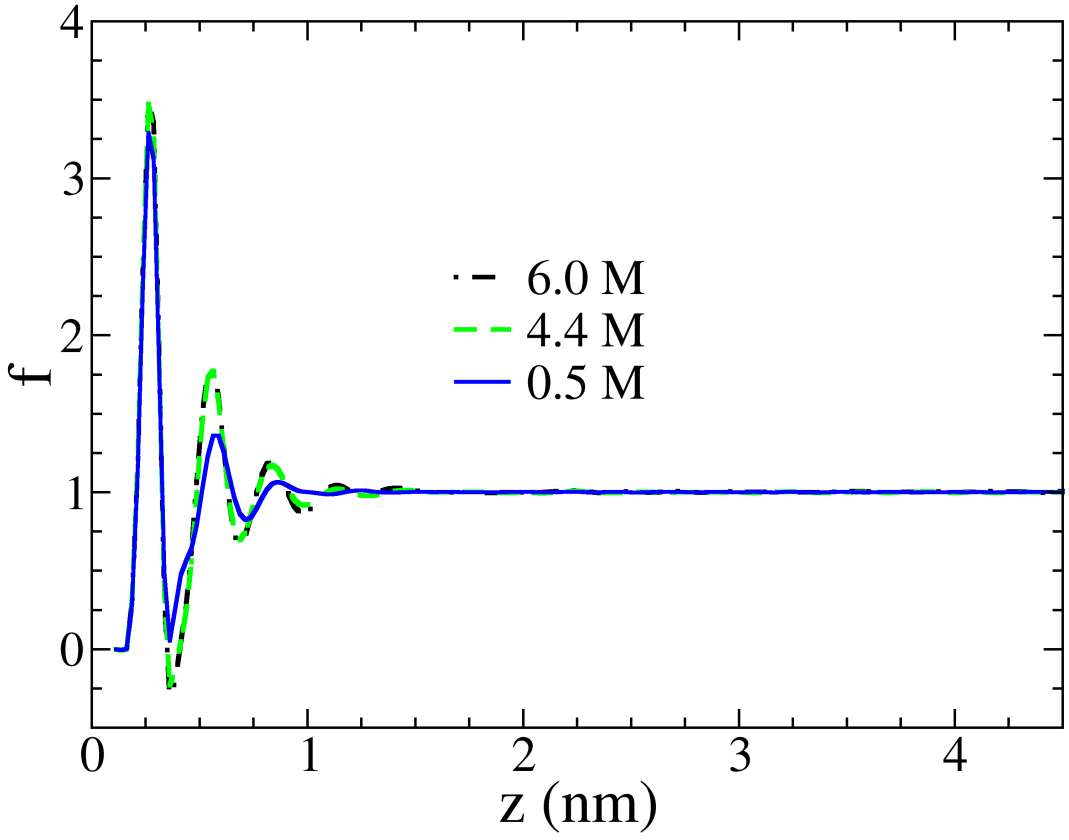

Figure S.21: Screening factor as defined in eq. (S.1) for the NaCl(aq) system using total charge of the electrolyte atoms (ions plus water molecules) We included only a subset of the concentrations without error bars for clarity.

References

[1] Abraham Savitzky and Marcel JE Golay. Smoothing and differentiation of data by simplified least squares procedures. *Analytical chemistry*, 36(8):1627–1639, 1964.

[2] Aaron R Finney, Ian J McPherson, Patrick R Unwin, and Matteo Salvalaglio. Electrochemistry, ion adsorption and dynamics in the double layer: a study of nacl (aq) on graphite. *Chemical science*, 12(33):11166–11180, 2021.