

Supporting Information

How Solvent Activity and Solute Solvation
Control Electrode Potentials: Quantitative Insights
from Li⁺ Insertion into TiO₂

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I. Electrolyte characterization

Table S1. Mole fraction x_i , conductivity, pH, density and water activity of the various LiCl aqueous electrolytes prepared, measured at 22°C.

molality (mol/kg)	x_i	Conductivity (mS/cm)	pH	density (kg/m³)	a_w
0.5	0.009	33.75	7.83	1012	0.98145
1	0.018	56.57	7.25	1029	0.96395
2	0.035	96.37	6.99	1044	0.9226
3	0.041	122.75	7.07	1059	0.87255
4	0.067	139.85	7.31	1080	0.81795
5	0.083	150.05	7.21	1098	0.7521
7	0.112	153.65	7.04	1132	0.61215
10	0.153	138.60	6.46	1176	0.4223
14	0.201	97.54	5.51	1220	0.239
18	0.245	68.68	4.77	1275	0.1402

II. Raman analysis

The ratiometric analysis of the Raman spectra was performed following the methodology reported by Wang et al.⁵², as detailed below.

Given that the aqueous solutions contain bulk (free) water molecules, water molecules bound within the ionic hydration shells of the solute, and the solute ions, the Raman spectrum at each salt concentration can be expressed as a linear combination of the spectra of these three components, *i.e.*:

$$I_{solution}(v) = I_{bulk}(v) + I_{hydration}(v) + I_{solute}(v) \quad (S1)$$

where I is the spectral intensity and v the frequency.

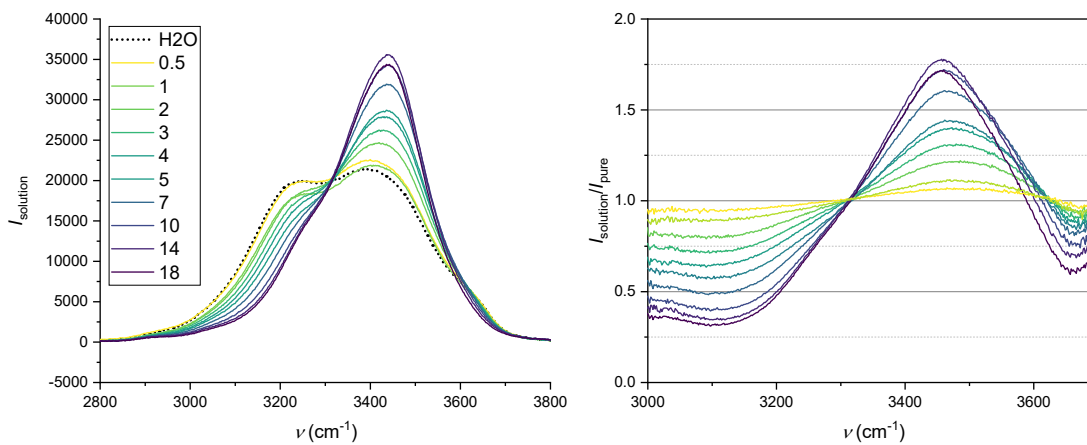
Assuming that the salt itself contributes negligibly to the O-H stretching band (2800-3700 cm^{-1}) and that the spectrum of bulk water in the solution is proportional to that of pure water (I_{pure}), the above expression can be rewritten as:

$$I_{solution}(v) = A \times I_{pure}(v) + I_{hydration}(v) \quad (S2)$$

where A is a proportionality coefficient (< 1).

Previous studies have shown that water molecules in the hydration shell do not contribute significantly to the Raman signal below 3100 cm^{-1} . Consequently, the proportionality coefficient can be determined from the ratio:

$$A = \frac{I_{solution}(v \sim 3100 \text{ cm}^{-1})}{I_{pure}(v \sim 3100 \text{ cm}^{-1})} \quad (S3)$$



Raman spectra were recorded for LiCl aqueous electrolytes over concentrations ranging from 0.5 to 18 mol/kg, and the corresponding data are presented in Figure S1.

Figure S1. (Left) Raman spectra of the O-H stretching vibration region of (dashed line) pure water and (plain lines) LiCl aqueous electrolytes with concentrations ranging from (yellow) 0.5 to (dark violet) 18 mol/kg. (Right) Corresponding ratio spectra calculated according to eq. 3.

From these data, the A parameter was determined at 3100 cm^{-1} (see Table S2). Based on this value, the spectrum corresponding to water molecules within the hydration shells of the ions can be calculated according to the following expression:

$$I_{\text{hydration}}(\nu) = I_{\text{solution}}(\nu) - A \times I_{\text{pure}}(\nu) \quad (\text{S4})$$

The resulting spectra were integrated over the $3100\text{-}3800 \text{ cm}^{-1}$ range to obtain $\int I_{\text{hydra}}(\nu)d\nu$ for each salt concentration, and $\int I_{\text{pure}}(\nu)d\nu$ was obtained by integrating the reference spectrum of pure water.

The hydration number is then defined as the ratio the number of water molecules in the hydrations shells ($n_{\text{hydration}}$) to the number of solute (n_{solute}), all being contained in the volume V analyzed:

$$h = \frac{n_{\text{hydration}}}{n_{\text{solute}}} = \frac{\frac{n_{\text{hydration}}}{n_{\text{water}}}}{\frac{n_{\text{solute}}}{n_{\text{water}}}} \quad (\text{S5})$$

The total water molecules in the volume V considered is:

$$n_{\text{water}} = n_{\text{bulk}} + n_{\text{hydration}} = B \times n_{\text{pure}} \quad (\text{S6})$$

with

$$n_{\text{hydration}} = \frac{\int I_{\text{hydration}}(\nu)d\nu}{k\sigma_{\text{hydration}}} \quad (\text{S7})$$

$$n_{\text{bulk}} = \frac{\int I_{\text{bulk}}(\nu)d\nu}{k\sigma_{\text{pure}}} = A \times n_{\text{pure}} \quad (\text{S8})$$

$$n_{\text{pure}} = \frac{\int I_{\text{pure}}(\nu)d\nu}{k\sigma_{\text{pure}}} \quad (\text{S9})$$

Where $\sigma_{\text{hydration}}$ and σ_{pure} are the Raman scattering cross section corresponding to hydration shell and pure (*i.e.*, bulk) water molecules, and k is a proportionality coefficient.

The parameter B (see Table S2) can be obtained from

$$n_{water} = \frac{\rho_{solution}}{\rho_{pure}} \times \frac{M_{H_2O}}{M_{H_2O} + M_{solute} \frac{x}{1-x}} \times n_{pure} \quad (S10)$$

Where x is the molar fraction of solute and $\frac{\rho_{solution}}{\rho_{pure}}$ is the density of the solution.

Introducing eqs. S7-S9 into eq. S6 leads to

$$B \times \frac{\int I_{pure}(v) dv}{k \sigma_{pure}} = \frac{\int I_{hydration}(v) dv}{k \sigma_{hydration}} + \frac{\int I_{bulk}(v) dv}{k \sigma_{pure}} \quad (S11)$$

and

$$\frac{\sigma_{hydration}}{\sigma_{pure}} = \frac{\int I_{hydration}(v)}{(B - A) \times \int I_{pure}(v)} \quad (S12)$$

Once this ratio has been determined for each concentration (see Table S2), then we access

$$\begin{aligned} \frac{n_{hydration}}{n_{water}} &= \frac{\int I_{hydration}(v) dv}{k \sigma_{hydration}} \div \left(\frac{\int I_{bulk}(v) dv}{k \sigma_{pure}} + \frac{\int I_{hydration}(v) dv}{k \sigma_{hydration}} \right) = \frac{\int I_{hydration}(v) dv}{\frac{\sigma_{hydration}}{\sigma_{pure}} \int I_{bulk}(v) dv + \int I_{hydration}(v) dv} \end{aligned} \quad (S13)$$

and finally:

$$h = \frac{\int I_{hydration}(v) dv}{\int I_{hydration}(v) dv + \frac{\sigma_{hydration}}{\sigma_{pure}} \int I_{bulk}(v) dv} \times \frac{n_{LiCl}}{n_{water}} \quad (S14)$$

Table S2. Data of the ratiometric Raman analysis for two sets of LiCl aqueous electrolytes.

C_i (mol/kg)	A	Density ^{S2}	B	$\frac{\sigma_{hydration}}{\sigma_{water}}$	h
0.5	0.943	1.01	0.98903	1.508	4.37
1	0.895	1.02	0.97851	1.321	4.63
2	0.800	1.04	0.9587	1.387	4.55
	0.796			1.345	4.33
3	0.718	1.06	0.94038	1.396	4.30
	0.716			1.384	4.04
4	0.644	1.08	0.92339	1.393	4.16
5	0.576	1.098	0.90594	1.339	4.03
7	0.488	1.134	0.87446	1.450	3.45
	0.581			1.517	2.70
10	0.398	1.173	0.82373	1.523	2.83
	0.409			1.474	2.78
14	0.347	1.23	0.77183	1.635	2.16
	0.365			1.586	2.08
18	0.319	1.273	0.72197	1.683	1.72
	0.330			1.633	1.66

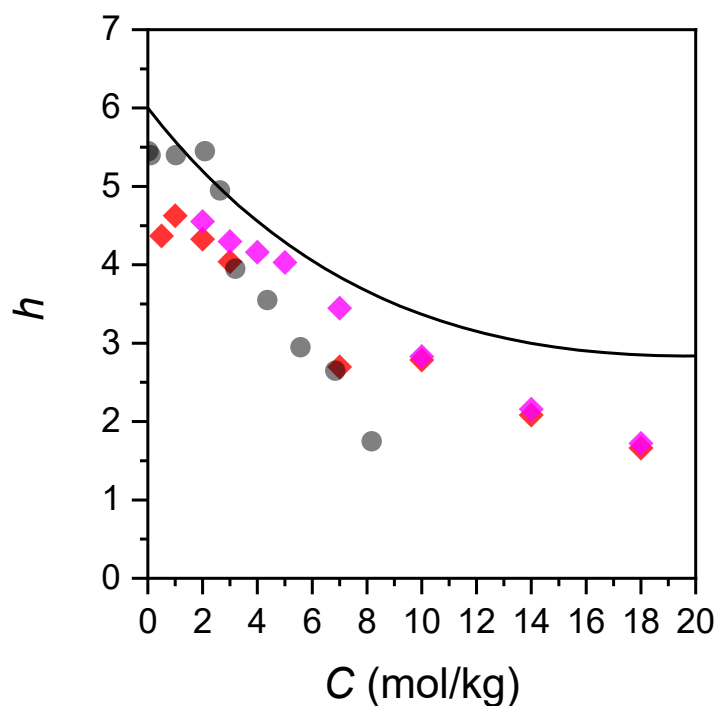


Figure S2. Dependence of h (red and magenta symbols) on the molal concentration of LiCl, together with (black dots) experimental data obtained by Jafeen et al.^{S3} and (black line) the quadratic expression derived by Y. Marcus from the fit of isothermal compressibility data.^{S4}

References

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- S3. M. J. M. Jafeen, M. A. Careem, S. Skaarup, Membrane Hydration Number of Li⁺ Ion in Highly Concentrated Aqueous LiCl Solutions. *Ionics* 2019, **25**, 3453–3460.
- S4. Y. Marcus, Concentration Dependence of Ionic Hydration Numbers. *J. Phys. Chem. B*, 2014, **118**, 10471–10476.