

Supporting information for: Charge hydration asymmetry: the basic principle and how to use it to test and improve water models

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Quadratic dependence of hydration free energy on ion charge for ions of the same sign

As inferred earlier by Latimer *et al.*,² we reconfirm the fact that the hydration free energies of ions with same sign of charge depend quadratically on the magnitude of the ion charge. To this end, we fit experimental hydration free energies¹ to the following equation,

$$\Delta G = - \left(1 - \frac{1}{\epsilon} \right) \frac{\gamma(q)}{2(R_i + C_{+/-})} \quad (1)$$

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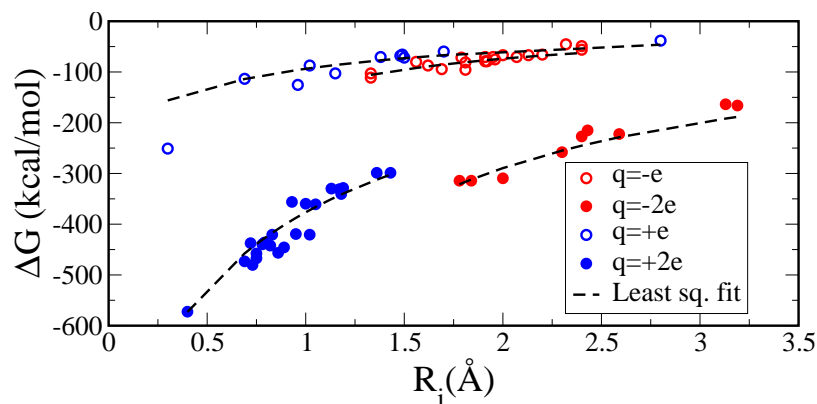


Figure S1: Experimental hydration free energy, ΔG , of monovalent and divalent cations and anions at 298 K and 1 mol/L as a function of ion radius.¹ The dashed lines correspond to the best fit ΔG 's exhibiting *almost* quadratic dependence on ion charge.

where C_+ and C_- are the corrections to the ion radii, specific to the sign of ion charge. Employing Eq. (1), we find the best fit (minimum RMSD to experimental ΔG , Figure S1) values of the $\gamma(q)$ for the each set of anions and cations, independently. We obtain $\Delta G(+2e)/\Delta G(+e) = \gamma(+2e)/\gamma(+e) = 4.02$ and $\Delta G(-2e)/\Delta G(-e) = \gamma(-2e)/\gamma(-e) = 3.92$, a 0.5% deviation from quadratic behavior for cations and 1.5% for anions.

Weak dependence of asymmetry factor η on water-water interaction

Free energy of ion hydration: first hydration shell approximation

To investigate the ion hydration asymmetry and its dependence on water-water interactions we utilize a simple first hydration shell model shown in the Figure S2. For many realistic ions, the number of water molecules in the first shell is close to six (Ref.³). This allows us to consider the ion surrounded by six water molecules with their centers fixed in space in octahedral configuration, making our analyses analytically tractable.

With only two allowed orientations for a water molecule dipole (+ and -), the canonical partition

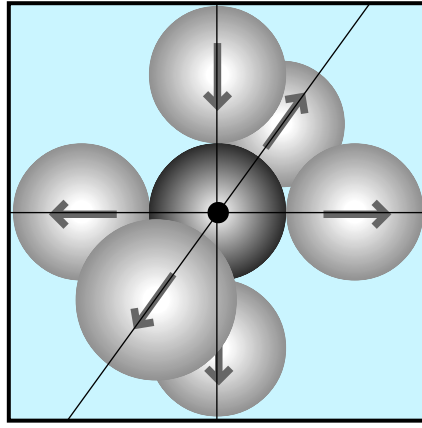


Figure S2: Schematic of the first hydration shell model used here. The ion (dark sphere with a charge q at its center) is surrounded by six water molecules (light spheres) with their centers fixed in space in an octahedral configuration. Each individual water molecule has two orientation states relative to the ion: its dipole directed away (+) or towards the ion (-).

Table S1: Configurational states of the water dipoles in the first-shell model of Figure S2. First row: schematic of configurations (i) of the ion-water system corresponding to different values of water-water interaction \mathcal{W}_i . Individual water dipole orientation states + or - are represented by \bullet or \circ respectively. The ion center is located at the origin of the axes formed by the water molecules. Second row: the degeneracy g_i of the i^{th} configuration. Third row: N_i^+ , the number of water molecules in state +.

	1	2	3	4	5	6	7	8	9	10	
Config.(i)											
g_i	1	6	3	12	12	8	3	12	6	1	
N_i^+	0	1	2		3		4		5	6	

function of the ion-water system shown in Figure S2 can be written as,

$$Z_{II} = \sum_i g_i \exp(-\beta (N_i^+ E^+ + (6 - N_i^+) E^- + \mathcal{W}_i)). \quad (2)$$

Here, g_i is the degeneracy of the energy of the i^{th} configuration (see Table S1), \mathcal{W}_i the Coulomb interaction energy between all the water molecules, N_i^+ the number of water molecules in the state +. The Coulomb interaction energy between the ion and one water molecule is characterized by E^+ , and E^- for the water molecule in the state + and -, respectively. Within this model the van

der Waals interactions are assumed to be constant and hence, are not explicitly incorporated in the calculations.

The partition function for a hydrated empty spherical cavity within this model can similarly be expressed as,

$$Z_I = \sum_i g_i \exp(-\beta \mathcal{W}_i). \quad (3)$$

Neglecting the tiny contribution pertaining to the cavity creation in water and the difference between ΔG and ΔF for the standard states of ions and using Eq. (2) and Eq. (3), the free energy of ion hydration is approximated by:

$$\Delta G^{1st} \approx \Delta F^{1st} = -\frac{1}{\beta} \ln \left(\frac{Z_{II}}{Z_I} \right) = -\frac{1}{\beta} \ln \left(\frac{\sum_i g_i \exp(-\beta (N_i^+ E^+ + (6 - N_i^+) E^- + \mathcal{W}_i))}{\sum_i g_i \exp(-\beta \mathcal{W}_i)} \right). \quad (4)$$

We now use our **2P** water model in Eq. (4) to calculate ΔG^{1st} for alkali and halide ions. We have already established (see Main text), that this two point water model is capable of causing charge hydration asymmetry.

The result is only 5.9% RMS deviation from the experimental⁴ values of hydration free energy. This agreement suggests that the simplified first shell, two-state model introduced here is a reasonable approximation for the energetics of ion hydration.

We will now show that this model can capture proper hydration asymmetry when used in the framework of the formalism based on the ansatz proposed in the Main text.

Evaluation of the asymmetry factor η

The asymmetry factor (see Main text) is defined as,

$$\eta = \Delta G_{2P} / \Delta G_{SPD} \approx \Delta G_{2P}^{1st} / \Delta G_{SPD}^{1st} \quad (5)$$

One can express ΔG_{SPD}^{1st} and ΔG_{2P}^{1st} within the first-shell approximation via Eq. (4). Further using Eq. (5), the asymmetry factor η is

$$\eta = \frac{\ln\left(\frac{\sum_i g_i \exp(-\beta(N_i^+ E_{2P}^+ + (6-N_i^+) E_{2P}^- + \mathcal{W}_i^{2P}))}{\sum_i g_i \exp(-\beta \mathcal{W}_i^{2P})}\right)}{\ln\left(\frac{\sum_i g_i \exp(-\beta(N^+(i) E_{SPD}^+ + (6-N_i^+) E_{SPD}^- + \mathcal{W}_i^{SPD}))}{\sum_i g_i \exp(-\beta \mathcal{W}_i^{SPD})}\right)}. \quad (6)$$

The above equation is analytically tractable. Using the ion radii from¹ and parameters for **2P** and **SPD** (see Main article) water models, one can hence calculate the hydration free energies for alkali and halide ions. Leading towards the goal of this section, *i.e.* to investigate the intensity of effect of water–water interactions in hydration free energy, we now scale the water–water interaction term in Eq. (6) with a multiplicative factor f , $\mathcal{W}_i \rightarrow f\mathcal{W}_i$, such that f can vary from 0 to 1. The resulting dependence of η calculated for mono–valent ions with ionic radius $R_i = 1$ and 2 \AA are presented in Figure S3.

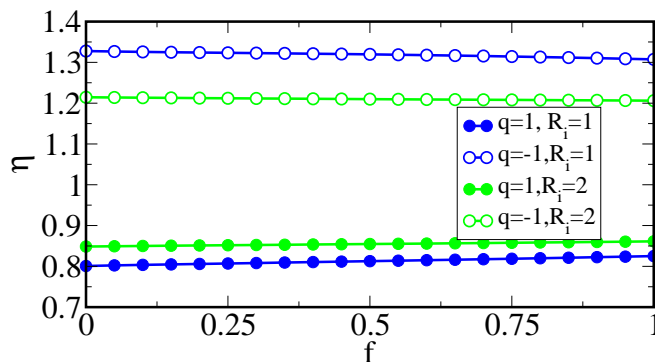


Figure S3: Dependence of the asymmetry factor η on the strength of water–water interaction. The calculation is for mono–valent ions of radius $R_i = 1$ and 2 \AA and charge $q = \pm 1e$, $f = 1$ corresponds to full strength of water–water interaction.

In Figure S3 we see that the relative change of $\eta(f)$ over the entire range of f , from 0 to 1, is very small, $\left| \frac{\eta(1) - \eta(0)}{\eta(1)} \right| \leq 3\%$. This allows one to neglect the water–water interactions in estimating

η which modifies Eq. (6) to the model discussed in the Main text. Mathematically,

$$\eta = \frac{\ln\left(\frac{e^{-\beta E_{2P}^+} + e^{-\beta E_{2P}^-}}{2}\right)}{\ln\left(\frac{e^{-\beta E_{SPD}^+} + e^{-\beta E_{SPD}^-}}{2}\right)}. \quad (7)$$

Employing our ansatz, $\Delta G = \Delta G_B(R_{eff})\eta$, in Eq. (7) provides us with:

$$\Delta G = \Delta G_B(R_{eff}) \frac{\ln\left(\frac{e^{-\beta E_{2P}^+} + e^{-\beta E_{2P}^-}}{2}\right)}{\ln\left(\frac{e^{-\beta E_{SPD}^+} + e^{-\beta E_{SPD}^-}}{2}\right)}, \quad (8)$$

where $R_{eff} = R_i + R_s$ with the quantity $R_s = 0.52\text{\AA}$ (see Main text).

Ion hydration energy expressed via water model parameters

The asymmetry factor in Eq. (7) utilizes two simplified water models, **2P** and **SPD**. Below we express the Coulomb energies of water molecule in the field of ion, $\vec{\mathcal{E}}$, through the parameters of these two models. Taking into account only two allowed orientations of the water molecule ($\sigma = +, -$) in our simplified first hydration shell model described in S2.1, these energies can be written as

$$E_{2P}^\pm = \frac{qq_O}{R_{iw}} + \frac{qq_H}{R_{iw} \pm R_{OH}^z}, \quad (9)$$

$$E_{SPD}^\pm = -(\vec{\mathcal{E}} \cdot \vec{p}_\pm) = -\left(\pm \frac{qq_H R_{OH}^z}{R_{iw}^2}\right), \quad (10)$$

where q_O , q_H are the negative (“oxygen”) and positive (“hydrogen”) charges in the **2P** model separated by the distance R_{OH}^z , R_{iw} the distance between center of ion and the center of water molecule (the “oxygen” point in **2P** model), and $|\vec{p}| = p = q_H R_{OH}^z$. Using the above expressions

for the energies and noting that $q_O = -q_H$, we can rewrite Eq. (8) as

$$\Delta G = \Delta G_B(R_{eff}) \frac{\ln \left(\frac{1}{2} \sum_{\sigma=-1,1} e^{-\beta q q_O \left(\frac{1}{R_{iw}} - \frac{1}{R_{iw} + \sigma R_{OH}^z} \right)} \right)}{\ln \left(\cosh(\beta q q_O R_{OH}^z / R_{iw}^2) \right)}. \quad (11)$$

Strong field limit for ion hydration

In this article as we used small ions, $R_i < 3\text{\AA}$ and $|q| \geq e$, the electric field of the ion acting on the first hydration shell water molecules satisfies $|\vec{\mathcal{E}}(R_{iw})| \gg (\beta p)^{-1}$. The energy of a water dipole in this field can exceed kT by orders of magnitude. With only two allowed water dipole orientations ($\sigma = +, -$) in our first shell model, this leads to the condition $|\beta E_\sigma| \gg 1$. Under these conditions, Eq. (11) simplifies significantly. This simplified form is most easily obtained from the strong field limit of Eq. (7), *i.e.*,

$$\eta = \frac{E_{2P}^{\sigma^*}}{E_{SPD}^{\sigma^*}}. \quad (12)$$

Here σ^* denotes the orientation of the water dipole with the lowest ion-water interaction energy (the orientation along the field of the ion: “+” for cations and “-” for anions). Using Eq. (9) and Eq. (10) in Eq. (12), the asymmetry factor can be expressed as

$$\eta = \frac{q q_H \left(\frac{1}{R_{iw}} - \frac{1}{R_{iw} + \text{Sgn}[q] R_{OH}^z} \right)}{q q_H \frac{\text{Sgn}[q] R_{OH}^z}{R_{iw}^2}} = \frac{R_{iw}}{R_{iw} + \text{Sgn}[q] R_{OH}^z} = \left(1 + \text{Sgn}[q] \frac{R_{OH}^z}{R_{iw}} \right)^{-1}. \quad (13)$$

With Eq. (13), the expression for ΔG (see Eq. (8)) in the strong field limit can thus be written as,

$$\Delta G = \Delta G_B(R_{eff}) \left(1 + \text{Sgn}[q] \frac{R_{OH}^z}{R_{iw}} \right)^{-1}. \quad (14)$$

Ion hydration Entropy estimation

The explicit form of free energy change upon ion hydration ΔG given by Eq. (14) allows us to estimate the ion hydration entropy using the general thermodynamics relation

$$\Delta S = - \left(\frac{\partial \Delta G}{\partial T} \right)_P \quad (15)$$

The temperature dependent parameters in Eq. (14) are the dielectric constant of water, ϵ , the solvent dependent effective position of the dielectric boundary, R_{eff} , and the ion-water distance, R_{iw} . At $T = 298\text{K}$, $\partial\epsilon/\partial T = -0.36$.⁵ Under our treatment, the thermal expansion of R_{eff} and R_{iw} are approximated to be the same as the thermal expansion of the mean intermolecular spacing of neighboring molecules ($R_{ww} = 2R_w$) in bulk water, *i.e.*, $\partial R_{eff}/\partial T \approx \partial R_{iw}/\partial T \approx \partial R_{ww}/\partial T$. Using the volumetric thermal expansion coefficient of water, $\alpha = 2.57 \cdot 10^{-4} \text{ K}^{-1}$ at $T = 298 \text{ K}$,⁶ one can express $\partial R_{ww}/\partial T$ as,

$$\alpha = \frac{3}{R_{ww}} \frac{\partial R_{ww}}{\partial T}. \quad (16)$$

Under the above assumptions and using Eq. (14) and Eq. (15) we obtain,

$$\Delta S = \Delta G_B(R_{eff}) \times \eta \left(-\frac{1}{\epsilon(\epsilon-1)} \frac{\partial \epsilon}{\partial T} + \frac{\alpha}{3} \left(\frac{R_{ww}}{R_{eff}} - \left(\frac{R_{ww}}{R_{iw}} \right) \frac{Sgn(q)R_{OH}^z}{R_{iw} + Sgn(q)R_{OH}^z} \right) \right). \quad (17)$$

which can be further simplified to,

$$\Delta S = \Delta G \left(-\frac{1}{\epsilon(\epsilon-1)} \frac{\partial \epsilon}{\partial T} + \frac{\alpha}{3} \left(\frac{R_{ww}}{R_{eff}} + (\eta - 1) \frac{R_{ww}}{R_{iw}} \right) \right). \quad (18)$$

Insensitivity to the number of water states

In this section we calculate the ion hydration free energy using 2P and SPD water models with all possible orientation states of a water molecule in the ion first hydration shell. The orientation of the water molecule is determined by the angle θ between the water dipole and the axis connecting

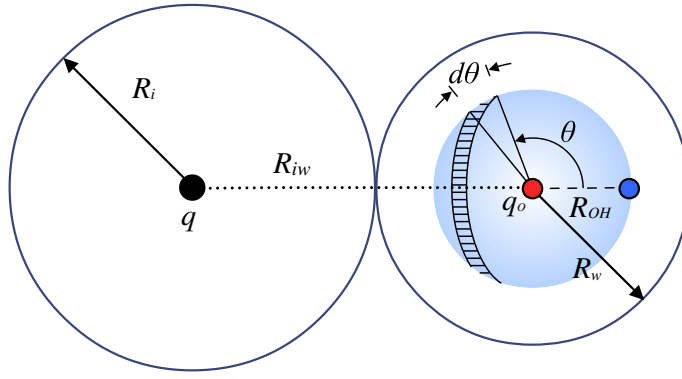


Figure S4: Schematic represents a simple ion (a sphere of radius R_i with a charge q at the center) interacting with $2P$ water molecule of radius R_w with the oxygen partial charge q_o (red dot) at the center. The light blue sphere represents all admissible states of the positive “hydrogen” charge (blue dot) at the distance R_{OH}^z from the center. θ is the angle between the axis connecting ion and water center, \vec{R}_{iw} and the water dipole moment, \vec{p} .

ion and water centers shown in Figure S4. The post-solvation canonical partition function for ion–water interaction with one water molecule is given by,

$$\zeta_1^I = \int_0^\pi e^{-\beta E(\theta)} \sin \theta d\theta, \quad (19)$$

where $E(\theta)$ is the ion-water Coulomb interaction energy. The equation for SPD water can be simplified taking into account that $E_{SPD}(\theta) = qq_o R_{OH}^z \cos \theta / R_{iw}^2$,

$$\zeta_{1,SPD}^I = \frac{2 \sinh\left(\frac{\beta qq_o R_{OH}^z}{R_{iw}^2}\right)}{\frac{\beta qq_o R_{OH}^z}{R_{iw}^2}}. \quad (20)$$

The pre-solvation partition function for both SPD and 2P models is given by $\zeta_1^I = \int_0^\pi e^0 \sin \theta d\theta = 2$.

Now, using our ansatz $\Delta G = \Delta G_B \times \eta$ and 6 from the main text, we can express the hydration

energy as,

$$\begin{aligned} \Delta G &= \Delta G_B(R_{eff}) \times \frac{\ln\left(\frac{\zeta_{1,2P}^H}{\zeta_{1,2P}^I}\right)}{\ln\left(\frac{\zeta_{1,SPD}^H}{\zeta_{1,SPD}^I}\right)} \\ &= \Delta G_B(R_{eff}) \frac{\ln\left(\frac{\int_0^\pi e^{-\beta\mathcal{E}(\theta)} \sin(\theta) d\theta}{2}\right)}{\ln\left(\frac{\sinh\left(\frac{\beta qq_O R_{OH}^z}{R_{iw}^2}\right)}{\frac{\beta qq_O R_{OH}^z}{R_{iw}^2}}\right)}. \end{aligned} \quad (21)$$

We use Eq. (21) to calculate the hydration free energies of alkali halide ions. The results of this calculation is compared with the analytical strong field limit result, Eq. (14) and experimental data in Figure S5. It clearly shows that incorporating more states (all orientation states in this example) does not provide any noteworthy difference in accuracy when compared to the simplified analytical formula, Eq. (14) *i.e.* the model based on just two orientation states.

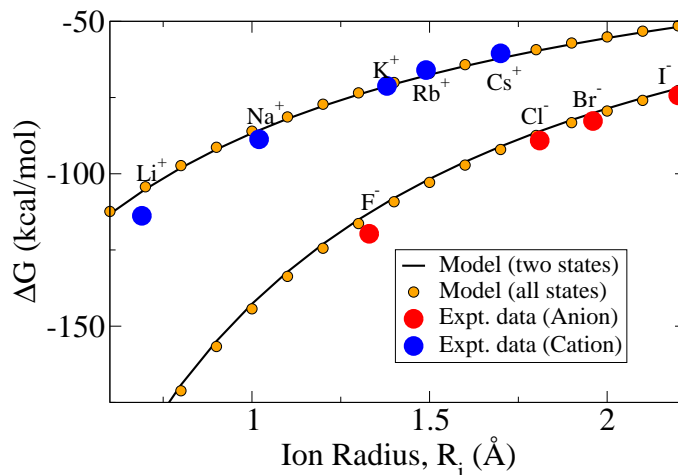


Figure S5: Comparison of the hydration free energies for monovalent anions and cations predicted using our main result, Eq. (14) based on only two orientation states (+/-) of the water molecule (solid black lines) and the results from the all states model, Eq. (21) (orange circles). The experimental data (red and blue circles) are taken from Ref.⁴

The “first principles” (MSA) universal shift in ion radius, R_s , is close to optimal.

We introduce a “first-principles” uniform shift, R_s , to the ion radius, $R_{eff} = R_i + R_s$, suggested by Ref.,⁷ a study based on the mean spherical approximation (MSA). Using the MSA formalism, we obtain $R_s = 0.52\text{\AA}$ at 298K and using the typical water radius, $R_w = 1.4\text{\AA}$. In Figure S6, we assess the sensitivity of the hydration energy, Eq. (14) by varying the R_s around the MSA calculated value. As seen in the Figure S6, the “first principles” MSA value of R_s is very close (within 9%) to its optimum value for Eq. (14). The hydration free energies based on this fitted optimal value is within 1% difference from the energies computed with the “first principles” MSA-based R_s used in the main text.

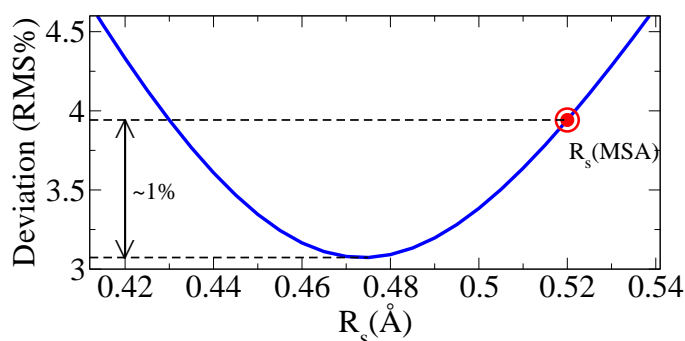


Figure S6: RMS% deviation of hydration free energy, Eq. (14) from experimental values⁴ plotted as a function of R_s . The “first principles” $R_s = 0.52\text{\AA}$ is marked by the red bullet.

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