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Electronic Supplementary Information.

to accompany

Absolute ion hydration enthalpies and the role of volume within hydration thermodynamics

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S1. Tables of Thermodynamic Data and Volume function $V^{-1/3}$.

Table S1. $\Delta_f H^o(M^+, g)$/kJ mol^{-1} and $\Delta_f G^o(M^+, g)$/kJ mol^{-1} data [1] for the proton and alkali metal ions and $\Delta_f H^o(X^-, g)$/kJ mol^{-1} and $\Delta_f G^o(X^-, g)$/kJ mol^{-1} for the halide ions.

Ion	**$\Delta_f H^o(M^+, g)$/kJ mol^{-1}**	**$\Delta_f G^o(M^+, g)$/kJ mol^{-1}**
H^+	1536.246	1516.99
Li^+	685.719	648.477
Na^+	609.343	574.317
K^+	514.007	480.947
Rb^+	490.129	457.771
Cs^+	458.402	426.897
Ion	**$\Delta_f H^o(X^-, g)$/kJ mol^{-1}**	**$\Delta_f G^o(X^-, g)$/kJ mol^{-1}**
F^-	−255.079	−261.997
Cl^-	−233.954	−240.167
Br^-	−219.008	−238.808
I^-	−194.591	−221.488

Table S2. Standard enthalpies and free energies of formation of cations and anions in aqueous solution, $\Delta_f H^o(M^+,aq)$ and $\Delta_f H^o(X^-,aq)$. The standard state is the hypothetical ideal solution with molality m = 1 mol kg^{-1}. [2-4]

Ion	$\Delta_f H^o(M^+, aq)$/kJ mol^{-1}	$\Delta_f G^o(M^+, aq)$/kJ mol^{-1}
H^+	0.0	0.0
Li^+	−278.5	−293.3
Na^+	−240.1	−261.9
K^+	−252.4	−283.3
Rb^+	−251.2	−284.0
Cs^+	−258.3	−292.0
Ion	**$\Delta_f H^o(X^-, aq)$/kJ mol^{-1}**	**$\Delta_f G^o(X^-, aq)$/kJ mol^{-1}**
F^-	−332.6	−278.8
Cl^-	−167.3	−131.2
Br^-	−121.6	−104.0
I^-	−55.2	−51.6

Table S3. Standard enthalpy of formation of alkali halide salts[3], $\Delta_f H^o(MX,s)$/kJ mol^{-1}

$\Delta_f H^o(MX,s)$/kJ mol^{-1}	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	−616.0	−576.6	−567.3	−557.7	−553.5
Cl^-	−408.6	−411.2	−436.6	−435.4	−443.0
Br^-	−351.2	−361.1	−393.8	−394.6	−405.8
I^-	−270.4	−287.8	−327.9	−333.8	−346.6

Table S4. Standard free energy of formation of alkali halide salts[3], $\Delta_f G^o(MX,s)$/kJ mol^{-1}

$\Delta_f G^o(MX,s)$/kJ mol^{-1}	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	−587.7	−546.3	−537.8	–	−525.5
Cl^-	−384.4	−384.1	−408.5	−407.8	−414.5
Br^-	−342.0	−349.0	−380.7	−381.8	−391.4
I^-	−270.3	−286.1	−324.9	−328.9	−340.6

Table S5. $\Delta_{latt}H^o(MX,s)$/kJ mol^{-1} calculated as [$\Delta_f H^o(M^+,g) + \Delta_f H^o(X^-,g) - \Delta_f H^o(MX,s)$] using data from Tables S1 and S3.

$\Delta_{latt}H^o$(MX,s)/kJ mol^{-1}	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	1046.6	930.9	826.2	792.8	756.8
Cl^-	860.4	786.6	716.7	691.6	667.4
Br^-	817.9	751.4	688.8	665.7	645.2
I^-	761.5	702.6	647.3	629.3	610.4

Table S6. U_{POT}(MX)/kJ mol^{-1} calculated as $\Delta_{latt}H^o(MX,s) + RT$

U_{POT}(MX)/kJ mol^{-1}	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	1049.1	933.3	828.7	795.2	759.3
Cl^-	862.6	789.1	719.1	694.1	669.9
Br^-	820.4	753.9	691.3	668.2	647.7
I^-	764.0	705.0	649.8	631.8	612.9

Table S7. Standard Enthalpy of solution[3], $\Delta_{soln}H^o$(MX, s)/kJ mol^{-1}

$\Delta_{soln}H^o$(MX, s)/kJ mol^{-1}	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	4.72	0.91	−17.73	−26.11	−36.86
Cl^-	−37.02	3.88	17.22	17.28	17.78
Br^-	−49.66	−0.6	19.87	21.88	25.98
I^-	−63.3	−7.53	20.33	25.1	33.34

Table S8. $V_m(MX)^{-1/3}$/nm^{-1} for alkali metal halide salts calculated from values of V_m(MX)

$V_m(MX)^{-1/3}$/nm^{-1}	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	3.94	3.43	2.97	2.81	2.64
Cl^-	3.08	2.81	2.52	2.41	2.24
Br^-	2.89	2.66	2.41	2.31	2.20
I^-	2.64	2.45	2.25	2.16	2.07

S2. Enthalpy of Hydration Relationships.

From the thermochemical cycle shown in Figure 3 we can infer the following relationships:

$$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)] = \Delta_f H^o(MX,s) - \Delta_f H^o(M^+,g) - \Delta_f H^o(X^-,g) + \Delta_{soln}H^o(MX,s) \quad (S1)$$

- this equation links Tables 1, 4, S1, S3 and S8.

$$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)] = \Delta_{soln}H^o(MX,s) - U_{POT}(MX) - n\mathrm{RT} \quad (S2)$$

- this equation links Tables 1, S7 and S8.

$$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)] = \Delta_{soln}H^o(MX,s) - \Delta_f H^o(M^+,g) - \Delta_f H^o(X^-,g) + \Delta_f H^o(MX,s) \quad (S3)$$

- this equation links Tables 1, S1, S3 and S8.

$$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)] = \Delta_f H^o(M^+,aq) + \Delta_f H^o(X^-,aq) - \Delta_f H^o(M^+,g) - \Delta_f H^o(X^-,g) \quad (S4)$$

- this equation links Tables 1, S1 and S2.

and

$$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)] = \Delta_f H^o(M^+,aq) + \Delta_f H^o(X^-,aq) - U_{POT}(MX) - n\mathrm{RT} - \Delta_f H^o(MX,s) \quad (S5)$$

- this equation links Tables 1, S2, S3 and S7.

S3. Free Energy of Hydration Relationships:

$$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(X^-,g)] = \Delta_f G^o(M^+,aq) + \Delta_f G^o(X^-,aq) - \Delta_f G^o(M^+,g) - \Delta_f G^o(X^-,g) \quad (S6)$$

- this equation links Tables 1, S1 and S2.

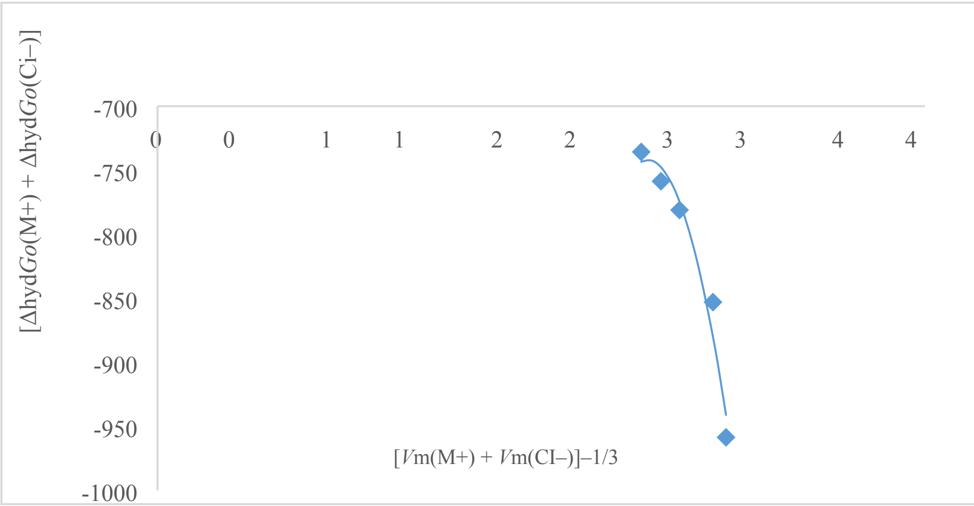
and

$$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(X^-,g)] = \Delta_f G^o(M^+,aq) + \Delta_f G^o(X^-,aq) - U_{POT}(MX) - n\mathrm{RT} - \Delta_f G^o(MX,s) \quad (S7)$$

- this equation links Tables 1, S2, S4 and S7.

S4. Hydration Sum Plots versus various functions of Volume.kJ mol^{-1}

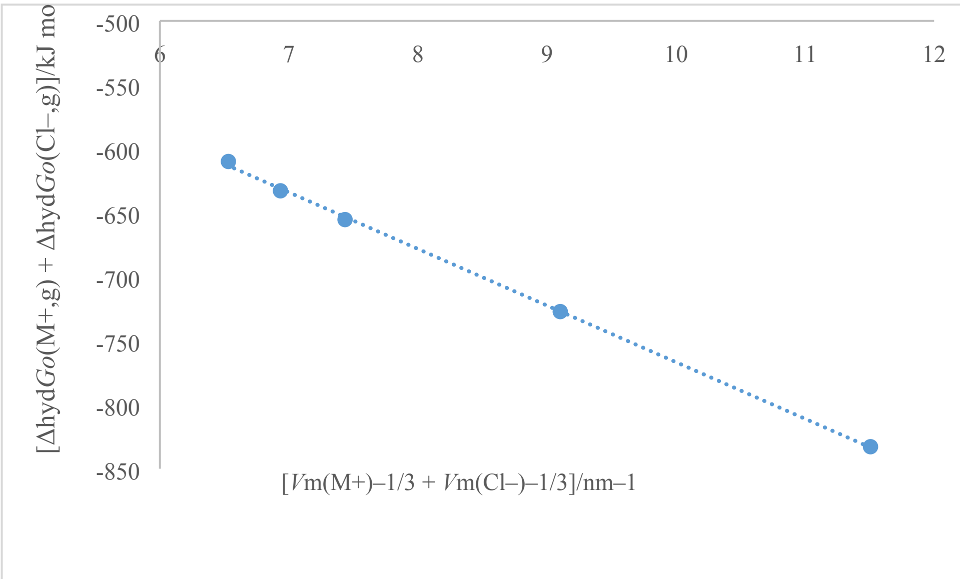
Figure S1. $[\Delta_{hyd}G^{o}(M^{+},g) + \Delta_{hyd}G^{o}(Cl^{-},g)]$/kJ mol^{-1} versus $[V_m(M^{+}) + V_m(Cl^{-})]^{-1/3}$/nm^{-1}



NON–LINEAR FIT

Figure S2. [$\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(Cl^-,g)$]/kJ mol^{-1} versus [$V_m(M^+)^{-1/3} + V_m(Cl^-)^{-1/3}$]/nm^{-1}

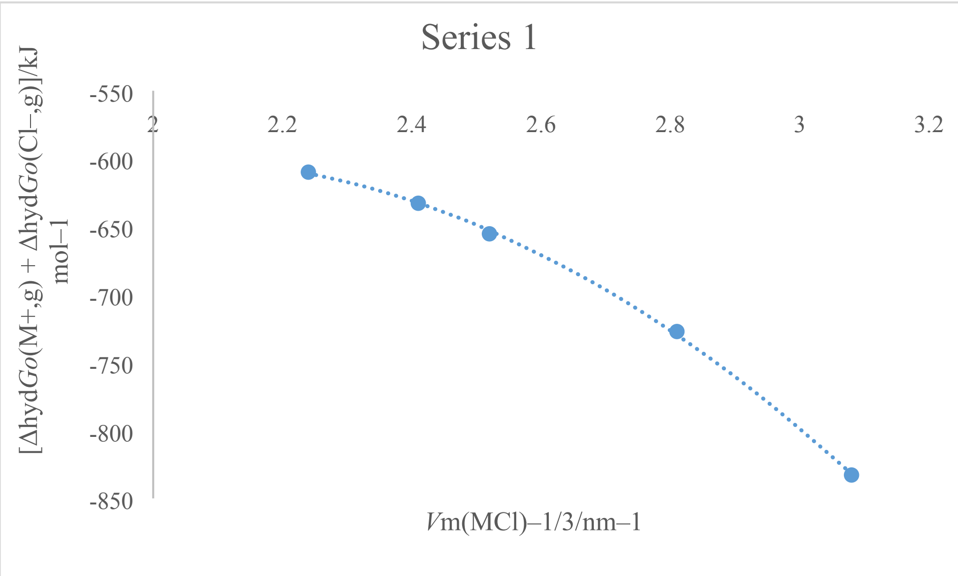
M = Li – Cs



LINEAR FIT

Figure S3.

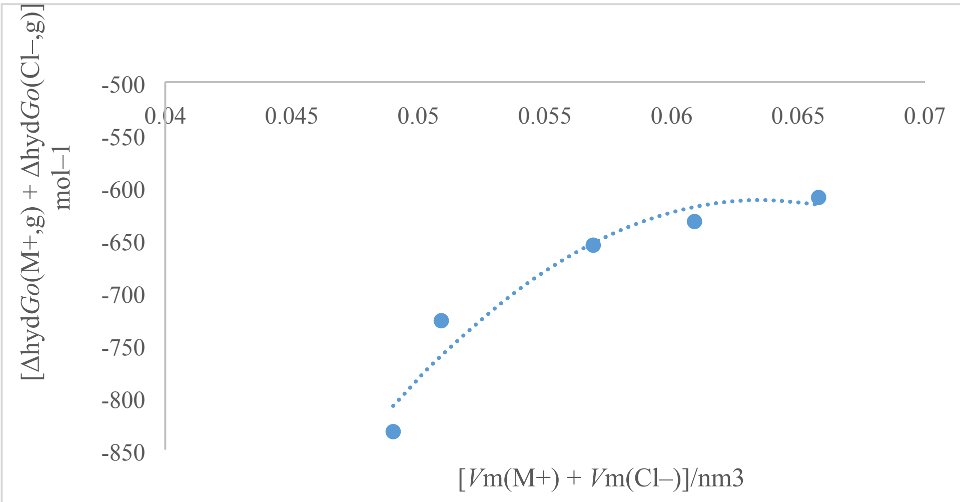
$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(Cl^-,g)]/kJ\ mol^{-1}$ versus $V_m(MCl)^{-1/3}/nm^{-1}$



POLYNOMIAL FIT

Figure S4.

$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(Cl^-,g)]$/kJ mol^{-1} versus $[V_m(M^+) + V_m(Cl^-)]$/nm^3



NON–LINEAR FIT

S5. Plot of [$\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)$] and [$\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(X^-,g)$]. versus [$V_m(M^+)^{-1/3} + V_m(X^-,g)^{-1/3}$].

Table S9. Data for [$\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(X^-,g)$]/kJ mol^{-1}

[$\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(X^-,g)$]/kJ mol^{-1}					
		F^-	Cl^-	Br^-	I^-
		−429.3	−303.5	−277.7	−239.5
H^+	−1104.5	**−1533.8**	**−1408.0**	**−1382.2**	**−1344.0**
Li^+	−529.3	**−958.6**	**−832.8**	**−807.0**	**−768.8**
Na^+	−423.7	**−853.0**	**−727.2**	**−701.4**	**−663.2**
K^+	−351.8	**−781.1**	**−655.3**	**−629.5**	**−591.3**
Rb^+	−329.3	**−758.6**	**−632.8**	**−607.0**	**−568.8**
Cs^+	−306.4	**−735.7**	**−609.9**	**−584.1**	**−545.9**

Table S10 Data for $[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}

$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}					
		F^-	Cl^-	Br^-	I^-
		−463.7	−319.5	−288.7	−246.8
H^+	−1150.1	**−1613.8**	**−1469.6**	**−1438.8**	**−1396.9**
Li^+	−578.1	**−1041.8**	**−897.6**	**−866.8**	**−824.9**
Na^+	−463.3	**−927.0**	**−782.8**	**−752.0**	**−710.1**
K^+	−380.3	**−844.0**	**−699.8**	**−669.0**	**−627.1**
Rb^+	−355.2	**−818.9**	**−674.7**	**−643.9**	**−602.0**
Cs^+	−330.6	**−794.3**	**−650.1**	**−619.3**	**−577.4**

Table S11. Data for $[V_m(M^+)^{-1/3} + V_m(X^-,g)^{-1/3}]/nm^{-1}$

$[V_m(M^+)^{-1/3} + V_m(X^-,g)^{-1/3}]/nm^{-1}$					
		F^-	Cl^-	Br^-	I^-
		3.420	2.771	2.614	2.404
H^+	20.676	**24.096**	**23.447**	**23.289**	**23.079**
Li^+	8.736	**12.156**	**11.507**	**11.350**	**11.140**
Na^+	6.331	**9.751**	**9.102**	**8.945**	**8.735**
K^+	4.664	**8.084**	**7.435**	**7.277**	**7.067**
Rb^+	4.163	**7.583**	**6.934**	**6.777**	**6.567**
Cs^+	3.760	**7.180**	**6.531**	**6.373**	**6.163**

S6. Analytical results for Graphical Fits of [$\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(X^-,g)$]/kJ mol^{-1} versus [$V_m(M^+)^{-1/3} + V_m(X^-,g)^{-1/3}$].

down columns

$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(F^-,g)] = -48.208\ [V_m(M^+)^{-1/3} + V_m(F^-,g)^{-1/3}] - 453.45$ ($R^2 = 0.9999$) (S8)

$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(Cl^-,g)] = -48.208\ [V_m(M^+)^{-1/3} + V_m(F^-,g)^{-1/3}] - 343.3$ ($R^2 = 0.9999$) (S9)

$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(Br^-,g)]$

$= -48.208\ [V_m(M^+)^{-1/3} + V_m(Br^-,g)^{-1/3}] - 317.32$ ($R^2 = 0.9999$) (S10)

$[\Delta_{hyd}H^o(M^+,g) + \Delta_{hyd}H^o(I^-,g)] = -48.208\ [V_m(M^+)^{-1/3} + V_m(I^-,g)^{-1/3}] - 285.55$ ($R^2 = 0.9999$) (S11)

Summarised in main text thus:

$[\Delta_{hyd}H^o(M^+,g) + \delta_{F-}\Delta_{hyd}H^o(F^-,g) + \delta_{Cl-}\Delta_{hyd}H^o(Cl^-,g) + \delta_{Br-}\Delta_{hyd}H^o(Br^-,g) + \delta_{I-}\Delta_{hyd}H^o(I^-,g)]$

$= -48.208\ [V_m(M^+)^{-1/3} + \delta_{F-}V_m(F^-,g)^{-1/3} + \delta_{Cl-}V_m(Cl^-,g)^{-1/3} + \delta_{Br-}V_m(Br^-,g)^{-1/3} + \delta_{I-}V_m(I^-,g)^{-1/3}]$

$- 453.45\ \delta_{F-} - 343.3\ \delta_{Cl-} - 317.32\ \delta_{Br-} - 285.55\ \delta_{I-}$ ($R^2 = 0.9999$) (18)

across rows

$[\Delta_{hyd}H^o(H^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}

$= -214.69\ [V_m(H^+)^{-1/3} + V_m(X^-)^{-1/3}]$/nm + 3560.6 ($R^2 = 0.9992$) (S12)

$[\Delta_{hyd}H^o(Li^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}

$= -214.69\ [V_m(Li^+)^{-1/3} + V_m(X^-)^{-1/3}]$/nm +1569.4 ($R^2 = 0.9992$) (S13)

$[\Delta_{hyd}H^o(Na^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}

$= -214.69\ [V_m(Na^+)^{-1/3} + V_m(X^-)^{-1/3}]$/nm + 1167.9 ($R^2 = 0.9992$) (S14)

$[\Delta_{hyd}H^o(K^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}

$= -214.69\ [V_m(K^+)^{-1/3} + V_m(X^-)^{-1/3}]$/nm + 892.8 ($R^2 = 0.9992$) (S15)

$[\Delta_{hyd}H^o(Rb^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}

$= -214.69\ [V_m(Rb^+)^{-1/3} + V_m(X^-)^{-1/3}]$/nm + 810.5 ($R^2 = 0.9992$) (S16)

$[\Delta_{hyd}H^o(Cs^+,g) + \Delta_{hyd}H^o(X^-,g)]$/kJ mol^{-1}

$= -214.69\ [V_m(Cs^+)^{-1/3} + V_m(X^-)^{-1/3}]$/nm + 748.4 ($R^2 = 0.9992$) (S17)

Summarised in main text by:

$$[\delta_{H+}\Delta_{hyd}H^{o}(H^{+},g) + \delta_{Li+}\Delta_{hyd}H^{o}(Li^{+},g) + \delta_{Na+}\Delta_{hyd}H^{o}(Na^{+},g) + \delta_{K+}\Delta_{hyd}H^{o}(K^{+},g) + \delta_{Rb+}\Delta_{hyd}H^{o}(Rb^{+},g) + \delta_{Cs+}\Delta_{hyd}H^{o}(Cs^{+},g) + {}_{-}\Delta_{hyd}H^{o}(X^{-},g)]$$

$$= -214.69\,[\delta_{H+}V_{m}(H^{+})^{-1/3} + \delta_{Li+}V_{m}(Li^{+})^{-1/3} + \delta_{Na+}V_{m}(Na^{+})^{-1/3} + \delta_{K+}V_{m}(K^{+})^{-1/3} + \delta_{Rb+}V_{m}(Rb^{+})^{-1/3} + \delta_{Cs+}V_{m}(Cs^{+})^{-1/3} + {}_{-}V_{m}(X^{-},g)^{-1/3}] + 3560.6\,\delta_{H+} + 1569.4\,\delta_{|Li+} + 1167.9\,\delta_{Na+} + 892.8\,\delta_{K+} + 810.5\,\delta_{Rb+} + 748.4\,\delta_{Cs+} \quad (R^{2} = 0.9992) \quad (20)$$

S7. Analytical results for Graphical Fits of [$\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(X^-,g)$]/kJ mol^{-1} versus [$V_m(M^+)^{-1/3} + V_m(X^-,g)^{-1/3}$].

down columns

$$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(F^-,g)] = -47.057\ [V_m(M^+)^{-1/3} + V_m(F^-,g)^{-1/3}] - 396.82\ (R^2 = 0.9996) \quad (S18)$$

$$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(Cl^-,g)] = -47.057\ [V_m(M^+)^{-1/3} + V_m(Cl^-,g)^{-1/3}] - 301.56\ (R^2 = 0.9996) \quad (S19)$$

$$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(Br^-,g)] = -47.057\ [V_m(M^+)^{-1/3} + V_m(Br^-,g)^{-1/3}] - 283.16\ (R^2 = 0.9996) \quad (S20)$$

$$[\Delta_{hyd}G^o(M^+,g) + \Delta_{hyd}G^o(I^-,g)] = -47.057\ [V_m(M^+)^{-1/3} + V_m(I^-,g)^{-1/3}] - 254.85\ (R^2 = 0.9996) \quad (S21)$$

Summarised in main text by:

$$[\Delta_{hyd}G^o(M^+,g) + \delta_{F-}\Delta_{hyd}G^o(F^-,g) + \delta_{Cl-}\Delta_{hyd}G^o(Cl^-,g) + \delta_{Br-}\Delta_{hyd}G^o(Br^-,g) + \delta_{I-}\Delta_{hyd}G^o(I^-,g)]$$
$$= -47.057\ [V_m(M^+)^{-1/3} + \delta_{F-}V_m(F^-,g)^{-1/3} + \delta_{Cl-}V_m(Cl^-,g)^{-1/3} + \delta_{Br-}V_m(Br^-,g)^{-1/3} + \delta_{I-}V_m(I^-,g)^{-1/3}]$$
$$- 396.82\ \delta_{F-} - 301.56\ \delta_{Cl-} - 283.16\ \delta_{Br-} - 254.85\ \delta_{I-} \quad (R^2 = 0.9996) \quad (22)$$

across rows

$$[\Delta_{hyd}G^o(H^+,g) + \Delta_{hyd}G^o(X^-,g)]/\text{kJ mol}^{-1} = -187.34\ [V_m(H^+)^{-1/3} + V_m(X^-)^{-1/3}]/\text{nm} + 2981.4 \quad (R^2 = 0.9993) \quad (S22)$$

$$[\Delta_{hyd}G^o(Li^+,g) + \Delta_{hyd}G^o(X^-,g)]/\text{kJ mol}^{-1} = -187.34\ [V_m(Li^+)^{-1/3} + V_m(X^-)^{-1/3}]/\text{nm} +1319.8 \quad (R^2 = 0.9993) \quad (S23)$$

$$[\Delta_{hyd}G^o(Na^+,g) + \Delta_{hyd}G^o(X^-,g)]/\text{kJ mol}^{-1} = -187.34\ [V_m(Na^+)^{-1/3} + V_m(X^-)^{-1/3}]/\text{nm} + 974.9 \quad (R^2 = 0.9993) \quad (S24)$$

$$[\Delta_{hyd}G^o(K^+,g) + \Delta_{hyd}G^o(X^-,g)]/\text{kJ mol}^{-1} = -187.34\ [V_m(K^+)^{-1/3} + V_m(X^-)^{-1/3}]/\text{nm} + 734.33 \quad (R^2 = 0.9993) \quad (S25)$$

$$[\Delta_{hyd}G^o(Rb^+,g) + \Delta_{hyd}G^o(X^-,g)]/\text{kJ mol}^{-1}$$

$$= -187.34\ [V_m(\mathrm{Rb}^+)^{-1/3} + V_m(\mathrm{X}^-)^{-1/3}]/\mathrm{nm} + 663.08 \quad (R^2 = 0.9993) \quad (S26)$$

$$[\Delta_{hyd}G^o(\mathrm{Cs}^+,\mathrm{g}) + \Delta_{hyd}G^o(\mathrm{X}^-,\mathrm{g})]/\mathrm{kJ\ mol}^{-1}$$

$$= -187.34\ [V_m(\mathrm{Cs}^+)^{-1/3} + V_m(\mathrm{X}^-)^{-1/3}]/\mathrm{nm} + 610.37 \quad (R^2 = 0.9993) \quad (S27)$$

Summarised in main text by:

$$[\delta_{H+}\Delta_{hyd}G^o(\mathrm{H}^+,\mathrm{g}) + \delta_{Li+}\Delta_{hyd}G^o(\mathrm{Li}^+,\mathrm{g}) + \delta_{Na+}\Delta_{hyd}G^o(\mathrm{Na}^+,\mathrm{g}) + \delta_{K+}\Delta_{hyd}G^o(\mathrm{K}^+,\mathrm{g}) +$$

$$\delta_{Rb+}\Delta_{hyd}G^o(\mathrm{Rb}^+,\mathrm{g}) + \delta_{Cs+}\Delta_{hyd}G^o(\mathrm{Cs}^+,\mathrm{g}) + {}_{-}\Delta_{hyd}G^o(\mathrm{X}^-,\mathrm{g})\ ]$$

$$= -187.34\ [\delta_{H+}V_m(\mathrm{H}^+)^{-1/3} + \delta_{Li+}V_m(\mathrm{Li}^+)^{-1/3} + \delta_{Na+}V_m(\mathrm{Na}^+)^{-1/3} + \delta_{K+}V_m(\mathrm{K}^+)^{-1/3} + \delta_{Rb+}V_m(\mathrm{Rb}^+)^{-}$$

$$+ \delta_{Cs+}V_m(\mathrm{Cs}^+)^{-1/3} + {}_{-}V_m(\mathrm{X}^-,\mathrm{g})^{-1/3}\ ] + 2981.4\ \delta_{H+} + 1319.8\ \delta_{|Li+}$$

$$+ 974.9\ \delta_{Na+} + 734.3\ \delta_{K+} + 663.1\ \delta_{Rb+} + 610.4\ \delta_{Cs+} \quad (R^2 = 0.9993) \quad (23)$$

S8. Tissandier et. al. Reference 52 Data in Table 1.

Solvation Free Energy, [$\Delta G_{aq}^{o}(M^{+},g) + \Delta G_{aq}^{o}(X–,g)$] versus $V(MX)^{-1/3}$

Table S12. The table assembles data for [$\Delta G_{aq}^{o}(M^{+},g) + \Delta G_{aq}^{o}(X^{-},g)$]/kJ mol^{-1} and V(MX)$^{-1/3}$/nm^{-1} taken from the computational results given in Table 1 of reference 52. Figure S7 displays a plot of the whole of this solvation Free Energy data = [$\Delta G_{aq}^{o}(M^{+},g) + \Delta G_{aq}^{o}(X^{-},g)$] as ordinate versus V(MX)$^{-1/3}$ as abscissa. [$\Delta G_{aq}^{o}(M^{+},g) + \Delta G_{aq}^{o}(X^{-},g)$] represents the free energy change brought about by placing a pair of separate and oppositely charged gaseous ions into water at 298K. The process is equivalent to what previously was labelled in the main paper: [$\Delta G_{hyd}^{o}(M^{+},g) + \Delta G_{hyd}^{o}(X^{-},g)$]/kJ mol^{-1}

Salt MX	V(MX)$^{-1/3}$/nm^{-1}	[$\Delta G_{aq}^{o}(M^{+},g) + \Delta G_{aq}^{o}(X^{-},g)$]/kJ mol^{-1}
LIF	3.94	–958.1
NaF	3.43	–852.6
KF	2.97	–780.8
RbF	2.81	–758.2
LiCl	3.08	–833.8
NaCl	2.81	–728
KCl	2.52	–656.2
RbCl	2.41	–633.6
LiBr	2.89	–807
NaBr	2.66	–701.2
KBr	2.41	–629.4
RbBr	2.31	–606.8
LiI	2.64	–769.5
NaI	2.45	–663.9
KI	2.25	–592.1
RbI	2.16	–569.4

LiOH	3.09	–960.2
NaOH	3.03	–854.6
KOH	2.88	–782.8
RbOH	2.79	–760.1

Table S13. Linear fit down columns of Table 1 of reference 52 compared to data in Table S9

[a] Prediction made from $\Delta G_{aq}^{o}(M^+ + X^-)$/kJ mol^{-1} = A $V_m(MX)^{-1/3}$ + B

	A /kJ mol^{-1}nm	B /kJ mol^{-1}	N	R^2	Predicted[a] $\Delta G_{aq}^{o}(Cs^+ + X^-)$ /kJ mol^{-1}	$\Delta G_{aq}^{o}(Cs^+ + X^-)$ /kJ mol^{-1} from Table S9 column 7	% age Difference
$\Delta G_{aq}^{o}(M^+ + F^-)$/kJ mol^{-1}	−176.45	−257.29	4	0.9949	−723.8	−735.7	1.6
$\Delta G_{aq}^{o}(M^+ + Cl^-)$/kJ mol^{-1}	**−296.10**	**88.05**	**4**	**0.9827**	**−575.2**	−609.9	5.7
$\Delta G_{aq}^{o}(M^+ + Br^-)$/kJ mol^{-1}	−342.39	193.00	4	0.9807	−560.3	—584.1	4.1
$\Delta G_{aq}^{o}(M^+ + I^-)$/kJ mol^{-1}	−415.95	339.16	4	0.9798	−521.9	−545.9	4.4

Table S14. Polynomial of degree 2 fit down columns of Table 1 of reference 52 compared to data in Table S9

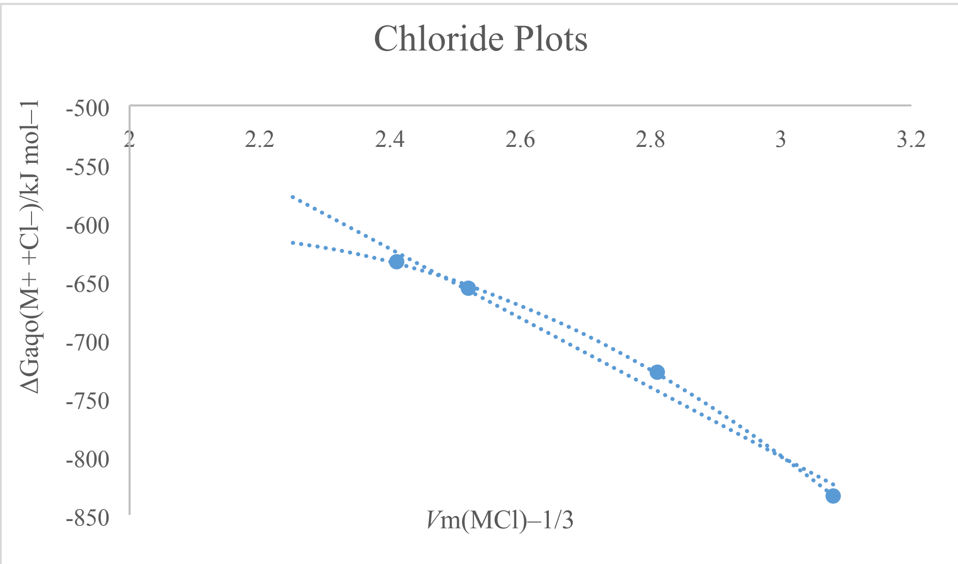
	C	D	E	N	R^2	Predicted[b]	$\Delta G_{aq}^{o}(Cs^+$	% age

	/kJ mol^{-1}nm^{2}	/kJ mol^{-1} nm	/kJ mol^{-1}			$\Delta G_{aq}{}^{o}(Cs^{+} + X^{-})$ /kJ mol^{-1}	+ X^{-}) /kJ mol^{-1} from Table S9 column 7	difference
$\Delta G_{aq}{}^{o}(M^{+} + F^{-})$/kJ mol^{-1}	−42.228	109.17	−731.71	4	0.9999	−738.3	−735.7	0.4
$\Delta G_{aq}{}^{o}(M^{+} + Cl^{-})$/kJ mol^{-1}	**−223.2**	**929.33**	**−1578.3**	**4**	**0.9996**	**−616.5**	−609.9	1.1
$\Delta G_{aq}{}^{o}(M^{+} + Br^{-})$/kJ mol^{-1}	−315.09	1296.3	−1921.1	4	0.9997	−594.3	—584.1	1.7
$\Delta G_{aq}{}^{o}(M^{+} + I^{-})$/kJ mol^{-1}	−468.01	1831.4	−2342.3	4	0.9999	−556.7	−545.9	2.0

[b] Prediction made from polynomial equation of the form:

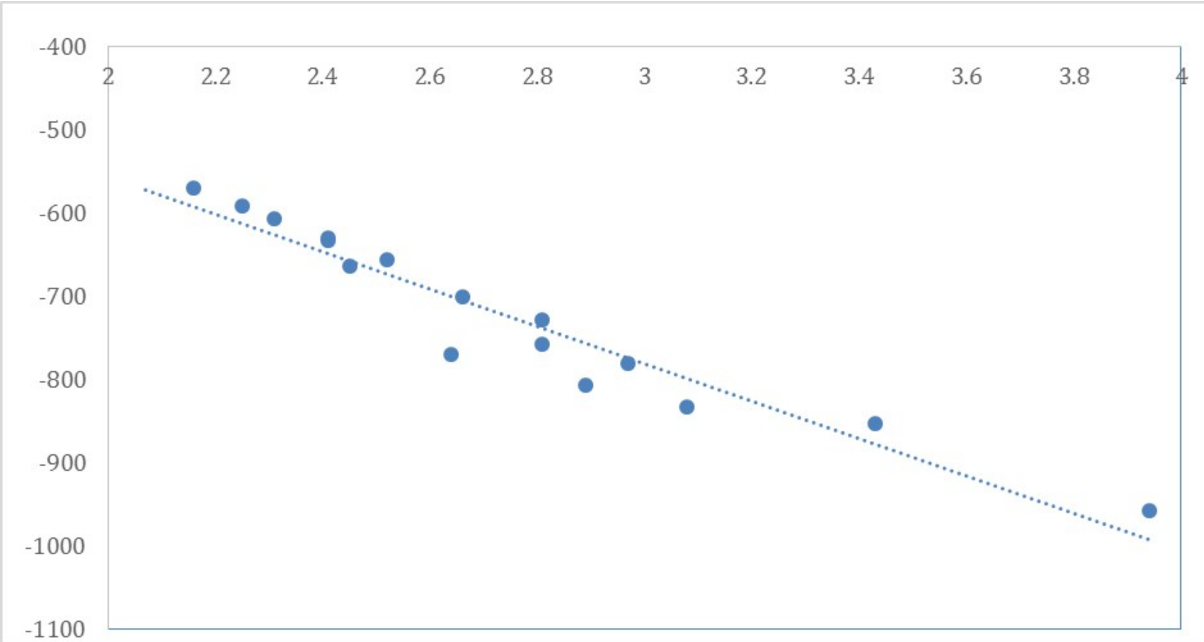
$$\Delta G_{aq}{}^{o}(M^{+} + X^{-})/\text{kJ mol}^{-1} = C\, V_m(MX)^{-2/3} + D\, V_m(MX)^{-1/3} + E$$

Figure S5. . Sample plot of $\Delta G_{aq}{}^{o}(M^{+} + Cl^{-})$/kJ mol^{-1} versus $V_m(MCl)^{-1/3}$ (highlighted rows in Tables S13 and S14 above showing linear fit and polynomial fit to data



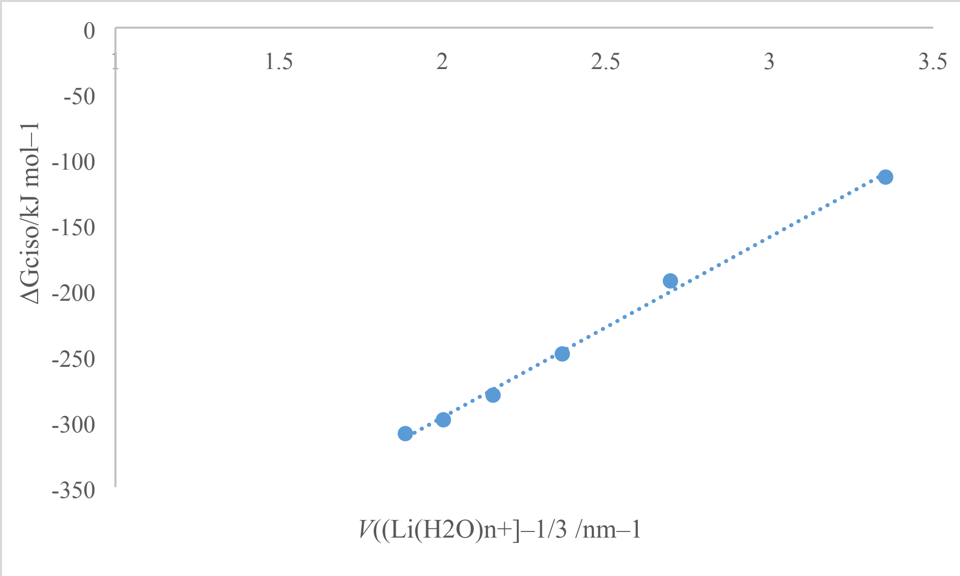
S9. Tissandier et. al. Reference 52 Data in Table 4.

Figure S6. Plot of Solvation Free Energy data as ordinate : $\Delta G_{aq}{}^{o}(M^{+} + X^{-}) = \Delta G_{aq}{}^{o}(M^{+},g) + \Delta G_{aq}{}^{o}(X^{-},g)$ versus $V(MX)^{-1/3}$ as abscissa for alkali halide salts (except Cs^{+} salts) listed in Table S11.



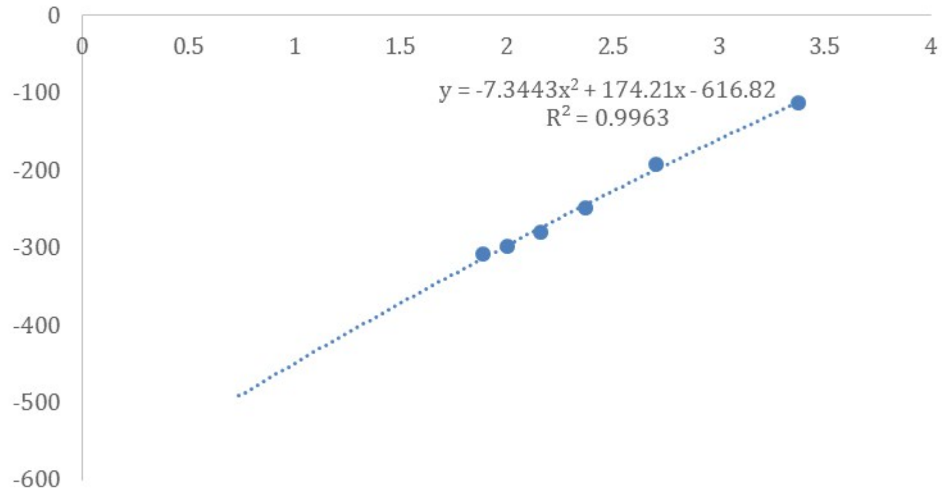
[ΔG_{aq}°(M^+,g) + ΔG_{aq}°(X^-,g)]/kJ mol^{-1} = –225.1 $V(MX)^{-1/3}$ – 106.0 (N = 15, R^2 = 0.9259) (32)

Figure S7 Cluster–ion Solvation Free Energy, ΔG_{cis}°/kJ mol^{-1} plotted as ordinate versus $V(Li(H_2O)_n^+)/nm^3$ with a least squares rectilinear fit.



$$\Delta G_{cis}^{o}/\text{kJ mol}^{-1} = 137.28\ V(Li(H_2O)_n^{+}) - 571.38 \quad (N = 6, R^2 = 0.9959) \quad (33)$$

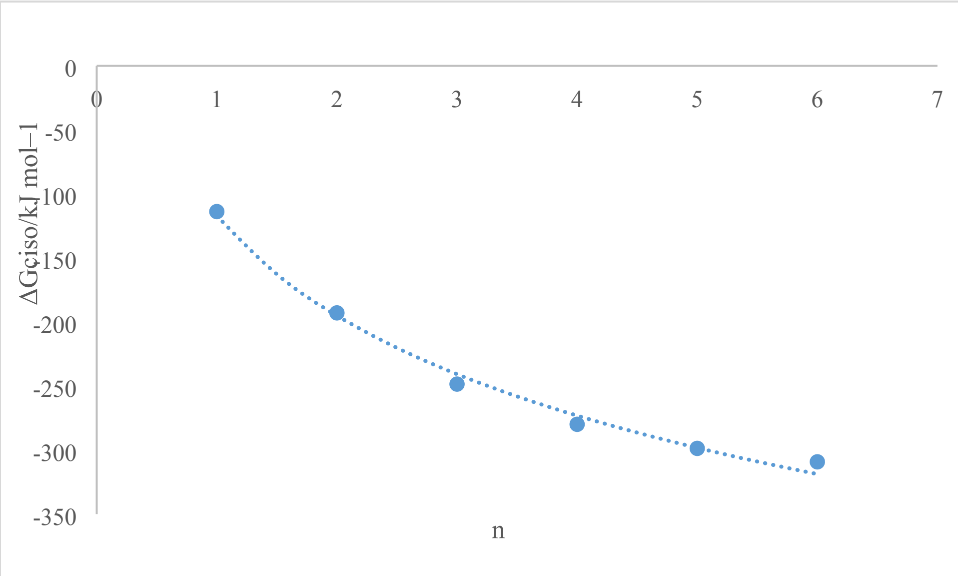
Figure S8. Cluster–ion Solvation Free Energy, ΔG_{cis}^{o}/kJ mol^{-1} plotted as ordinate versus $V(Li(H_2O)_n^+)$/nm^3 as abscissa with a least squares polynomial fit of degree 2.



ΔG_{cis}^{o}/kJ mol^{-1}

$= -6.45\ V(Li(H_2O)_n^+)^{-2/3} + 171.15\ V(Li(H_2O)_n^+)^{-1/3} - 613.95$ (N = 6, $R^2 = 0.9963$) (S30)

Figure S9. **ΔG_{cis}°/kJ mol^{-1} plotted versus n**



References

1. **http://kinetics.nist.gov/janaf/**

2. D. R. Lide, "*Handbook of Chemistry & Physics*", 80th Edition, 1999–2000, C R C Press, Boca Raton. Page 5–85.

3. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nutall, "NBS Tables of Chemical Thermodynamic Properties", *J. Phys. Chem. Ref. Data, Volume 11, Supplement 2,* 1982.

4. J. F. Zemaitis, D. M. Clark, M. Rafal, N. C. Scrivner, "*Handbook of Aqueous Electrolyte Thermodynamics"*, American Institute of Chemical Engineers, New York, 1986.