## 1 Supplementary Information - A Study of the Relationship between Water and Anions of the 2 Hofmeister Series Using Pressure Perturbation Calorimetry

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9 The calculated values for the coefficient of thermal expansion determined using the equation derived in Lin et. al. 2002 using the conventional apparent partial volume (V) values from Millero 10 1971<sup>2</sup> and experimental results for 100 mM salt solutions are shown in Figures S1. The coefficient of 11 12 thermal expansion for sodium chloride, sodium bromide, sodium iodide, sodium thiocyanide and 13 sodium perchlorate are simplar but the two sodium salts with high charge density anions sodium fluoride and disodium sulphate have markedly different calculated coefficients of thermal 14 expansion. For the two high charge density salts sodium flouride and disodium sulphate, the 15 conventional apparent partial volume ( $\overline{V}$ ) values differ significantly from the intrinsic volumes ( $V_{int}$ ), 16 as shown in Figure S2. It was the observation that the coefficient of thermal expansion calculated for 17 18 high charge density anions was problematic that led the authors to develop the alternative 19 mathetical approach where the hydration layer was treated as a discrete population of water with 20 an average volume and coefficient of thermal expansion. This idea is supported by a range of analytical methodologies that suggest that water in the first and second layer around an ion is 21 significantly different to pure or bulk water, see the main paper. 22







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32 Figure S2: The conventional apparent partial volume ( $V_0$ ) (from Millero 1971)<sup>2</sup> versus intrinsic volume

33 (V<sub>int</sub>) calculated from the ionic radii (from Marcus 1997)<sup>3</sup> of disodium sulphate (=), sodium chloride

34 ( $\square$ ), sodium bromide (+), sodium iodide ( $\oplus$ ) and sodium perchlorate ( $\square$ ).

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## 36 References

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- 39 3. Y. Marcus, Ions Properties, CRC Press, Boca Raton, 1997.