Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

# Understanding Specific Ion Effects and the Hofmeister Series

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## *Supporting Information*

### Hofmeister's Original Experiments

Hofmeister's initial discussion of specific ion effects was in a weight per volume concentration scale. This was due to these units of concentration initially being used in the conducted experiments (Figure S1(a)). This meant large polyatomic ions with high molecular weights such as citrate ($C_3H_5O(CO_2)_3{}^{3-}$) would require higher concentrations with respect to their molar counterparts. For example, chromates ($CrO_4{}^{2-}$) and chlorides ($Cl^-$) required almost identical weights to precipitate the protein.

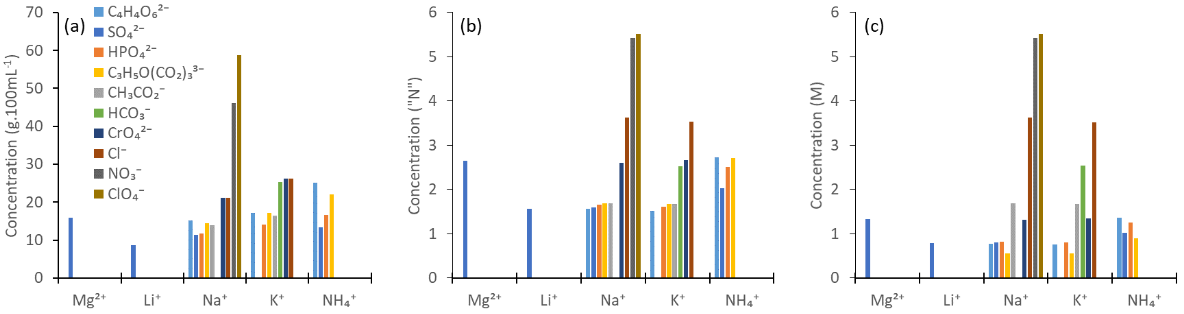

**Figure S1:** Concentration of salt required to precipitate egg white proteins in a) g·100mL$^{-1}$, b) molar concentration of the cation and c) the molar concentration. Data obtained from Refs. 1,2.

Hofmeister then attempted to account for the molecular weight of the salts. It appears the calculations were for the number ("N") of metal ions in solution (Figure S1(b)). For divalent anions the concentration values are therefore double the concentration of the salt. In fact, it appears the value for $MgSO_4$ (the only multi-valent cation salt in this series) was also doubled, such that the concentration was reported to be twice the value of the salt. So, on a per ion basis of $Mg^{2+}$, the "N" value should be half what was reported. This would switch it from having the least to the most "precipitating power" on a per ion basis. Considering the orders of the anions on this "N" concentration scale are what are on the commemorative plaque at Charles University, inconsistencies in reported *Hofmeister series* are not surprising.

If instead the molar salt concentration is used (Figure S1(c)), which, for these salts gives us the concentration of anions present in solution. On this basis we get a different series to what is on Hofmeister's commemorative plaque (given in the main text) as charge factors are no longer calculated out of the effect (e.g., $C_3H_5O(CO_2)_3^{3-}$ and $CrO_4^{2-}$). The three anionic series from each concentration form may be written as,

> Anions (g·100mL$^{-1}$): $SO_4^{2-} > HPO_4^{2-} > CH_3CO_2^- > C_3H_5O(CO_2)_3^{3-} > C_4H_4O_6^{2-} > HCO_3^- > CrO_4^{2-} > Cl^- > NO_3^- > ClO_3^-$
>
> Anions ("N"): $C_4H_4O_6^{2-} > SO_4^{2-} > HPO_4^{2-} > C_3H_5O(CO_2)_3^{3-} > CH_3CO_2^- > HCO_3^- > CrO_4^{2-} > Cl^- > NO_3^- > ClO_3^-$
>
> Anions (M): $C_3H_5O(CO_2)_3^{3-} > C_4H_4O_6^{2-} \approx SO_4^{2-} > HPO_4^{2-} > CrO_4^{2-} > CH_3CO_2^- > HCO_3^- > Cl^- > NO_3^- > ClO_3^-$

Moreover, the difference between ions from a quantitative standpoint appears more definitive on a molar concentration (Figure S1(a)), which is primarily the concentration scale that contemporary "Hofmeister Series" are now reported. However, caution is still advised, as counterion concentration should not be disregarded in mixed salts or mixed-valance binary salts. Ionic strength may aid in this regard, especially for re-entrant effects. Still, coupling of the cation and anion concentrations into a single ionic strength term for may lead to erroneous insight in other circumstances and mechanistic understanding may be required for a proper concentration analysis. For example, in a circumstance where counterions or coions act as a "spectators",[3,4] their concentration effects might occur indirectly from an entropic or crowding standpoint. Alternatively, each of the ions present in solution could have opposing effects, and additionally be dependent on concentrations of a cosolute (*i.e.*, saturation of binding sites).

The qualitative ordering of ions, such as those presented in the Hofmeister series also requires caution. Unsubstantial perturbations on a quantitative scale can cause ions to swap positions in the sequence and become subject to conclusions about mechanistic differences or changes where there are none. The series is especially prone to anomalous orders at series reversal conditions, where specific ion effects could be masked, or subject to non-dominant intermolecular forces. Instead of qualitative series reporting, a more valuable representation to academically signal SIE that appear to correspond with Hofmeister effects, would be a quantitative correlation with a fundamental ion parameter (such as the electrostatics as represented by þ, which correlates with a majority of reported "Hofmeister series" and the more well defined Lyotropic series).

## Salt Solubility

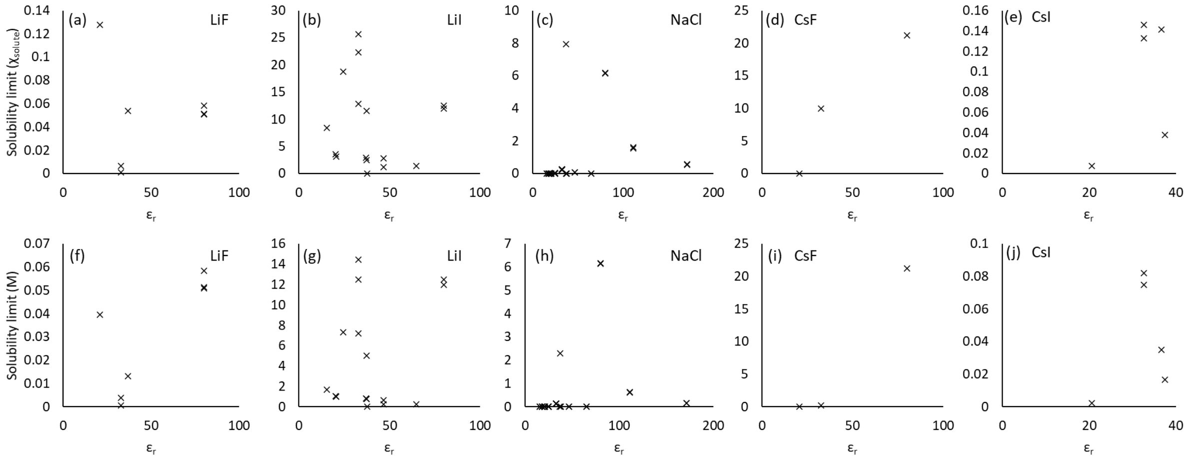

**Figure S2:** (a-e) Mole fraction and (f-j) molar concentration solubility limit of various salts representing (a,f) small cation, small anion (LiF), (b,g) small cation, large anion (LiI), (c,h) moderate cation, moderate anion (NaCl), (d,i) large cation, small anion (CsF) and (e,j) large cation, large anion (CsI) in aqueous and nonaqueous solvents. Data from Mazzini.[5,6]

**Table S1:** Surface sensitive experimental techniques available to investigate ionic presence at vapor-liquid interfaces

| **Experimental Technique** | **Probing depth** | **Information obtained** |
|---|---|---|
| **X-ray Photoelectron spectroscopy (XPS)** | 20 – 80 Å for primary kinetic energy of 200 - 1000 KeV[7]<br>Dependent upon Inelastic mean free- path of electrons (IMFP). | Measures surface concentration of elements present in the system through emitted photoelectron signal.<br>Requires high- energy X-ray sources and measurements can only be performed in UHV conditions hence requires special setup. |
| **Metastable Induced Electron Spectroscopy (MIES)** | One molecular layer[8] | Measure the surface composition through deexcitation of metastable Helium atoms ($He^*$) at the surface.<br>Only probes elements present in the outermost layers and requires special setup as MIES measurements are done under UHV conditions |
| **Neutral Impact Collision Ion Scattering Spectroscopy (NICISS)** | 2 – 300 Å (depends on primary energy of projectile from 1- 10 KeV) with resolution of ~2 Å[9,10] | Measures Concentration depth profiles of elements through energy loss experience by He neutrals backscattering through the matter.<br>High-Vacuum conditions requirement is one limitation. Water as a solvent can be measured but requires special setup.<br>Harder to measure lighter elements present in lower concentrations. |
| **Non- Linear Optical (NLO) techniques (Sum frequency generation (SFG) and Second harmonic generation (SHG) spectroscopies)** | MD simulations suggest probing depth of 4- 6 Å.[11,12]<br>However, probing depth for NLO techniques depends on the non-centrosymmetric region nearby liquid-vapour interface which differs between electrolyte solutions. | Measures the change in non-centrosymmetric signals present at vapor-liquid interface formed due to interfacial asymmetry. Provides important specific ion interactions present at vapor-liquid interface.<br>Indirectly measures the presence of ions at vapor-liquid interface.<br>Provides information of net ion contribution. |
| **Charge transfer to the solvent- UV-SHG (CTTS-UV-SHG)** | MD simulations suggest probing depth of 4- 6 Å.[11,12] | Measures ion's charge transfer to the solvent which exhibits large non-linear cross-section that can be separated from solvent non-resonant contribution.[13]<br>This separated contribution is fitted to a Langmuir adsorption model to obtain Gibb's surface free energy of adsorption of ion. (See Table S3 for so far available data for anions)<br>Separating contribution of ions from solvent non-resonant contribution is harder for simple halide ions especially in intermediate concentration regime (0.1 to 2 moles/litres). |

**Table S2:** Gibbs Free Energy of Adsorption of anions (mentioned in brackets) derived using CTTS-UV-SHG.

| **Salt** | **Anion** | **Gibbs Free Energy of Adsorption (Kcal/mole)** | **Ref.** |
|---|---|---|---|
| NaI | $I^-$ | -6.1 ± 0.2 | Petersen[14] |
| KI | $I^-$ | -6.3 ± 0.2 | Petersen[14] |
| NaSCN | $SCN^-$ | -1.80 ± 0.03 | Petersen[15] |
| $K_4Fe\ (CN)_6$ | $Fe\ (CN)_6^{4-}$ | -6.8 | Petersen[16] |
| $NaN_3$ | $N_3^-$ | -9.9 ± 0.3 | Petersen[17] |

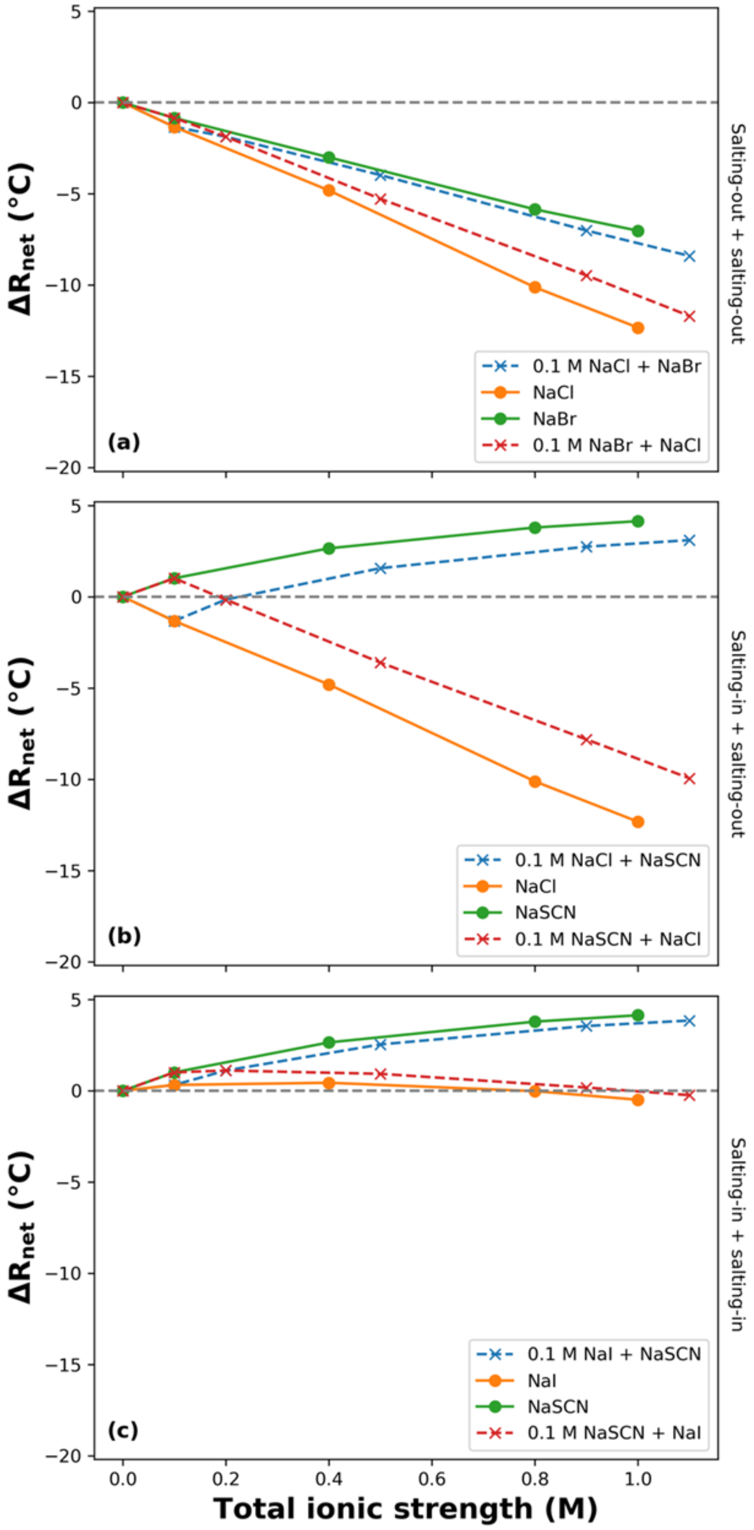

**Figure S3:** The net response in LCST ($\Delta R_{net}$; change relative to the LCST of PPO in water) of ungrafted PPO as a function of the total ionic strength for various binary electrolyte compositions: same end of Hofmeister series anions (a) and (b); opposite end (c). Data obtained and reproduced with permission from Moghaddam and Thormann.[18]

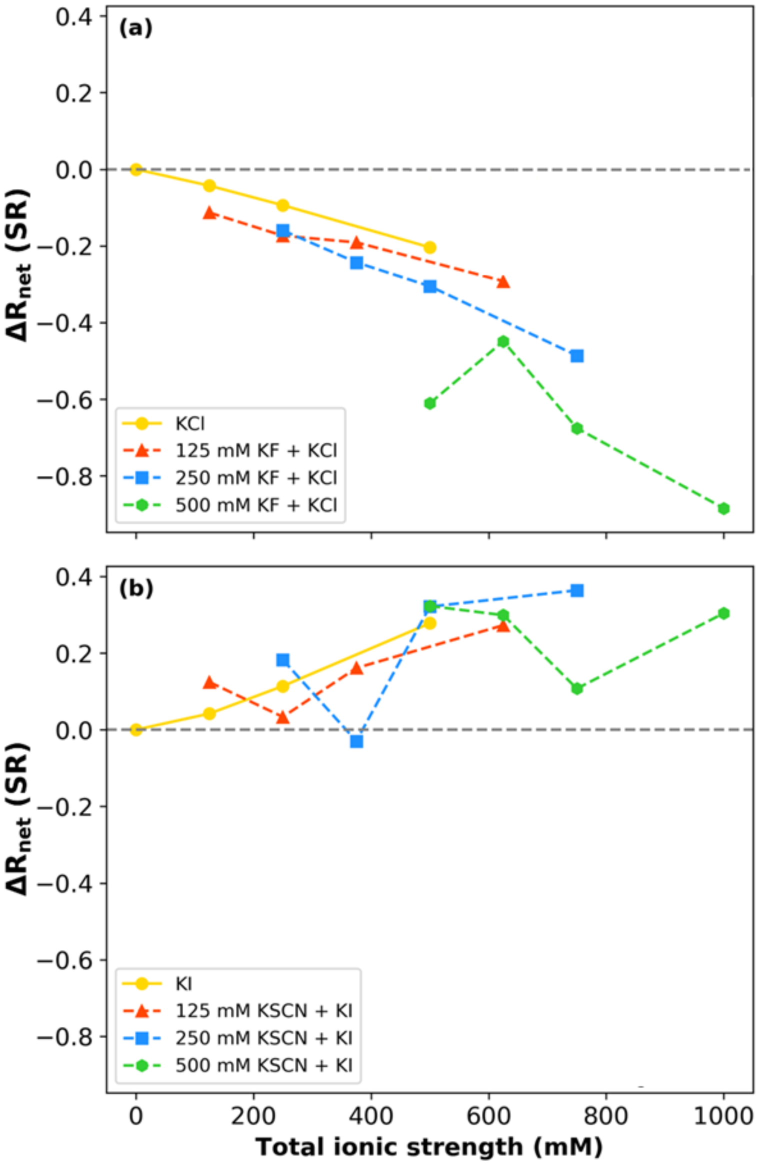

**Figure S4:** The net response ($\Delta R_{net}$ (SR); change in swelling ratio relative to the response in water) of a P(MEO$_2$MA-*stat*-OEGMA$_{300}$) 80:20 mol% copolymer brush at 15 °C in binary electrolytes composed of (a) salting-out and (b) salting-in ions. After Ref. 19.

**Table S3:** Experimental values of the static relative permittivity ($\varepsilon_r$) of aqueous solutions of NaCl at varying concentrations.

| Concentration [M] | Static Relative Permittivity ($\varepsilon_r$) | Reference |
|---|---|---|
| 1.02 | 62.8 | Christensen[20] |
| 2.083 | 52.2 | Christensen[20] |
| 4.366 | 37.6 | Christensen[20] |
| 5.619 | 32.1 | Christensen[20] |
| 0.125 | 78 | Hasted[21] |
| 0.33 | 73 | Hasted[21] |
| 0.66 | 68.7 | Hasted[21] |
| 1 | 65 | Hasted[21] |
| 1 | 68.48 | De Ninno[22] |
| 2 | 53.67 | De Ninno[22] |
| 3 | 45.39 | De Ninno[22] |
| 4 | 39.2 | De Ninno[22] |
| 5 | 34.5 | De Ninno[22] |
| 0.11086 | 76.48 | Buchner[23] |
| 0.11086 | 76.79 | Buchner[23] |
| 0.19193 | 75.45 | Buchner[23] |
| 0.19193 | 75.71 | Buchner[23] |
| 0.40412 | 72.59 | Buchner[23] |
| 0.40412 | 73.22 | Buchner[23] |
| 0.5974 | 70.29 | Buchner[23] |
| 0.5947 | 70.8 | Buchner[23] |
| 0.79496 | 68.22 | Buchner[23] |
| 0.79496 | 68.75 | Buchner[23] |
| 0.97854 | 66.46 | Buchner[23] |
| 0.97854 | 66.82 | Buchner[23] |
| 1.4581 | 62.18 | Buchner[23] |
| 1.4581 | 62.5 | Buchner[23] |
| 1.9381 | 58.21 | Buchner[23] |
| 1.9381 | 58.39 | Buchner[23] |
| 2.3937 | 55.24 | Buchner[23] |
| 2.3937 | 55.08 | Buchner[23] |
| 2.8316 | 52.43 | Buchner[23] |
| 2.8316 | 52.75 | Buchner[23] |
| 3.7118 | 47.37 | Buchner[23] |
| 3.7118 | 47.99 | Buchner[23] |
| 4.5212 | 43.48 | Buchner[23] |
| 4.5212 | 44.63 | Buchner[23] |
| 2 | 59.5 | Harris[24] |
| 4 | 46 | Harris[24] |
| 5 | 42 | Harris[24] |
| 0.33 | 71.8 | Haggis[25] |
| 0.66 | 67.2 | Haggis[25] |
| 1 | 63 | Haggis[25] |

The above data was fitted using the Levenberg-Marquardt algorithm implemented in the lmfit package.[26] The data was fitted to both an exponential function and a function described by Gavish and Promislow.[27] The data and fits are shown in Figure S5, with the functional fit of the exponential given by:

$$\varepsilon_r = Ae^{-kc} \tag{1}$$

And the Gavish-Promislow function:

$$\varepsilon_r = \varepsilon_w - \beta\mathcal{L}\left(\frac{3\alpha c}{\beta}\right) \tag{2}$$

Where $\mathcal{L}(v) = \coth(v) + 1/v$ is the Langevin function. The fitted parameters are:

**Table S4:** Parameters for above models, fitted using the Levenberg-Marquardt algorithm

| Parameter | Value |
|---|---|
| $\boldsymbol{A}$ | 76.5070678 ± 0.65792307 |
| $\boldsymbol{k}$ | 0.14224695 ± 0.00464290 |
| $\boldsymbol{\varepsilon_w}$ | 76.6175509 ± 0.82668694 |
| $\boldsymbol{\beta}$ | 61.8706296 ± 5.79490317 |
| $\boldsymbol{\alpha}$ | 10.4036673 ± 0.81235523 |

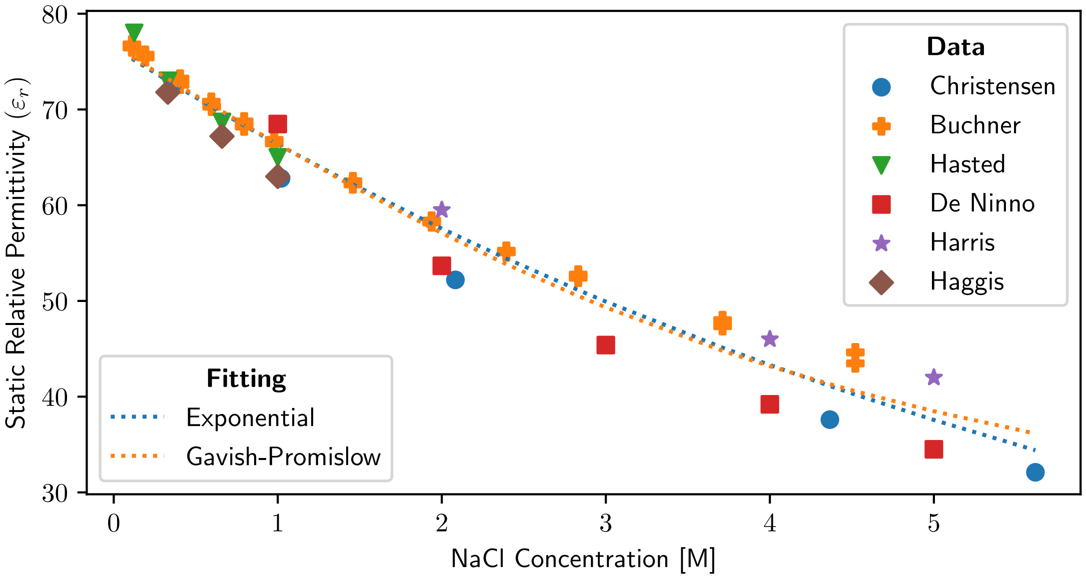

**Figure S5:** Fitting of experimental data for the static relative permittivity (static dielectric constant) for aqueous solutions of NaCl.

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