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Hofmeister effects at low salt concentration due to surface charge transfer

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Abstract

We present a theoretical comparison of the surface forces between two graphite-like surfaces at salt concentrations below 10 mM with surfaces charged by various mechanisms. Surface forces include a surface charging or chemisorption contribution to the total free energy. Surfaces are charged by charge regulation (H\textsuperscript{+} binding), site competition (H\textsuperscript{+} and cation binding) and redox charging with electrodes coupled to a countercell. Constant surface charge is also considered. Surface parameters are calibrated to give the same potential when isolated. Nonelectrostatic physisorption energies of the potential determining ions provide a specific and significant contribution to the charging energy. Consequently ion specificity is found in the surface forces at concentrations of 1-10 mM, which is not observed under constant charge conditions. The force between redox electrodes continues to show Hofmeister effects at 0.01 mM. We refer to this low concentration Hofmeister effect as “Hofmeister charging”, and suggest that the more common high concentration ion specific effects may be known as “Hofmeister screening”. Hofmeister series are considered over LiCl, NaCl, KCl and NaNO\textsubscript{3}, NaClO\textsubscript{4}, NaSCN with the cations (or H\textsuperscript{+}) being the potential determining ions. A K\textsuperscript{+} anomaly is attributed to the small size of the weakly hydrated chaotropic K\textsuperscript{+} ion, with Li\textsuperscript{+} and Na\textsuperscript{+} explicitly modelled as strongly hydrated cosmotropes.

Keywords: surface forces, redox electrode, specific ion effects, nonelectrostatic ion interaction, Hofmeister effects

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1. Introduction

Specific ion (Hofmeister) effects are those variations in properties which are not anticipated from classical electrostatic theory of salt solutions. Li⁺, Na⁺, K⁺ all have the same single positive charge, but cause different degrees of protein aggregation [1]. Likewise Cl⁻, NO₃⁻, ClO₄⁻, SCN⁻ have identical negative charges, but give a broad variation in zeta potentials [2, 3].

Hofmeister effects are typically reported at “physiological” salt concentrations around 100 mM or greater [4]. The general reason for a critical Hofmeister concentration of 100 mM can be understood in terms of the interaction potential (chemical potential) of an ion near a charged surface [5, 6]. The total interaction potential is a sum of both the electrostatic and the nonelectrostatic energy of the ion. Typical ionic nonelectrostatic adsorption energies (ionic dispersion energies at the surface) are around $-2kT$ to $-4kT$ per ion [7, 8] but diminish rapidly with the cube of the distance of the ion from the surface to around $-0.2kT$ when 0.3 nm from the surface. A typical surface potential is of the order of 100 mV (around $4kT$ per monovalent ion) and screened weakly at low salt concentrations. But at 100 mM concentrations with a Debye length of 1 nm the typical surface potential may be reduced by charge screening to 5–10 mV (0.2–0.4$kT$). Hence above 100 mM salt concentration the electrostatic energy within the diffuse layer of physisorbed ions is screened to a level comparable to the nonelectrostatic energy, enabling specific ion effects to become observable. We might refer to this high concentration mechanism of ion specificity as “Hofmeister screening” since the specific value of the screened potential (zeta potential) will exhibit a Hofmeister effect depending on the identity of the background salt.

Nevertheless, low concentration Hofmeister effects have been reported. Pashley and coworkers reported cation-specific forces between mica surfaces at salt concentrations below 10 mM [9–11] and anion-specific effects between quaternary ammonium bilayers [12]. Mahiuddin et al. observed specific ion effects in the adsorption of dihydroxybenzoic acid to alumina surfaces below 5 mM salt concentrations [13, 14], attributed to finite ion size effects affecting the distance of closest approach of ions to the surface. Liu et al. found cation exchange selectivity on montmorillonite below 5 mM [15], for which a satisfactory mechanism has not been determined. Salis et al. reported buffer-specific effects in pH measurements [16] and enzyme activities [17] with buffer concentrations below 10 mM. Hofmeister series in lysozyme electrophoretic mobilities can be measured in 10 mM buffer solutions [3].

The Hofmeister relationship between surface charge and surface potential is not always simple. Intuition about concentration effects by electrostatic screening can be developed naturally for surfaces with constant charge. But
many, perhaps most, real surfaces do not have a constant charge. Metal oxides and silica commonly have pH-sensitive zeta potentials and surface charges [18], as do proteins [19–21]. The chief mechanism for pH dependence can be understood as chemisorption of the H\textsuperscript{+} ion to oxide or carboxylate sites, known as charge regulation [22–24] and is affected by Hofmeister screening due to the “inert” background salt. Hofmeister series in the charge/potential relationship have been predicted [25, 26] and measured [27, 28] for electrode capacitances, where the electrode charge depends on the applied potential.

Chemisorption, or “specific adsorption”, may occur for ions other than H\textsuperscript{+}. Pashley et al. invoked site binding of Br\textsuperscript{–} to quaternary ammonium surfactant headgroups to interpret bilayer force measurements [12]. Pashley used competitive site binding to interpret cation effects on mica surface forces [9–11], with metal cations competing with H\textsuperscript{+} to bind to surface sites. Charge regulation models were extended by Miklavic and Ninham [29] to include competitive ion binding with finite ion size effects. Parsons and Salis developed a competitive ion binding model that includes nonelectrostatic physisorption of the ions [30].

A different surface charge mechanism is found at redox electrodes, where the electrode charge develops due to transfer of electrons between the electrode and ions in solution [8]. Electrochemical Hofmeister effects have been measured in the streaming current of membrane electrodes [2, 31], activity of redox proteins [32] and glucose electrodes [33].

In each of these cases the result is ion specificity in the surface charge, arising from charge transfer between surface and solution. Consider that the classic pH-dependent zeta potential is sensitive to trace levels of H\textsuperscript{+} typically less than 1 mM (pH > 3). So too, we suggest, low concentration Hofmeister effects can arise from chemisorption of Hofmeister ions. We refer to this mechanism as “Hofmeister charging”.

In summary, we identify different classes of Hofmeister effects. The classic effect is Hofmeister screening, arising from ion-specific physisorption of all ions in solution and observable at high concentrations above 100 mM. The second effect is Hofmeister charging, involving chemisorption or charge transfer between the surface and ions in solution, which may be observable at 1 mM concentrations. A third regime of “Hofmeister correlations” may also be identified at very high salt concentrations [34] above 1M due to ion-ion correlations [35].

In this paper we present an estimate of the impact that Hofmeister charging may have on surface forces. We compare forces calculated for four different charging mechanisms: constant charge, classic charge regulation (H\textsuperscript{+} binding only), competitive site binding (metal ion competing with H\textsuperscript{+}) and
redox (metal reduction). To facilitate direct comparison of the different mechanisms, we use the same graphene (graphene oxide) surface in all cases, calibrating the various mechanisms against experimental zeta potentials [36].

2. Charging graphite-like surfaces

We model the Hofmeister effect of various low-concentration cations and anions on the forces between spherical particles of a graphite (or graphene) like material, under different charging mechanisms. Graphite is chosen since it enables a potentially more realistic comparison between the different mechanisms. Site binding (charge regulation) corresponds to cation binding at oxide sites (i.e. modelling graphene oxide). Redox electrode charging corresponds to transfer of electrons to a conductive graphite (or graphene) electrode. Constant surface charge is less realistic for a graphite surface but might correspond to defects or immobile intercalation of ions analogous to the relatively pH-insensitive charge of mica.

To facilitate a direct comparison between the four charging mechanisms, we adopt an identical surface potential for each case at each salt concentration. We match our parameters against an experimental zeta potential measured for reduced graphene oxide by Konkena and Vasudevan [36] (we assume the zeta potential was measured under 10 mM NaCl). Calculations are made at pH 7, for which the measured zeta potential is $-27.2$ mV. The fitted parameter for each charging mechanism, adjusted to generate the same surface potential is

1. $H^+$ charge regulation: oxide site density
2. site competition: $Na^+$ binding constant
3. constant charge: surface charge density
4. redox: concentration of countercell

2.1. $H^+$ Charge Regulation

The experimental zeta potential involves $H^+$ binding (more precisely, $H^+$ dissociation),

$$\text{GOH} \leftrightarrow \text{GO}^- + H^+ \ (pK_{H}) \quad (1)$$

GO$^-$ refers to an oxide site on the graphite surface. We adopt Konkena’s $H^+$ dissociation constant $pK_{H}$, but specify that their value of 7.9 corresponds to equilibrium with $H^+$ in bulk solution. Our model instead uses the intrinsic dissociation constant for $H^+$ physisorbed at the graphite surface. The difference between the two pKs arises from the physisorption energy $\mu_{ps}^{H^+}$ of $H^+$, with $pK_{H} = pK_{H}^{bulk} + \mu_{ps}^{H^+}/(kT \ln 10)$. We calibrate the oxide site density for $H^+$ charge regulation at high pH where the zeta potential reaches a
plateau. So the electrostatic part of the physisorption energy is taken from the zeta potential $-43.36$ mV at pH 11. The nonelectrostatic component is estimated from the ion dispersion energy [37] at contact with the surface as $-14.58kT$. Hence we use $pK_H = 0.8346$. If the bulk $pK_{H}^{bulk} = 7.9$ is used instead, then $H^+$ binding is too strong (or the site density deviates strongly from estimates by pH titration) and the experimental zeta potential is not reproduced. When nonelectrostatic physisorption (ion dispersion interactions) of all ions is included, the fitted oxide site density is $-0.01181 \text{ Cm}^{-2}$.

2.2. H-cation Site Competition

For the site competition model we add site binding of cation $M^+$, competing with $H^+$ binding (Eq. 1),

$$GOM \rightleftharpoons GO^- + M^+ \ (pK_M) \ (2)$$

In this case we fit $pK_{Na}$ to reproduce the zeta potential, maintaining the same H dissociation constant $pK_H = 0.8346$. In order to simplify analysis by employing only a single fitted parameter, we adopt Konkena’s site density of $-0.0179 \text{ Cm}^{-2}$ obtained by Gouy-Chapman analysis of pH titration data, which is reasonably close to our site density fitted above for $H^+$ charge regulation. The equilibrium constant is taken with the cation physisorbed (with both electrostatic and nonelectrostatic interactions) at the surface. Best fitted value is then $pK_{Na} = 0.6992$.

Experimental data for binding of $Li^+$ or $K^+$ to graphene oxide sites is not available. Instead we present an indicative evaluation of low concentration Hofmeister charging by assuming $Li$ binding lies between $H$ and $Na$, taking $pK_{Li} = 0.7669$. We then assume the relative difference between $Na$ and $K$ is the same as between $Na$ and $Li$, with $K^+$ binding more weakly, $pK_K = 0.6316$. Naturally a larger difference in these site dissociation constants will generate a larger Hofmeister charging effect.

2.3. Constant Charge

The surface charge density used in constant charge calculations is that which reproduces the surface potential calculated for the H-Na site competition model for each Na salt concentration at pH 7.

2.4. Redox electrode charging

Redox electrode charging requires a more complex model. We follow the approach of a split concentration cell described recently [8], which considers the force between two electrodes in the active cell coupled to a single electrode in a countercell. A schematic diagram of the redox system is given in
Figure 1: Schematic diagram of two interacting graphite cathodes in an Na$^{+}$ → Na concentration cell, coupled to a graphite anode in an MgSO$_4$ (Mg → Mg$^{2+}$) countercell.

Fig. 1. In order to facilitate a direct comparison between charging mechanisms, the active cell must contain the same low-concentration salt solution at pH 7 used in the other cases. Since the real zeta potential is negative (relative to bulk solution), the redox reaction (in equilibrium with an open circuit) must be reduction of metal atoms which are assumed to be bound to the electrode (cathode) surface but scarce enough so as not to affect the material properties (dielectric function) of the graphite surface. We find that MgSO$_4$ provides an appropriate countercell (via oxidation of Mg atoms in the graphite counterelectrode to Mg$^{2+}$) which at reasonable concentrations allows us to obtain an anode potential (relative to bulk solution) which matches the same surface potential used in the other cases.

The concentration of metal cations [M$^{+}$] in the active cell and Mg$^{2+}$ in the countercell determines the potential difference $\Delta \psi$ between cathodes and anode via the Nernst equation (neglecting ion-ion interactions, i.e. activity coefficients), $\Delta \psi = \Delta \psi^0 - (kT/e) \ln[Mg^{2+}]^{1/2}/[M^{+}]$. Standard reduction potentials are −3.0401 V (Li), −2.71 V (Na) or −2.931 V (K), and −2.70 V for Mg. Any given potential difference $\Delta \psi$ is partitioned into cathode and anode potentials so as to maintain charge balance between electrodes [8, 26], $2\sigma_{\text{cat}} + \sigma_{\text{an}} = 0$. The concentration of MgSO$_4$ (and therefore the potential difference $\Delta \psi$) is fitted to reproduce the desired surface potential at the isolated cathodes (with the two cathodes separated from each other) while maintaining electrode charge balance. Only homeopathic concentrations of MgSO$_4$ are required to maintain the cathode potential in the Li cell. The required MgSO$_4$ concentrations in the countercell are 2.88 × 10$^{-6}$ mM and 9.16 mM for 10 mM salt concentrations in the main cell of LiCl and NaCl respectively (10 mM KCl calculations did not converge numerically). The required MgSO$_4$ countercell concentrations are 3.71 × 10$^{-8}$ mM, 0.0731 mM and 2.7201 × 10$^{-4}$ mM for 0.1 mM main cell concentrations of LiCl, NaCl,
KCl respectively.

The case of redox charging is conceptually related to the classic “constant potential” case. The key difference is that in a redox cell the potential difference between cathodes and anodes is constant, determined by Nernstian equilibrium from bulk electrolyte concentrations. As two cathodes move towards each other, the potential difference between cathodes and anode remains constant at all separations. Consequently the individual electrode potentials (and electrode charges) vary with cathode separation.

By contrast in the classic constant potential case, the cathode potential would remain constant at all cathode separations. This condition can only be met if the potential is actively maintained at a constant level using an external energy source. For this reason we consider the classic “constant potential” case to be somewhat artificial and do not address it further.

3. Theory of Surface Forces

The force $f(L)$ between a sphere of radius $R$ and a flat surface (geometry of atomic force microscopy, AFM) or between two crossed cylindrical surfaces with radius $R$ (geometry of a surface forces apparatus, SFA) can be estimated by applying the proximity force approximation (Derjaguin approximation), $f(L) = 2\pi RG(L)$. $L$ is the separation between the two surfaces, and $G(L)$ is the interaction free energy between two flat surfaces of the same material. When considering the role of nonelectrostatic ion interactions and surface charging, it is convenient to split the total free energy into three components:

$$G = G_{DLVO} + G_{NES} + G_{charge}$$

$G_{DLVO}$ is the classic interaction free energy described by the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory of surface forces. For brevity we omit details, but note that it is composed of a Casimir-Lifshitz (Hamaker or van der Waals) energy (typically attractive) [38], an entropic component due to deviation of ion concentrations away from bulk levels [39] (typically repulsive) [40] and an electrostatic component due to surface and ionic charges (typically attractive) [40].

$G_{NES}$ describes the contribution to the total free energy arising from nonelectrostatic ion interactions $U_{i}^{NES}(z)$ at a distance $z$ from the surface (nonelectrostatic physisorption),

$$G_{NES}(L) = \sum_{i} \int_{0}^{L} dz c_{i}(z) U_{i}^{NES}(z)$$

This term relates directly to “Hofmeister screening” (high-concentration ion specificity), although there is also an indirect specific ion effect on $G_{DLVO}$ as
$U_i^{\text{NES}}(z)$ modulates ion concentration profiles $c_i(z)$. Note that $G_{\text{NES}}$ can be expected to become larger if $c_i(z)$ becomes larger, that is at higher concentrations. Conversely we expect $G_{\text{NES}}$ to become negligible at low concentrations where $c_i(z)$ is small.

$G_{\text{charge}}(L)$ describes the free energy required to bring the surface from an uncharged reference state to its final charged state [8, 30]. Since it often involves a chemical reaction between the surface and ions in solution, it is sometimes referred to as the chemical [39, 41] or chemisorption term [24]. The detail of $G_{\text{charge}}$ depends on the specific surface charging mechanism and drives the “Hofmeister charging effect”, the main focus of this paper.

In each case (apart from constant charge), $G_{\text{charge}}$ contains a surface electrostatic term $-\sigma \psi$ (where $\sigma$ and $\psi$ are the surface charge and surface potential, respectively) that partially cancels [24, 40] against the electrostatic energy in $G_{\text{DLVO}}$. The remainder of $G_{\text{charge}}$ involves the nonelectrostatic physisorption energy of the potential determining ions, multiplied by the surface charge.

A third class of Hofmeister effect could also be considered. Salt has an effect on protein stability at high concentrations above 500 mM distinct from that observed at physiological concentrations of 100–300 mM [34]. Ion-ion correlations become significant at very high salt concentrations, exceeding 1M, and introduce an additional contribution to the total free energy which may, for instance, induce charge inversion [35]. We might refer to these effects as “Hofmeister correlations”.

### 3.1. $H^+$ Charge Regulation

In the charge regulation mechanism the potential determining ion is $H^+$ with dissociation constant $pK_H$, and the charging free energy is [24]

$$G_{\text{charge}} = -\sigma \psi - \frac{\sigma}{e} \mu_{\text{H}}^{\text{NES}} + kTN_s \ln \left( \frac{c_H/K_H}{1 + c_H/K_H} \right)$$

(5)

$e$ is the charge of a proton. $\mu_{\text{H}}^{\text{NES}}$ is the nonelectrostatic physisorption energy of the hydrogen ion in solution but at the surface (i.e. the value of the nonelectrostatic interaction $U_{\text{H}}^{\text{NES}}(z)$ at $z = 0$). The third term describes the entropy of unbound oxide sites. $N_s$ is the surface site density.

### 3.2. Site Competition

When a cation $M^+$ competes with $H^+$ to bind to an oxide site, the charging energy is similar to Eq. 5 but controlled by both $pK_H$ and $pK_M$. The term
is [30]

\[ G_{\text{charge}} = -\sigma \psi - N_s \mu_H^{\text{NES}} \left( \frac{c_H}{K_H} - 1 \right) - N_s \mu_M^{\text{NES}} \frac{c_M}{K_M} + kTN_s \ln \frac{c_H}{K_H} A \]

A = 1 + c_H/K_H + c_M/K_M is a measure of the total degree of dissociation of the oxide sites. Note the role of the nonelectrostatic physisorption terms \( \mu_H^{\text{NES}} \) and \( \mu_M^{\text{NES}} \). Site competition may be invoked in a pure DLVO model neglecting nonelectrostatic physisorption [9–11], in which case \( G_{\text{charge}} = -\sigma \psi \). By including nonelectrostatic physisorption (here and also in the cases of simple charge regulation and redox charging), a more complete and more nuanced description of Hofmeister effects is enabled.

3.3. Constant Charge

This is the trivial case where the surface charge remains fixed at all surface separations, such that \( G_{\text{charge}} = 0 \).

3.4. Redox electrode charging

At a redox electrode no specific surface sites are involved, so the site entropy term involving \( kTN_s \) does not appear. The redox charging free energy is then [8]

\[ G_{\text{charge}} = -\sigma \psi - \frac{\sigma}{e} \Delta \mu_M^{\text{NES}} \]

This expression must be evaluated at each electrode (two cathodes and one anode). \( \Delta \mu_M^{\text{NES}} \) refers to the difference in the nonelectrostatic physisorption of the ions involved in each half reaction. At the cathodes, reducing \( M^+ \), this is the nonelectrostatic physisorption energy of the monovalent cation, so \( \Delta \mu_M^{\text{NES}} = \mu_M^{\text{NES}} \). At the anode in the countercell where Mg is oxidised, \( \Delta \mu_{Mg}^{\text{NES}} = \mu_{Mg}^{\text{NES}} / 2 \) with the factor \( 1/2 \) appearing due to the stoichiometry of the half-reaction for the divalent \( M^{2+} \) ion. \( \mu_{Mg}^{\text{NES}} \) is the nonelectrostatic physisorption energy of the \( M^{2+} \) ion at the anode.

3.5. Computational Details

Ion concentration profiles and electrostatic potentials are calculated using a modified Poisson-Boltzmann model, with Boltzmann concentration profiles including nonelectrostatic ion interactions \( U_i^{\text{NES}}(z) \) alongside the electrostatic \( \psi(z) \),

\[ c_i(z) = c_{i0} \exp \left[ -q_i \psi(z) + U_i^{\text{NES}}(z) / kT \right] \]

The nonlinear Poisson-Boltzmann equation is solved with a finite element approach using Dolfin/FEniCS [42].
The nonelectrostatic ion interactions are represented by the Mahanty-Ninham ionic dispersion potential \[43, 44\], modelling ions as a polarisable Gaussian sphere with Gaussian radius \(a_i\) embedded in the solvent (i.e. including the finite size of the ion but neglecting effects due to the ionic cavity \[45–47\]). The dispersion interaction with one surface is given by

\[
\mu_i^{\text{disp}}(z) = \frac{B_i}{z^3} g(z) \tag{9}
\]

where \(g(z) = 1 + \left(\frac{2z}{\sqrt{\pi}a_i}\right) \left(\frac{2z^2}{a_i^2} - 1\right) \exp\left[-\frac{z^2}{a_i^2}\right] - \left(1 + 4\frac{z^4}{a_i^4}\right) \text{erfc}\left[\frac{z}{a_i}\right].\)

\(U_i^{\text{NES}}(z)\) is the sum of two of these interactions, one for each surface. In the redox \(\text{MgSO}_4\) countercell (with a single electrode), only a single \(\mu_i^{\text{disp}}\) is deployed in \(U_i^{\text{NES}}.\) \(B_i\) is a dispersion parameter determined by the dynamic polarisability at optical/UV frequencies, modulated by the dielectric spectrum of the solvent and the surface \[37\]. The ionic dispersion interaction at a solid interface is typically attractive \((B_i < 0)\) but may in some systems be repulsive, e.g. cations at a hydrophobic surface \[40\]. Dielectric functions derived from experimental data for water \[48\] and graphite \[49\] are deployed. Polarisabilities and ion radii for \(\text{Li}^+\) and \(\text{Na}^+\) explicitly include the inner hydration shell (five and three water molecules respectively \[50\]), representing their cosmotropic nature. \(\text{K}^+\) is taken as unhydrated (chaotropic), which leads to consequences for the calculated Hofmeister series discussed below. \(\text{Mg}^{2+}\) is treated as an implicitly hydrated cosmotropic ion, that is the polarisability of the water molecules (18, including the second hydration layer) in its hydration shell are added to that of the bare \(\text{Mg}^{2+}\) ion and the thickness of the hydration shell (1.5 water radii) is added to that of the bare ion \[7, 8, 51\]. The Gaussian radii, \(B_i\) dispersion coefficients and nonelectrostatic physisorption energies \((\mu_i^{\text{disp}}(z)\) at \(z = 0\)) are listed in Table 1.

A steric energy \[8\] is also included in \(U_i^{\text{NES}},\) which caps ion concentrations at a maximum concentration estimated as “close packing” with \(c_i^{\text{max}} = 1/V_i\), using the ion volume \(V_i = \pi \sqrt{\pi}a_i^3.\) The excess chemical potential corresponding to this concentration cap is \(\mu_i^{\text{cap}} = -kT \ln\left(c_i^{\text{cap}}/c_i^{0}\right),\) where \(c_i\) is the bulk concentration. The steric energy, then, is \(\mu_i^{\text{steric}} = \max\{0, \mu_i^{\text{cap}} - \mu_i'\},\) where \(\mu_i'\) is the excess chemical potential of the ion \((q_i\psi(z) + U_i^{\text{NES}}(z))\) that would be computed in the absence of steric hindrance. In practice since concentrations are small, this serves only to cap the \(\text{SO}_4^{2–}\) concentration in the redox countercell at 24.68 M and \(\text{Mg}^{2+}\) concentration at 17.40 M when coupled against \(\text{Na}^+\) or \(\text{K}^+\) solutions. By included an explicit steric energy term, the proper energy contribution of capped concentrations can be accounted for in the total free energy, rather than artificially imposing a concentration cap \[14\].
Ion | $a_i$ (Å) | $B_i$ ($10^{-50} \text{Jm}^3$) | $\mu_{\text{disp}}(0)$ ($kT$)
--- | --- | --- | ---
Li$^+$.5H$_2$O | 2.56 | -2.789 | -1.21
Na$^+$.3H$_2$O | 2.25 | -0.800 | -0.513
K$^+$ | 0.96 | -1.656 | -13.68
Cl$^-$ | 1.86 | -3.780 | -4.290
nitrate | 2.01 | -4.736 | -4.25
 perchlorate | 2.17 | -6.024 | -4.29
thiocyanate | 2.18 | -7.211 | -5.10
H$_3$O$^+$ | 0.97 | -1.843 | -14.58
OH$^-$ | 2.39 | -5.233 | -2.79
Mg$^{2+}$+18H$_2$O | 2.58 | -43.184 | -18.42
SO$_4^{2-}$ | 2.29 | -7.819 | -4.73

Table 1: Gaussian radii $a_i$ of ions, static polarisability $\alpha_0$ (in vacuum), dispersion coefficients $B_i$ and nonelectrostatic physisorption energy (ion dispersion energy at contact) for ions in water interacting with a graphite-like electrode.

4. Results

4.1. Constant Charge

The constant charge case provides a baseline since the charge is insensitive to salt concentrations. The force (normalised against radius of the surface) for various salts at 10 mM concentration is shown in Fig. 2. Apart from a K$^+$ anomaly (discussed below), the Hofmeister effect on surface forces is mild. The force in NaSCN can be seen to be marginally less attractive than other salts. Only a small Hofmeister effect is expected here since $G_{\text{NES}}$ is small at low concentrations, and $G_{\text{charge}} = 0$ for the case of constant surface charge.

4.2. H$^+$ Charge Regulation

With the surface charge determined by H$^+$ binding, a clear Hofmeister effect is found in both cations and anions at 10 mM salt concentrations, see Fig. 3a. The repulsive peak is 520 mN/m higher in NaCl than in LiCl, i.e. repulsion becomes 25% stronger. Repulsion due to SCN$^-$ (NaSCN) is 130 mN/m (5%) weaker than other anions.

At 1 mM salt concentrations, shown in Fig. 3b, the gap in the repulsive peak between NaCl and LiCl diminishes down to 230 mN/m (5% difference), and a strong K$^+$ discrepancy is found. Below 1 mM a Hofmeister charging effect is no longer observed (apart from the K$^+$ effect, discussed below).

4.3. Site Competition

Unsurprisingly, the cationic Hofmeister charging effect is even stronger than the charge regulation case when the surface charge is established by
Figure 2: Force (normalised by radius) between two graphite-like surfaces with constant surface charge $-0.004021 \text{C m}^{-2}$ in 10 mM salt solution at pH 7 (generating a surface potential for isolated surfaces of $-21 \text{mV}$).

Figure 3: Force (normalised by radius) between two graphite-like surfaces with surface charge regulation (H$^+$ binding) in 10 mM salt solution at pH 7. (a) 10 mM salt solution (generating a surface potential for isolated surfaces of $-17 \text{mV}$). (b) 1 mM salt solution (isolated surface potential $-27 \text{mV}$).
site competition between H\(^+\) and metal cations. The forces in 10 mM salt are shown in Fig. 4. The difference between repulsive peaks of LiCl and NaCl is 700 mN/m (NaCl is 50% stronger). The anion effect is similar to the charge regulation case, with NaSCN repulsion being 150 mN/m or 8% weaker than other Na salts.

At still lower concentrations, a reduction in the Hofmeister charging effect is found, following the same pattern seen for the H\(^+\) charge regulation case (cf. Fig. 3b). At 1 mM ion-specific differences are still clear, with the repulsive LiCl peak being 5% lower than NaCl. Below 1 mM concentration the Hofmeister differences (apart from the K\(^+\) anomaly) are negligible.

4.4. Redox electrode charging

Fig. 5a shows the force between two cathodes reducing the cation in 10 mM salt solution, coupled to a MgSO\(_4\) countercell. The force in NaCl is found to be more attractive than in LiCl, although the difference is not as large, around 0.3 mM/m (18% stronger) at 2 Debye lengths (6 nm), as that found for 10 mM concentration in the cases of charge regulation or site competition. A negligible anion effect is found. A solution to the Poisson-Boltzmann equation for KCl did not converge numerically, hence KCl is not shown here.
At 0.1 mM salt concentrations, a numerical solution for KCl becomes accessible. 0.1 mM forces are shown in Fig. 5b. LiCl and NaCl forces are again attractive. The difference between LiCl and NaCl has become relatively larger with a difference of 0.2 mN/m at separation of 2 Debye lengths (60 nm) meaning the attractive force in NaCl is twice as strong as that of LiCl. The cathode forces for KCl have a repulsive peak, unlike the attractive forces for LiCl and NaCl. At still lower concentrations (0.01 mM) the differences in forces between these salts becomes smaller but is still significant (with differences of 0.2 mN/m at a separation of one Debye length).

4.5. Comparison of Surface Charging Mechanisms

The forces between graphite-like surfaces in 10 mM NaCl for the four charging mechanisms considered here are collected in Fig. 6. A contrast with classic DLVO theory can be drawn here. When analysing experimental force curves from a surface forces apparatus (SFA) or atomic force microscope (AFM), it is common practice to compare the experimental data with theoretical DLVO curves neglecting nonelectrostatic ion interactions. Typically both the classic constant charge and constant potential cases are compared [52, 53], with the potential at large separation fitted so that the theoretical curves match the experimental data a large separation.

The match between theory and experimental is typically poor at small separations (partly due to neglect of surface roughness [54]). A rule of thumb is that the constant charge curve is more repulsive and lies above the experimental data. The constant potential curve is less repulsive and lies below the experimental data. Charge regulation with an appropriately selected site density and $pK_H$ is usually found to match experimental data more reliably, lying between the two extremes of constant charge and constant potential.
Figure 6: Force (normalised by radius) between two graphite-like cathodes in 10 mM NaCl salt solution at pH 7 for various charging mechanisms. The surface potential for isolated (separated) surfaces is $-20.6$ mV in each case except H charge regulation, for which the isolated surface potential is $-17.4$ mV.

That is the typical case when nonelectrostatic ion physisorption is unaccounted for.

The force curves in Fig. 6 have not been calibrated against experimental force curves. Rather, they are calibrated to give equivalent surface potentials on separated surfaces. Nevertheless it is interesting to note that the force for both site binding models (charge regulation and site competition) lie above the constant charge curve rather than below, in fact showing a repulsive peak where the constant charge curve is attractive at all separations. This can be attributed to the appearance of the nonelectrostatic physisorption energies $\mu_{\text{H}}^{\text{NES}}$ and $\mu_{\text{M}}^{\text{NES}}$ in the charging free energies $G_{\text{charge}}$ in Eq. 5 and Eq. 6. If system parameters are recalibrated to give equal long range forces then the typical relationship (charge regulated force less repulsive than constant charge) may be recovered, but at the same time generating different surface potentials for each charging mechanism [24]. However, deviation from the normal understanding of the relationship between constant potential and charge regulated force curves has been anticipated in theory by Borkovec and Behrens [56], with the charge regulated curve in their study becoming more attractive than the classic constant potential case.
4.6. The $K^+$ Anomaly

In many of the force curves calculated here, $K^+$ often exhibited a behaviour discrepant to that of $Li^+$ or $Na^+$. Under constant charge conditions in 10 mM salt (Fig. 2) and also in redox conditions at 0.1 mM salt (Fig. 5b), KCl gave a repulsive force curve while LiCl and NaCl generated attractive curves. Under $H^+$ charge regulated conditions in 1 mM salt, Fig. 3b (and also for site competition at 1 mM) the repulsive peak for KCl was significantly weaker than for LiCl or NaCl.

The computational origin of the $K^+$ anomaly is the hydration model used to represent $Li^+$ and $Na^+$ as strongly hydrated cosmotropes. Radii for $Li^+$ and $Na^+$ included hydration waters (see Table 1) and consequently are larger than the bare ion radius used for $K^+$. The $K^+$ anomaly arises largely due to this size difference. The dispersion $B_i$ coefficient for $K^+$ is actually larger than that of $Na^+$, even though the value for $Na^+$ includes the polarisability of 3 hydration waters. But $B_i$ for $Li^+$ is larger than $K^+$. But because the ion size of $K^+$ is much smaller, its nonelectrostatic physisorption energy is 10 times larger than that of $Li^+$.

The nonelectrostatic physisorption energy applied here (an ion dispersion energy for a Gaussian-shaped ion embedded in the solvent) is relatively crude. An alternative model has been developed [57] that successfully reproduces experimental solvation energies [46], partial molar volumes and ion entropies [58], surface tensions at the air-water interface [47, 59]. This model did not invoke explicit hydration waters to distinguish cosmotropic from chaotropic ions. Instead the model included the formation energy of the ion cavity and higher order ion polarisabilities [60, 61]. The impact of the cavity energy on ions at the air-water interface was studied [47, 59]. The impact of the cavity energy at the interface with solid surfaces has not yet been fully resolved, and may potentially remove the $K^+$ anomaly. Just as the cavity interaction energy at the air-water interface involves loss of air-water surface tension [47], so too at a solid interface the loss of interaction of the surface with its first hydration layer must be accounted for [62–64].

Nevertheless, the mechanism of ion size dependence is in general real and radical specific ion effects comparable to the $K^+$ anomaly have been observed experimentally. 10 mM citrate buffer inverts the direction of lysozyme electrophoretic mobilities compared to other buffers [21]. Didodecylidimethylammonium (DDA) surfactant forms spherical micelles in OH$^-$ solution, but forms cylindrical micelles, lamellar phases or gels in Br$^-$ solution [65, 66].
5. Conclusion

Hofmeister effects are typically reported at high salt concentrations exceeding 100 mM. These are readily modelled with Boltzmann concentration profiles that include nonelectrostatic ion interactions alongside electrostatic energies. We therefore might think of this Hofmeister effect as “Hofmeister screening” due to the modification that the nonelectrostatic interactions introduce to ion concentration profiles or Debye screening lengths.

But nonelectrostatic physisorption energies also contribute to the charging energy of a surface. This contribution appears when the surface charge is not constant, but is controlled by binding of H\(^+\) ions (charge regulation), competitive binding of other ions, or charging by redox reactions.

By including the surface charging contribution to forces between two graphite-like surfaces and including a representation of nonelectrostatic ion interactions with the surface, we find that a Hofmeister effect emerges at low concentrations down to 1 mM. We call this effect “Hofmeister charging”. In the force between redox electrodes coupled to a counterelectrode, Hofmeister charging is still predicted at concentrations as low as 0.01 mM.

A third regime of “Hofmeister correlation” effects may appear at very high salt concentrations above 1M, acting through ion-ion correlations.

6. Acknowledgements

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[26] D. F. Parsons, Supercapacitors have an asymmetric electrode potential and charge due to nonelectrostatic electrolyte interactions, Colloids Surf., A 460 (0) (2014) 51 – 59.


Graphical Abstract