

## LETTERS

### Hofmeister Effects in pH Measurements: Role of Added Salt and Co-Ions

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Measurements of pH with a glass electrode that reveal a strong dependence on the ion pair of the background electrolyte and on the salt concentration are presented. Although such phenomena are well known, they are inexplicable in the classical theory based on the Nernst equation. It is shown that this (Hofmeister) effect can be understood once neglected ionic dispersion potentials acting between ions and the glass–water interface are taken into account. At high concentrations, those of interest in biology ( $\geq 0.1$  M), co-ions, are shown to play a profound and previously overlooked role in pH changes near glass–water interfaces.

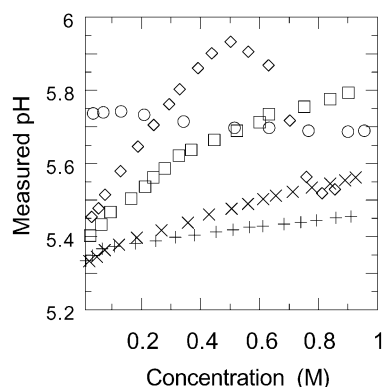
Measurements of pH via the response of oxide glasses is a long-established and commonly used technique.<sup>1,2</sup> Some controversy exists as to the true origin of the pH–glass electrode potential. The phenomena at the interface and within the glass electrode are very complex and are not yet fully understood. However, for a long time, it has been taken as axiomatic that the Nernst equation can be used to interpret the experimental results.<sup>3,4</sup> According to this equation, a potential is set up across a glass electrode that separates a reference electrolyte solution and an unknown electrolyte. This potential difference depends on the concentrations (or, strictly speaking, the activities) of hydronium ions in the different compartments. It can then be used to deduce the pH of the unknown electrolyte solution. The Nernst equation does not predict any dependence on the ion pair of the background salt or on its concentration. Consequently, few experiments have focused on these specific ion effects, which, where they occur, are generally assigned to solid-state glass properties. We report pH measurements that depend strongly on both the choice of salt solution and concentration. We then show that ionic dispersion forces acting between ions

and interfaces can account for the phenomenon. The measured pH will in general also be influenced by structural changes in the glass electrode and ion-specific changes in the bulk hydronium activity coefficient.

Hofmeister effects that are common in biology have presented a mystery to physical chemistry for more than 100 years.<sup>5</sup> A large number of applications in biology and physical chemistry depend strongly on the supposedly irrelevant choice of background salt and especially on the co-ion. Examples include double-layer forces,<sup>6,7</sup> the surface-tension increment with added salt at an air–water interface<sup>8</sup> and at an oil–water interface,<sup>9</sup> bubble–bubble interactions,<sup>10</sup> and pH measurements.<sup>3,11,12</sup> Experiments on colloid interactions have furthermore recently revealed an important and previously ignored role of co-ion specificity<sup>13</sup> and dissolved gas.<sup>14</sup> Since the only ionic property included in theories of double layers was the ionic charge, all monovalent salt solutions are expected to give the same result. However, this is not what is seen experimentally. It is clear that electrostatics is not the full story. It is often the case that dispersion forces acting on ions dominate, particularly at biological salt concentrations. High-frequency correlations that give rise to ion-specific dispersion effects are only weakly screened, and above 0.1 M, salt can dominate electrostatic

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**Figure 1.** Measured pH as a function of electrolyte concentration using a glass electrode. Data are shown for NaBr (○), NaCl (□), NaClO<sub>4</sub> (◇), NaNO<sub>3</sub> (×), and KBr (+).

effects that are strongly screened in electrolyte solutions. The DLVO theory that underpinned colloid science has never accounted for specific counterion effects. Co-ion effects were dismissed as counterintuitive. We earlier proved this to be incorrect in general<sup>15,16</sup> and here present a corrected theory that appears to accommodate the apparent pH dependence on background salt. The dispersion forces are dictated in part by the polarizabilities of the ions, which in turn are very ion-specific. We have recently demonstrated that the ionic dispersion potential is one main reason that the surface tension of salt solutions is ion-specific.<sup>17,18</sup> We have also demonstrated that these ionic dispersion potentials play a similarly important role in the ion-specific double-layer force between charged surfaces<sup>19</sup> and in the ion specificity of micelles and polyelectrolytes.<sup>20</sup>

The outline of this letter is as follows. We first describe the results of experiments that measure pH with a glass electrode. These demonstrate a strong dependence on what ought to be the supposedly irrelevant choice of background salt and on salt concentration. More importantly, they demonstrate that co-ions play a very important role in pH measurements. We then solve the Poisson–Boltzmann equation in the presence of ionic dispersion potentials to obtain the self-consistent electrostatic potential. This potential is used to evaluate the hydronium concentration near the glass–water interface. An explanation of the experimental result is offered in terms of ion-specific changes in the surface hydronium concentration, with an important and previously ignored role for the co-ions.

A standard pH meter (Metrohm 654) with a typical glass electrode (Metrohm 6.0203.100) has been employed to measure the apparent pH of a series of aqueous salt solutions. Distilled water was used. Salts were AR grade and used without further purification. All measurements were made in a constant-temperature room at 20 °C in a closed Pyrex beaker. After the addition of each aliquot of concentrated salt solution, the solution under investigation was stirred for 2 min and allowed to rest for 1 min before the pH value was recorded. pH values measured in this manner were stable, except the values for pure water, where the very low electrolyte levels lead to slow equilibration. The results are presented in Figure 1. Significant changes in measured pH that are consistent with the polarizability of the anions present in solution were observed. The apparent pH decrease with added [NaBr] can be understood to be due to attractive ionic dispersion potentials acting on the co-ions (Br<sup>−</sup>). Our result is consistent with osmotic pressure measurements that could only be understood if the bromide ions were assumed to bind much more strongly to the interface than chloride ions.<sup>7</sup> The observed cation effects are consistent with potassium being a more polarizable ion than sodium. The addition of salt to

aqueous phosphate buffer solutions has revealed similar trends and changes of the same magnitude, indicating that the observed changes cannot be attributed to trace contaminants of acidic or basic materials. The unusual behavior of the chlorate salt was also observed in the buffered system but at a slightly higher concentration. The origin of this behavior is being investigated.

The theoretical model system that we use to explore the ion-specific properties of pH measurements is a planar glass surface with ionizable surface groups, each with a surface area  $S$  (700 Å<sup>2</sup>) that gives a surface potential between 30 and 40 mV. We use an effective dissociation constant  $Z$  (10<sup>−2</sup>). A fraction  $\delta$  of these groups to be determined self-consistently are dissociated:<sup>21</sup>

$$Z = \frac{\delta[\text{H}^+]_s}{(1 - \delta)} \quad (1)$$

The surface concentration of hydronium ions follows a Boltzmann distribution

$$[\text{H}^+]_s = [\text{H}^+]_r e^{-\beta[e\phi(s) + U_H(s)]} \quad (2)$$

where  $[\text{H}^+]_r$  (10<sup>−7</sup> M) is the bulk concentration of hydronium ions,  $e$  is the electric charge,  $\phi$  is the electrostatic potential at the surface,  $\beta = 1/k_B T$ ,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. In general, one must also take into account that the hydronium ions near an interface experience both image and ionic dispersion potentials ( $U_H$ ). However, we can neglect the effect of these potentials here since it is only at much higher hydronium concentrations that this particular potential influences the surface charge. In fact, the surface charge is more or less constant at this low hydronium concentration. (At lower pH values, this and the exact value for the dissociation constant become much more important.) The expression for the surface charge ( $\sigma = -(e\delta)/S$ ) depends on the surface potential and must in general be determined self-consistently with the nonlinear Poisson–Boltzmann equation:

$$\frac{d^2\phi}{dx^2} = -\frac{e(c_+ - c_-)}{\epsilon_w \epsilon_0} \quad (3)$$

$$\frac{d\phi}{dx^s} = -\frac{\sigma}{\epsilon_w \epsilon_0} \quad (4)$$

$$\frac{d\phi}{dx^{x=\infty}} = 0 \quad (5)$$

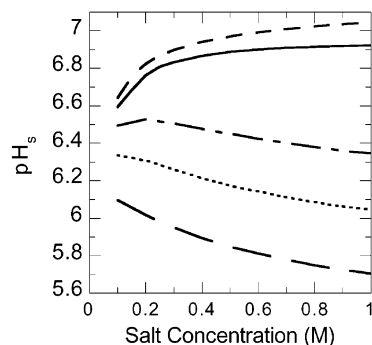
The Poisson–Boltzmann equation is solved numerically using the method of relaxation with the above boundary conditions. The ion concentrations are given by

$$c_{\pm} = c_0 \exp[-\beta(\pm e\phi + U_{\pm})] \quad (6)$$

Here,  $c_0$  is the bulk salt concentration (where  $c_0 \gg [\text{H}^+]$ ), and  $\epsilon_w$  the dielectric constant of water. The interaction potential ( $U_{\pm}$ ) receives important contributions from the ionic dispersion potential between an ion and an interface:

$$U_{\text{dispersion}} \approx \frac{B}{x^3} \quad B \approx \frac{(n_w^2 - n_{\text{glass}}^2)\alpha^*(0)\hbar\omega_i}{8} \quad (7)$$

Here,  $n_w$  ( $n_{\text{glass}}$ ) is the refractive index of water (glass),  $\hbar\omega_i$  is the electron affinity (or ionization potential) for the ion, and  $\alpha^*(0)$  is the static excess polarizability of the ion in water. The static excess polarizability of anions in water is typically around



**Figure 2.** Surface pH at glass-water interface for five different combinations of ionic dispersion constants. We assume in this case no ionic dispersion interaction potential acting on the cations. The dispersion constants acting on the anions are (in units of  $10^{-50}$  J m<sup>3</sup>) 30 (—), 0 (---), -20 (- · - ·), -25 (- - -), and -30 (—).

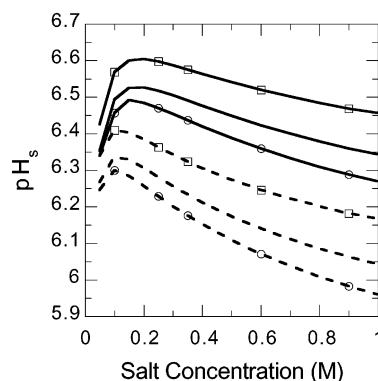
$5 \text{ \AA}^{-3}$ . The electron affinity of the ions in water is not known experimentally with any real certainty, but it should be between an IR and a UV frequency. The ionic dispersion potential depends on the optical properties of the ion, water, and glass. A reasonable estimate for the ionic dispersion constant should be around  $B_+ \approx \pm 5 \times 10^{-50} \text{ J m}^3$  for relevant cations and around  $B_- \approx \pm 30 \times 10^{-50} \text{ J m}^3$  for highly polarizable anions. We recently demonstrated that the surface tension of several chloride salts at an air-water interface can be accommodated if  $B_{\text{Cl}} \approx 30 \times 10^{-50} \text{ J m}^3$ . At a mica-water interface, estimates<sup>20</sup> suggest that the ionic dispersion coefficient should be around  $B_{\text{Cl}} \approx -50 \times 10^{-50} \text{ J m}^3$ . The ionic dispersion constant near the particular glass electrode is unknown, but it should not be larger than that near a mica interface. The point is that the potentials that are chosen are consistent with those that explain ion-specific interfacial tensions at air-water and oil-water interfaces<sup>17</sup> and the specificity of direct-force measurements.<sup>19</sup> The interaction potential also has a contribution from the image potential between each ion and the interface,

$$U_{\text{image}}(x) \approx \frac{e^2 \exp[-2\kappa_D x]}{16\pi\epsilon_w\epsilon_0 x} \quad (8)$$

where  $\Delta = (\epsilon_w - \epsilon_{\text{glass}})/(\epsilon_w + \epsilon_{\text{glass}}) \approx 1$  and  $\epsilon_{\text{glass}}$  is the dielectric constant of glass. The inverse Debye length is  $\kappa_D = \sqrt{(2\beta e^2 c_0)/(\epsilon_w \epsilon_0)}$ . There will in general also be contributions from ionic dispersion potentials acting between the bulk ions that affect bulk activities. We neglect these here.

In this work, we approximate pH by  $-\log_{10}[\text{H}^+]$ . In fact, pH depends on the activity coefficient rather than the molar concentration of hydronium ions. However, the purpose of this approximation is to demonstrate, with the simplest possible extension of existing theories, why the pH near a glass electrode surface will be very ion-specific. In the numerical evaluation of surface pH, we have taken image potentials acting on the hydronium ions into account but not its ionic dispersion potential.

We have calculated surface pH as a function of salt concentration for the model glass electrode described above for different combinations of ionic dispersion potentials acting on the ions of the background salt. It is clear from Figure 2 that there is an important and previously ignored role for the co-ions. When ionic dispersion potentials acting on the anions are neglected, the surface pH increases with added salt concentration. This is easy to understand. The increasing concentration of counterions (cations) near a negatively charged surface competes with and effectively decreases the attraction of



**Figure 3.** Surface pH at the glass-water interface for six different combinations of ionic dispersion constants (in units of  $10^{-50}$  J m<sup>3</sup>). The solid (dashed) line is for an attractive potential of -20 (-25) acting on the anions. Three different examples are shown for the cations: -5 (□), 0 (○), and 5 (△).

hydronium ions toward the surface. The same is true if the co-ions experience a repulsive (or a very small attractive) ionic dispersion potential. However, depending on the optical properties of the glass electrode, highly polarizable ions such as  $\text{Br}^-$  can experience moderately large attractive ionic dispersion potentials. When this happens, the ionic dispersion potentials can overcome the electrostatic repulsion above  $\sim 0.15$  M. The key to understanding the increased hydronium surface concentration (decreased pH) with added salt is to understand that co-ions (anions) due to attractive ionic dispersion potentials can become attracted to a negatively charged surface. It is clear in Figure 3 that there will also be very important counterion effects similar to those seen in the experimental results both described above and in similar work that has explored counterion effects on indicator equilibria.<sup>11,12</sup>

The observed shift downward in the theoretical curves compared with the expected results ( $\text{pH} \approx 7$ ) at low concentrations is most likely due to several other different ignored effects. First, adding an ionic dispersion potential of around  $6 \times 10^{-50} \text{ J m}^3$  acting on the hydronium ions could by itself explain this shift. An attractive ionic dispersion potential acting on hydronium ions near an air-water interface is consistent with the fact that the surface tension decreases with added HCl. In most pH measurements, there will also be buffer present. Buffer effects reflecting competition between the anions of the buffer and co-ion are as ubiquitous as they are ignored.<sup>13</sup> One should also remember that what is actually measured is a potential difference between two sides of a glass electrode (or, more specifically, a current that is related to this potential difference). The measured pH is well known to depend on both the measurement technique and the buffer. Therefore, what is of interest is the general behavior rather than an exact comparison between the experimental pH and the theoretical surface pH.

The main conclusion of this letter is that ionic dispersion potentials acting on ions play a very important role in interpreting measured specific ion pH. In particular, we have demonstrated a previously ignored role for the co-ions for the experimentally measured ion-specific pH. In a purely electrostatic model, the role of co-ions in colloid interactions<sup>13,14</sup> and in pH measurements has been a great mystery. Even if other complications such as bulk activity coefficients, water structure,<sup>22</sup> silicic acid diffuse layers, ion size, counterion and co-ion exclusion,<sup>23</sup> and dielectric constant variation near the interface or other factors play a role, it is clear that ionic dispersion forces consistent with interfacial tensions and force measurements alone can accommodate the pH dependence on

salt type and concentration. Clearly, they cannot be ignored. Attractive ionic dispersion potentials acting on anions can explain the experimentally observed pH decrease with added salt that is directly opposite to what should be expected from purely electrostatic estimates. The results and theory also make sense in terms of the well-known difficulties in making pH measurements on any system containing surfactant. Surfactant adsorption, generally a dynamic fluctuating process, will change the dielectric properties of the substrate to those that are more reminiscent of "oil" and will totally change the specific ion adsorption due to dispersion forces. This letter shows the importance of including ionic dispersion potentials in any realistic modeling of pH measurements. Soon, we intend to use hypernetted chain calculations to take ion size and ionic dispersion potentials into account, acting both between ions and interfaces and between ions, to investigate bulk activity coefficients and pH measurements in more detail.

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