

Effects of Weak Electrolytes on Electric Double Layer Ion Distributions

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Cite This: *J. Phys. Chem. Lett.* 2020, 11, 8302–8306



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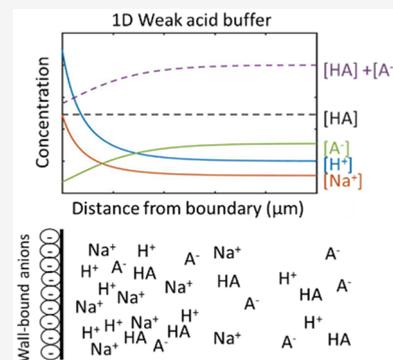


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ABSTRACT: Many common experimental systems have electric double layers containing weak electrolytes, including systems with buffers. The pH at the boundary of the diffuse layer is an important parameter for determining the physicochemical state of the system, including surface charge density. We show that the Boltzmann equilibrium relation can be used as an exact solution for weak electrolyte electric double layers. Using these results, we provide a closed-form relation for the maximum pH change in a buffered electric double layer, in terms of the boundary potential. Importantly, our results suggest that equilibrium electric double layer concepts developed for strong electrolytes can be expanded to include weak electrolytes.



Many physicochemical phenomena are underpinned by an electric double layer (EDL) at the interface between two phases. Classic EDLs are characterized by having two locally parallel layers of charge of opposite sign: one fixed to a solid interface, the other free to diffuse within the liquid. EDLs are pivotal to understanding the stability of particle suspensions, electrophoresis, ion transport, and other systems wherein ion-containing liquids interact with another phase, particularly charged walls.^{1–3} By far, most common EDL models assume strong electrolytes governed by a Boltzmann distribution, which implies an equilibrium balance between electromigration and diffusion. Of interest here is the effect of chemical reactions with weak electrolytes. For example, one intuition for such systems is that a pH buffer would attempt to counteract the extreme pH gradient imposed by high potential and ionic gradients, thereby altering local ion distributions, relative to the strong electrolyte case. The current work suggests this intuition is incorrect. We show that the ion distributions in the diffuse part of an EDL containing a weak electrolyte can be treated in a manner analogous to the strong electrolyte case and leads to a strong, steady-state pH gradient in the EDL.

The EDL for systems of strong electrolytes has been well-studied.^{1–5} Many models also include treatments of one or more adsorbed species (e.g., the Stern layer) and/or treatments of surface-to-solution reaction balances (e.g., the deprotonation of acidic surface groups). The various treatments establish relationships among the potential at the boundary of the diffuse ion region, the surface charge density at this boundary, and the ionic strength far from the interface. Here, we focus on the diffuse charge region of the EDL (see Figure 1).

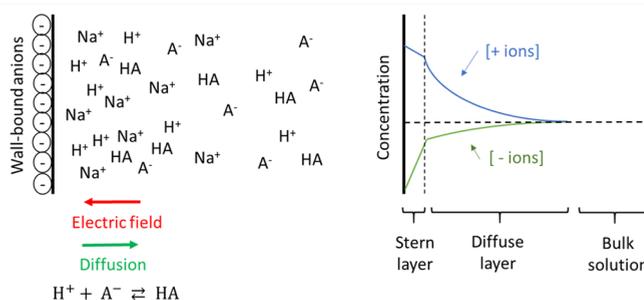


Figure 1. Schematic for electric double layers, resulting from a balance of electromigration, diffusion, and chemical equilibrium. The sign of the ion at the interface boundary can be either positive or negative. Here, we show the negative case. Classic models may or may not include treatments of one or more adsorbed species (e.g., the Stern layer) and/or treatments of surface-to-solution reaction balances (e.g., the deprotonation of acidic surface groups).

Here, we consider the more general case of an electrolyte mixture containing one or more weak electrolytes and the effects therein on the diffuse layer of the EDL. Important theoretical analysis of EDLs and electrokinetic flow of weak electrolytes has been presented by Baygents and Saville.⁶ They considered only reactions consisting of association–dissocia-

Received: July 22, 2020

Accepted: September 11, 2020

Published: September 11, 2020

tion reactions between ions with charge that is opposite in sign and equal in magnitude, which can combine to form neutral species. Their perturbation analysis used an (externally) applied potential normalized by the thermal voltage as a smallness parameter (β) and was applied to electrophoresis of a sphere. Consistent with association–dissociation reaction rates being significantly faster than either diffusion or advection, their first-order solution was reduced to local reactions at equilibrium and with ionic species in Boltzmann equilibria. Their order β solution (significant applied field) showed deviation from Boltzmann equilibria. In this paper, we consider a treatment of the quasi-steady-state EDL case where bulk velocity and bulk advection of species are negligible. Our approach allows for a broader range of chemical equilibria but is restricted to slow motions of the fluid.

The conservation equation includes a divergence of the Nernst–Planck flux (\vec{j}_i) and a chemical reaction source term (R_i):⁷

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \vec{j}_i + R_i \quad (1)$$

Here c_i is the local concentration of species i (mol m⁻³), t the time (s), \vec{j}_i the flux of species i (mol m⁻² s⁻¹), and R_i the net local reaction rate of species i (mol m⁻³ s⁻¹). The Nernst–Planck flux is written as the sum of three terms: bulk motion ($c_i \vec{u}$), electromigration ($\mu_i F z_i c_i \nabla \varphi$), and a (dilute system) diffusion flux ($D_i \nabla c_i$);⁸ it is a commonly used approximation based on infinite dilution

$$\vec{j}_i = c_i \vec{u} + \mu_i F z_i c_i \nabla \varphi + D_i \nabla c_i \quad (2)$$

Here, μ_i is the ion mobility (mol m² V⁻¹ s⁻¹ C⁻¹), F the Faraday constant (C mol⁻¹), z_i the ion charge (unitless, but signed), φ the electric potential (V), and D_i the diffusion coefficient (m² s⁻¹).

The Nernst–Einstein equation⁹ relates the diffusion coefficient and ion mobility via a temperature-dependent constant (with units of electric potential), known as the thermal voltage V_T :

$$V_T = \frac{D_i}{\mu_i F} = \frac{k_b T}{e} \quad (3)$$

where k_b is the Boltzmann constant, T the temperature (K), and e the charge on an electron. Combining eqs 1, 2, and 3 yields

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (c_i \vec{u}) + D_i \nabla \cdot \left(\frac{z_i}{V_T} c_i \nabla \varphi + \nabla c_i \right) + R_i \quad (4)$$

For the purposes of scaling, we can decompose the total potential into the components associated with the effects of charged surfaces, φ_{int} ; an externally applied potential, φ_{ext} ; and a reference potential, φ_o :

$$\varphi = \varphi_{\text{int}} + \varphi_{\text{ext}} + \varphi_o \quad (5)$$

Combining eqs 4 and 5

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (c_i \vec{u}) + D_i \nabla \cdot \left(\frac{z_i}{V_T} c_i \nabla \varphi_{\text{int}} + \nabla c_i \right) + D_i \nabla \cdot \left(\frac{z_i}{V_T} c_i \nabla \varphi_{\text{ext}} \right) + R_i \quad (6)$$

In the [Supporting Information](#), we present a scaling analysis that explores limits where the behavior is quasi-steady, bulk flow is negligible, and externally applied potential gradients are

small, relative to the thermal voltage. Under these assumptions, eq 6 reduces to

$$0 = D_i \nabla \cdot \left(\frac{z_i}{V_T} c_i \nabla \varphi_{\text{int}} + \nabla c_i \right) + R_i \quad (7)$$

Equation 7 is the set of species-specific governing partial differential equations (PDEs). The chemical reaction term (R_i) is dependent on the concentration of other species in the system. Hence, the PDEs are all coupled via the electrical potential and the chemical reaction term. We seek a solution to the ion concentration equations (c_i) for this set of PDEs.

We explore the possibility that the same Boltzmann distribution that holds for the strong electrolyte case also applies to the ionized species of the weak electrolyte mixture. To account generally for confined (albeit still diffuse and approximately dilute) nanoscale spaces and overlapped EDLs, we consider the following form of the Boltzmann distribution:

$$c_i = c_i^0 \exp \left[-\frac{z_i}{V_T} (\varphi_{\text{int}} - \varphi_o) \right] \quad (8)$$

Here, c_i^0 is the ion concentration of species i at a reference point where the potential is φ_o . For systems that include some region outside of the EDL (where net neutrality applies) and where $\varphi_o = 0$, c_i^0 is the ionic concentration in this bulk region.

We simplify the notation in eq 8 by introducing a difference for the internal potential from the reference potential $\Delta \varphi \equiv \varphi_{\text{int}} - \varphi_o$, and therefore write

$$c_i = c_i^0 \exp \left[-\frac{z_i}{V_T} (\Delta \varphi) \right] \quad (9)$$

We substitute our hypothesized Boltzmann distribution eq 9 into the governing equation for the weak electrolyte PDE given in eq 7 as follows:

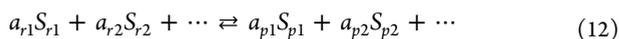
$$0 \stackrel{?}{=} D_i \nabla \cdot \left\{ \frac{z_i}{V_T} c_i^0 \exp \left(-\frac{z_i}{V_T} \Delta \varphi \right) \nabla \varphi_{\text{int}} + \nabla \left[c_i^0 \exp \left(-\frac{z_i}{V_T} \Delta \varphi \right) \right] \right\} + R_i \quad (10)$$

The question mark in eq 7 indicates that this is not a new governing equation but rather a condition to be met for eq 9 to be a solution to eq 7.

Evaluating the gradient in the second term on the right-hand side of eq 10, we see that the first two terms cancel identically (as expected from a local balance between electromigration and diffusion). The resulting condition is

$$0 \stackrel{?}{=} R_i(x, y, z) \quad (11)$$

Again, this equation expresses a condition to be met for the set of Boltzmann equations (eq 9) to be consistent with a solution to the set of governing eqs (eq 7). This condition $R_i(x, y, z) = 0$, is that of chemical equilibrium everywhere. We can explore chemical equilibrium in terms of a reaction quotient (Q) definable for any generic set of chemical equilibria.¹⁰ A system is in chemical equilibrium if Q is equal to the effective, system-wide equilibrium constant K at all locations. We are assuming the activities in the reaction quotient and equilibrium constant can be safely replaced by concentrations. Note that any complex set of simultaneous chemical equilibria can then be rewritten as a single equilibrium of the form given in eq 12 with a single equilibrium constant defined by eq 13:



$$K = \prod_i^{\text{all equilibria}} K_i = \frac{\prod_j^{\text{all products}} (c_j^o)^{a_j}}{\prod_k^{\text{all reactants}} (c_k^o)^{a_k}} \quad (13)$$

where a_{ri} and a_{pi} are stoichiometric coefficients for the i th reactant and product, respectively. S_{ri} and S_{pi} denote the species of the i th reactant and product.

The equilibrium described by eq 12 has the following reaction quotient:

$$Q(x, y, z) \equiv \frac{(c_{p1})^{a_{p1}}(c_{p2})^{a_{p2}}\dots}{(c_{r1})^{a_{r1}}(c_{r2})^{a_{r2}}\dots} = \frac{\prod_j^{\text{all products}} c_j^{a_j}(x, y, z)}{\prod_k^{\text{all reactants}} c_k^{a_k}(x, y, z)} \quad (14)$$

where c_{ri} and c_{pi} are the concentrations (c_i) of species S_{ri} and S_{pi} , respectively. Substituting in eq 9 yields

$$Q(x, y, z) = \frac{\prod_j^{\text{all products}} (c_j^o)^{a_j} \exp\left(-a_j \frac{z_j}{V_T} \Delta\phi(x, y, z)\right)}{\prod_k^{\text{all reactants}} (c_k^o)^{a_k} \exp\left(-a_k \frac{z_k}{V_T} \Delta\phi(x, y, z)\right)} \quad (15)$$

Extracting the exponential from the product, we obtain

$$Q(x, y, z) = \left(\frac{\prod_j^{\text{all products}} (c_j^o)^{a_j}}{\prod_k^{\text{all reactants}} (c_k^o)^{a_k}} \right) \times \exp\left[-\frac{\Delta\phi(x, y, z)}{V_T} \left(\sum_j^{\text{all products}} a_j z_j - \sum_k^{\text{all reactants}} a_k z_k \right) \right] \quad (16)$$

Conservation of charge for a chemical reaction states that the net charge on the reactants must be equal to the net charge on the products (see eq 17):

$$\sum_j^{\text{all products}} a_j z_j - \sum_k^{\text{all reactants}} a_k z_k = 0 \quad (17)$$

The left-hand side of eq 17 is in the exponent of eq 16. This cancels the exponential portion of eq 16, leaving only

$$Q_o = \frac{\prod_j^{\text{all products}} (c_j^o)^{a_j}}{\prod_k^{\text{all reactants}} (c_k^o)^{a_k}} \quad (18)$$

For our hypothesized solution, we see that spatial dependences associated with the various Boltzmann distributions all cancel, so that the resulting reaction quotient is a single uniform value, Q_o , for the entire system. A comparison of eqs 13 and 18 shows that

$$Q_o = K \quad (19)$$

As previously stated, if eq 19 is true, then, for weak electrolytes,

$$R_i(x, y, z) = 0 \quad \text{for all } x, y, z \quad (20)$$

Thus, we have established that eq 9 is an exact solution to the governing equation (eq 7) for the case of weak electrolytes at chemical equilibrium. Hence, we conclude that, for our assumptions, chemical equilibrium is consistent with a Boltzmann distribution of ions. This is a powerful principle that we can use to study weak electrolyte EDL systems and show their strong analogy to the strong electrolyte situation.

Before exploring this solution further, we note that the governing equation (eq 7) is a set of coupled nonlinear PDEs. Hence, the existence of the aforementioned exact solution does not necessarily imply that it is a unique or stable solution to this problem.

Next, we discuss the analogies of the weak electrolyte solution to that of a strong electrolyte system (i.e., traditional Boltzmann). Our treatment of the types of chemical reactions is fairly general; for example, it applies to multivalent species. Simply stated, the analogous strong electrolyte system should have the same ion concentrations in the bulk as the ionic concentrations of the weak electrolyte case. For example, consider a strong electrolyte system of one cation, a monovalent anion, and a divalent anion. The analogous weak electrolyte should have a pH equilibrium¹¹ in the bulk such that the concentration of species ionized to +1, -1, and -2 should be equal to those of the strong electrolyte bulk region. We see that ionic concentration is different than the often-reported analytical (i.e., total) concentration, which is the sum of all ionization states of a species.¹¹

Note that analytical concentrations do not necessarily follow a Boltzmann distribution. For example, the analytical concentration of a strong electrolyte species is always equal to its ionized concentration; but, the sum of Boltzmann distributions of the analytical concentration of ionized weak electrolyte species (with different arguments in the exponential) is not itself a Boltzmann distribution.

Let us briefly specialize this to a common buffer solution comprising a univalent weak acid buffer, as indicated in eq 21 with the acid dissociation constant K_A given in eq 22. The resulting EDL (using the sodium salt of the weak acid for the buffer) is shown in Figure 2.



$$K_A = \frac{c_H c_A}{c_{HA}} \quad (22)$$

This has an analytical concentration in the bulk of

$$c_{A,anal}^o \equiv c_A^o + c_{HA}^o \quad (23)$$

The superscript "o" indicates a concentration in the bulk so that c_A^o is the concentration of the conjugate base in the bulk and $c_{A,anal}^o$ is the sum of the conjugate base and weak acid concentrations (c_{HA}^o) in the bulk.

Substitution of eq 23 into eq 22 and rearranging yields eq 24 for converting from analytical concentrations to the individual concentration for univalent weak acid buffers.

$$c_A^o = \frac{K_A c_{A,anal}^o}{c_H^o + K_A} \quad (24)$$

The distribution of the conjugate base of the weak acid in the EDL is then given by $c_A = c_A^o \exp\left[-\frac{z_A}{V_T}(\Delta\phi)\right]$ while the acid concentration is uniform throughout the EDL at the value set by the bulk equilibrium, that is, $c_{HA} = c_{HA}^o$. A similar technique can be applied to more complex buffers to determine the ionic concentrations from the analytical concentrations.

The solution for weak electrolytes described above includes the interesting conclusion that the concentration of hydronium ions also follows a Boltzmann balance,

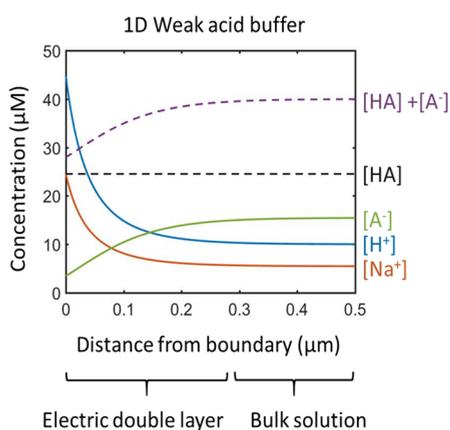


Figure 2. One-dimensional case of a buffered EDL with a negatively charged wall (25 °C, 1.5 thermal volts or 38.5 mV), and univalent weak acid buffer (e.g., 40 μM weak acid, $\text{p}K_a$ 5.2, titrated with sodium hydroxide to create a pH 5 buffer). Solid lines denote concentrations of species found in both the weak and strong electrolyte cases (with the same distribution). Shown are analytical concentration of the weak acid family (purple), weak acid (black, HA), conjugate base of weak acid (green, A^-), Na^+ ion (orange, Na^+), and hydroxide ion (blue, H^+). The hydroxide anion is very low in concentration and not shown for the sake of simplicity. Shown are exact solutions to the Poisson–Boltzmann equation for both strong and weak electrolyte systems. The former is from Hunter,² and the latter follows from the current work.

$$c_{\text{H}}(x, y, z) = c_{\text{H}}^0 \exp\left(-\frac{1}{V_T} \Delta\varphi(x, y, z)\right) \quad (25)$$

which rearranges to

$$\text{pH}(x, y, z) = \text{pH}^0 + \frac{\Delta\varphi(x, y, z)}{V_T \ln(10)} \quad (26)$$

From eq 26, the extreme in pH is clearly located at the extreme of φ , which is typically at the boundary of the diffuse layer of the EDL:

$$\text{pH}^b = \text{pH}^0 + \frac{\Delta\varphi^b}{V_T \ln(10)} \quad (27)$$

Here, the superscript “b” indicates a quantity evaluated at the charged boundary of the diffuse layer of the EDL, while superscript “o” again indicates value in the bulk. This boundary potential (i.e., zeta potential) is often measured directly, as in the case of electro-osmotic flows, streaming potential flows, or electrophoretic mobility of finite-sized particles.^{1,2} The pH at the boundary of the diffuse layer is, of course, an important parameter for determining the physicochemical conditions at the boundary.

The formulations described here represent a compact method of generalizing steady-state solutions to EDLs involving weak electrolytes. This is an important point as classical formulations of electrokinetics and colloids theory have almost exclusively relied on the assumption of strong electrolytes and most commonly binary and symmetric electrolyte mixtures (two species with valences of equal magnitude and opposite sign). Such theory has typically decoupled the weak electrolyte behavior of fixed surface groups (e.g., acidic silanol on a glass surface) from the behavior of weak electrolytes in the diffusion region. As one example, treatments of acidic surface groups (e.g., on glass surfaces)

have relied on correlations between the surface charge and the pH in the bulk, while also assuming strong electrolytes to describe the distributions of diffuse ions of the EDL.⁴

Intuitively, the correct treatment of proton equilibrium between ionizable surface groups and weak electrolyte mixtures (e.g., pH buffers) should involve the balance of all chemical reactions, both bulk and surface. For example, EDL models often assume a fixed surface charge density boundary condition to relate bulk ionic strength on EDL length scale and potential drop across the diffuse ion layer (i.e., the zeta potential). The current work suggests that such treatments are overly contrived, and a realistic EDL treatment should consider the entire coupled problem, including the pH equilibrium in the diffuse region, the surface charge density at the boundary, and the dramatic deviation of pH near the boundary, as expressed by eq 27.

The key assumptions of the current work is that it was derived strictly for (quasi-steady-state) equilibrium conditions with fast electromigration rates, relative to advective dispersion and effects of external potentials on the EDL (e.g., polarization of the EDL of a sphere). A second key assumption is that the behavior of all ions can be approximately described by the Nernst–Einstein relation, which implies a proportionality between diffusivity and electromigration mobility for transport in the limit of infinite dilution. Such proportionality does not necessarily hold for charged species, particularly at significant ion concentrations.⁹ For such non-Nernst–Einstein transport, the current formulation suggests the spatial dependencies in Q will likely be further dependent on the individual ion mobilities and diffusivities. In such a case, eq 16 is not useful and classic Boltzmann balances do not hold.

Here, we have further used the Nernst–Planck equation (eq 2), which also assumes infinite dilution and the linear superposition of the various sources of transport, including a diffuse treatment of Fick’s law and its superposition to an electromigration flux. This again neglects finite dilution effects, as well as noncontinuum considerations. We have also assumed that the equilibrium constant is independent of the electric potential.

In conclusion, EDLs often imply steep ion gradients. Here, we have considered the simple case of negligible bulk flow and diffuse and dilute ion transport with negligible effects caused by an externally applied electric field. For such a regime, remarkably, all quasi-steady solutions for ion gradients yield Boltzmann distributions. These spatial distributions are inter-related, such that chemical equilibrium is an exact solution to the weak electrolyte EDL problem. Specification of this equilibria to the hydronium ion yields a pH jump for the diffuse section of an equilibrium EDL, allowing calculation of the pH at the boundary of the diffuse layer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c02247>.

The Supporting Information contains details of the scaling used between eqs 6 and 7 and a worked-out example of a system containing a univalent buffer made from a weak acid, HA and its sodium salt, NaA (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by a fellowship from the Center for Molecular Analysis and Design at Stanford University, the National Institutes of Health (under Award No. 1R01EB025867), and the Air Force Office of Scientific Research through Basic Research Initiative grant (No. AFOSR FA9550-12-1-0400).

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