

Simple Estimate of the Potential Drop across an Amphiprotic Liquid–Liquid Interface

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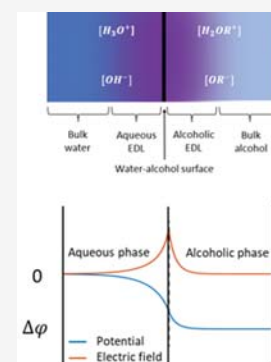


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ABSTRACT: Two immiscible liquids in contact with each other can have different internal electrostatic potentials. An associated electric double layer (EDL) therefore exists within each liquid. For amphiprotic liquids, the exchange of protons between the two liquids gives rise to two EDLs, a positively charged EDL in one of the liquids and negatively charged EDL in the other. Using the pK_a and pK_b of one liquid dissolved in the other and the pH equivalent within each amphiprotic liquid, we can estimate the potential drop, $\Delta\phi$, between the interior of the two liquids, also known as the Galvani potential or liquid–liquid junction potential. This estimation is independent of surface charge and ionic strength. By using the ionic strength to find the thickness of the EDL, we also estimate the average electric field strength across the interface. For the special case of water (H_2O) in contact with an immiscible alcohol (ROH), the potential drop across the interface from the water to the alcohol is $\Delta\phi = 2.303V_T (pK_b + pH - pK_w - pH_2OR)$, where V_T is the thermal voltage at a given temperature T .



INTRODUCTION

Electric field effects on local chemistry have been seen in a variety of different systems.^{1–9} When electric fields are applied to liquids, an electric double layer (EDL) forms at the liquid interface that screens the interior bulk of the liquid from the electric field. Recently, systems with chemical reactions at the interface, bypassing the normal screening of the electric field by the EDL, have gained interest as they can promote unique new chemistry at the interface.^{10–16} As the chemistry is dependent on the electric field strength, it is of great interest to know the electrostatic potential drop and electric field strength across the interface. Given that EDLs have dimensions that are typically less than the optical diffraction limit, direct measurements of the electric field strength are difficult to obtain. Further complicating the issue, surfactant ions often accumulate at the interface surface, creating a surface charge density and an associated surface potential. The associated surface potential is highly system-dependent, varying with the ions present and even the ionic strength of the solution.

Typically, the bulk of a liquid is taken as the zero reference point for the electrostatic potential. This becomes more complicated for systems with two liquids, as only one of them can be used as the reference. While neither liquid has an internal electric field due to screening from their respective EDLs, they are not necessarily at the same potential. The electric field is the negative slope of the potential, thus any difference in potential between the liquids directly gives rise to an electric field at their interface.

In this work, we derive an approximation for the difference in electric potential between the two liquids that are in contact, which also allows us to estimate the average electric field strength across the interface. This approximation is obtained from easily measurable parameters of the system. Our parameter of interest is the pH, or pH equivalent, in the bulk solutions. Thus, we restrict this derivation to amphiprotic liquids in which the solvent can act as both a Brønsted–Lowry acid and a Brønsted–Lowry base giving a protonated solvent species that can be used as a pH equivalent for each liquid. The derivation in this work can be generalized to the interface of any two amphiprotic immiscible liquids. Common amphiprotic solvents are water and alcohols. To make this treatment concrete, we refer specifically to an interface between water (H_2O) and an alcohol (ROH), although technically either of those can be substituted with any amphiprotic solvent.

Amphiprotic solvents are conductors due to ions formed by autoionization as well as any other dissolved ions within them. Metals move electrons to their surface in order to prevent any electric fields within their bulk. Similarly, amphiprotic solvents move ions to their surface to prevent electric fields within their bulk. The ions moved to the surface form an EDL of nonzero

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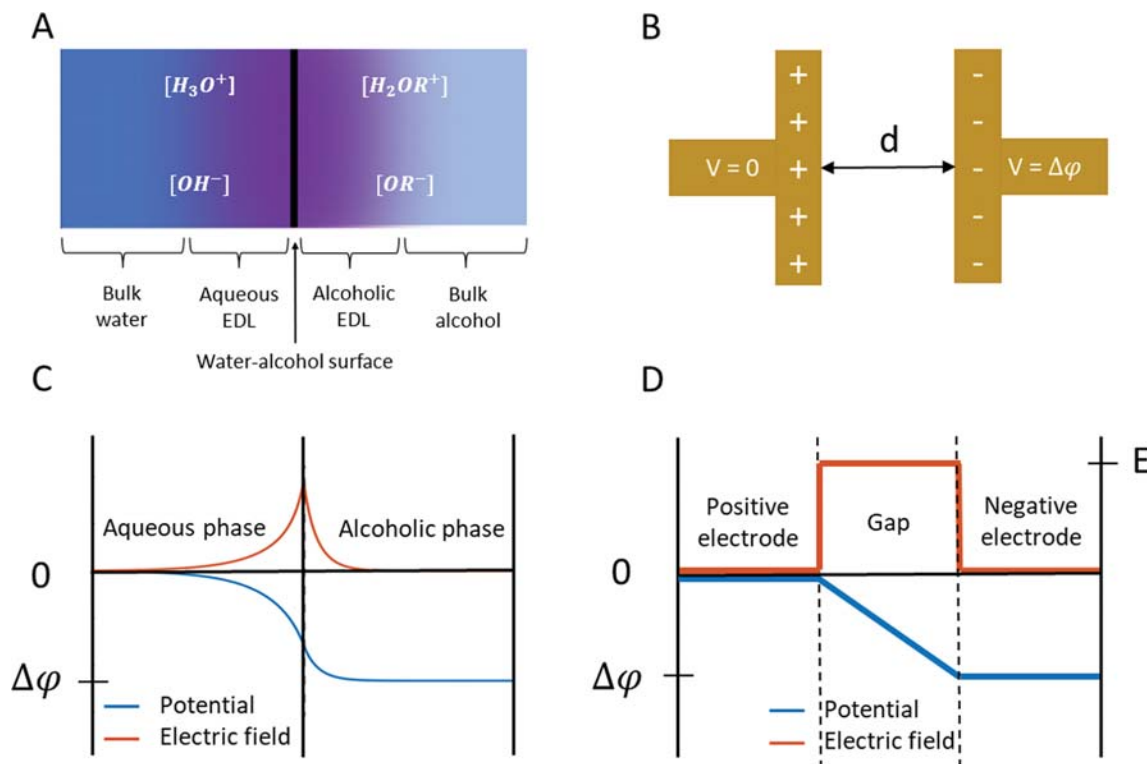
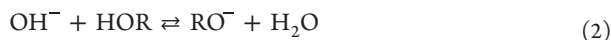
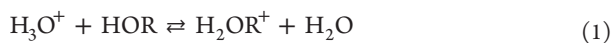


Figure 1. (A) Sketch of the structure of the water–alcohol interface. (B) Sketch of a parallel plate capacitor. (C) Sketch of a potential (blue) and electric field (orange) from EDLs in (A). (D) Sketch of a potential (blue) and electric field (orange) from the parallel plate capacitor in (B).

net charge that counteracts any static externally applied electric field.

We divide the interface into five parts as shown in Figure 1A: (1) the bulk solution of the water, (2) the aqueous EDL, (3) the water–alcohol surface, (4) the alcoholic EDL, and (5) the bulk alcohol. Strictly speaking, the water–alcohol surface is a boundary located at the intersection of two volumes while the other locations each have distinct volumes. At the water–alcohol surface, two reactions take place.



Each reaction has an associated equilibrium constant for the reaction happening at the surface. The main approximation made in this work is to estimate the combined effect of these surface equilibria using the K_a and K_b of the alcohol dissolved in the water. The exchange of protons (and other ionic species) across the amphiprotic liquid–liquid interface results in equal but opposite net charges on the two EDLs.

For amphiprotic liquid–liquid interfaces, the EDLs have opposite net charges, each screening its own bulk solution from the electric field of the other. An analogy can be made to a charged parallel plate capacitor. There is no electric field within the bulk of the wires on either side of the capacitor and equal but opposite charges on the surface of the two plates (Figure 1B). Between the two charged plates there is an electric field. The negative integral of the electric field across the capacitor is the change in potential (Figure 1D), i.e., the voltage applied to the capacitor. The average electric field strength within the capacitor can be calculated by dividing the change in potential by the distance, d , that the charges in the capacitor are separated.

The water–alcohol interface has a similar structure (Figure 1C). There is no electric field in either bulk solution, with two oppositely charged EDLs at the interface. The potential changes across the interface with a corresponding electric field. The average electric field strength can be estimated by dividing the potential difference between the two liquids, by a distance that encompasses the width of the two EDLs.

DERIVATION

The distribution of ions in a diffuse EDL can be described with a Boltzmann distribution.¹⁷

$$[i](x, y, z) = [i]_{\text{bulk}} \exp\left[-\frac{z_i}{V_T}(\varphi(x, y, z) - \varphi_0)\right] \quad (3)$$

Here, $[i](x, y, z)$ is the concentration of the i th species at a location (x, y, z) with electric potential φ , $[i]_{\text{bulk}}$ is the ion concentration of species i at a reference point where the potential is φ_0 , z_i (unitless) is the charge on the ion, and V_T is the thermal voltage, which is the Boltzmann constant k times the temperature T divided by the charge on the electron. We define the reference spot for aqueous ions inside the bulk aqueous solution with $\varphi_0 = 0$ and a reference for alcohol ions inside the bulk of the alcohol layer where $\varphi_0 = \Delta\varphi$, and $\Delta\varphi$ represents the net potential drop across the interface from the aqueous solution to the alcoholic solution. This has received a variety of names in the literature, including the Galvani potential, the liquid-junction potential, and the diffusion potential.¹⁸ It is the quantity $\Delta\varphi$ that we wish to calculate.

The derivation of the Boltzmann distribution is often derived specifically for nonreactive ions that are not part of a chemical equilibrium. We have previously shown that a Boltzmann distribution for an EDL maintains the chemical

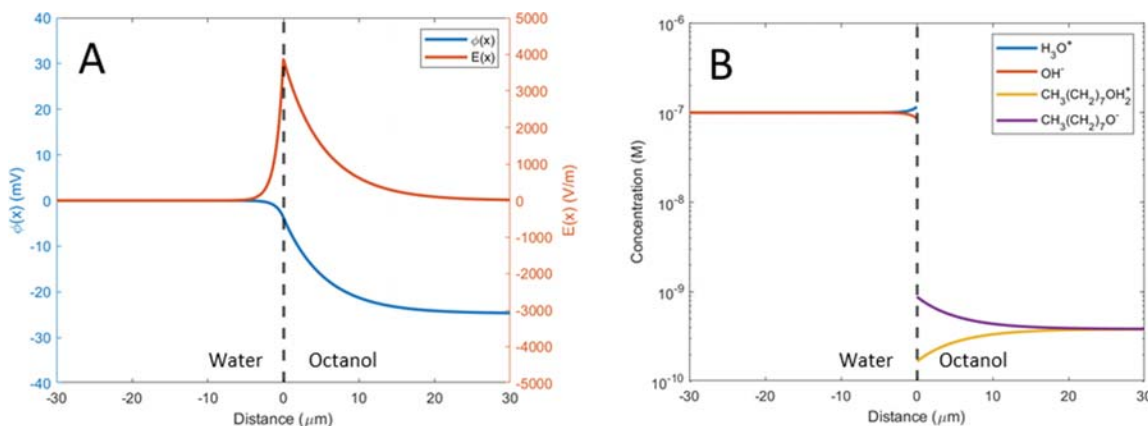


Figure 2. EDLs of a pure water–octanol interface with neutral bulk octanol ($\text{pH}_2\text{OR} = \text{pOR}$) and neutral bulk water ($\text{pH} = \text{pOH}$) and no surfactant ions. (A) Potential (blue) and electric field (orange) of the interface EDLs. (B) Ion gradients of interface EDLs. The surface is located at 0, with negative distances traveling into the water and positive distances traveling into the octanol. The temperature is 20 °C.

equilibrium of species within it.¹⁹ This includes the Boltzmann distribution of the H^+ ion concentration; even in buffered solutions, H^+ ion concentration gradients exist inside EDLs at chemical equilibrium.

The concentrations of species at the liquid–liquid surface are of particular interest to us, which we designate with a subscript S. Furthermore, we assign φ_s as the potential at the interface. Specifying our location of interest as the surface, surface concentrations $[\text{H}_3\text{O}^+]_s$ and $[\text{OH}^-]_s$ for the aqueous EDL and $[\text{H}_2\text{OR}^+]_s$ and $[\text{OR}^-]_s$ for the alcohol EDL are defined according to eq 3:

$$[\text{H}_3\text{O}^+]_s = [\text{H}_3\text{O}^+]_{\text{bulk water}} \exp(-\varphi_s/V_T) \quad (4)$$

$$[\text{OH}^-]_s = [\text{OH}^-]_{\text{bulk water}} \exp(\varphi_s/V_T) \quad (5)$$

$$[\text{H}_2\text{OR}^+]_s = [\text{H}_2\text{OR}^+]_{\text{bulk alcohol}} \exp[-(\varphi_s - \Delta\varphi)/V_T] \quad (6)$$

$$[\text{OR}^-]_s = [\text{OR}^-]_{\text{bulk alcohol}} \exp[(\varphi_s - \Delta\varphi)/V_T] \quad (7)$$

We approximate the reactivity of the alcohol functional group at the surface with the K_a and K_b of the dilute alcohol dissolved in water

$$K_a \cong \frac{[\text{H}_3\text{O}^+]_s [\text{OR}^-]_s}{a_{\text{ROH}}} \quad (8)$$

$$K_b \cong \frac{[\text{H}_2\text{OR}^+]_s [\text{OH}^-]_s}{a_{\text{ROH}}} \quad (9)$$

where a_{ROH} is the activity of the alcohol, which for a dilute species is simply its concentration, but is not well defined at the liquid–liquid interface. Fortunately, this quantity cancels by taking the ratio of K_a to K_b

$$\frac{K_a}{K_b} = \frac{[\text{H}_3\text{O}^+]_s [\text{OR}^-]_s}{[\text{H}_2\text{OR}^+]_s [\text{OH}^-]_s} \quad (10)$$

Substitution of eqs 4–7 into eq 10 yields

$$\frac{K_a}{K_b} = \frac{[\text{H}_3\text{O}^+]_{\text{bulk water}} \exp(-\varphi_s/V_T) [\text{OR}^-]_{\text{bulk alcohol}} \exp((\varphi_s - \Delta\varphi)/V_T)}{[\text{H}_2\text{OR}^+]_{\text{bulk alcohol}} \exp(-(\varphi_s - \Delta\varphi)/V_T) [\text{OH}^-]_{\text{bulk water}} \exp(\varphi_s/V_T)} \quad (11)$$

which can be simplified and solved for $\Delta\varphi$, with the surface potential φ_s canceling out of the equation.

$$\Delta\varphi = -\frac{V_T}{2} \ln \left(\frac{K_a}{K_b} \times \frac{[\text{OH}^-]_{\text{bulk water}} [\text{H}_2\text{OR}^+]_{\text{bulk alcohol}}}{[\text{H}_3\text{O}^+]_{\text{bulk water}} [\text{OR}^-]_{\text{bulk alcohol}}} \right) \quad (12)$$

Converting the concentrations and equilibrium constants to their p values (that is, their negative logarithm to the base 10 values) yields

$$\Delta\varphi = \frac{1}{2} V_T \ln(10) (pK_b + pH + pOR - pK_a - pOH - pH_2OR) \quad (13)$$

Finally, we can approximate the alcohol's autoionization equilibrium constant from the alcohol's K_a and K_b values in water.

$$K_{\text{ROH}} = [\text{H}_2\text{OR}^+][\text{RO}^-] \cong K_a K_b / K_w \quad (14)$$

with

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] \quad (15)$$

Substitution of eq 14 twice and eq 15 into eq 12 yields

$$\Delta\varphi = -\frac{V_T}{2} \ln \left(\frac{K_w^2 [\text{H}_2\text{OR}^+]_{\text{bulk alcohol}}^2}{K_b^2 [\text{H}_3\text{O}^+]_{\text{bulk water}}^2} \right) \quad (16)$$

Converting the concentrations and equilibrium constants to their p values yields the following simple equation for the change in potential across the interface.

$$\Delta\varphi = 2.303 V_T (pK_b + pH - pK_w - pH_2OR) \quad (17)$$

■ WATER–OCTANOL EXAMPLES

There are some unintuitive results from this equation. For example, consider a pure water–alcohol interface with neutral bulk water ($\text{pH} = \text{pOH}$) and neutral bulk octanol ($\text{pH}_2\text{OR} = \text{pOR}$). Octanol has a $\text{p}K_a$ value of 16.84 and a $\text{p}K_b$ value of 15.99.²⁰ At room temperature, these substitutions into eq 13 yield

$$\Delta\varphi = \frac{1}{2} \times (25.3 \text{ mV}) \times 2.303 \times (15.99 - 16.84) = -25 \text{ mV} \quad (18)$$

One might expect that neutral water and neutral octanol would not have a potential drop across their interface. Instead, we predict a small potential with the bulk potential in the octanol to be 25 mV less than the potential in the bulk water. The equilibrium concentrations of $\text{CH}_3(\text{CH}_2)_7\text{OH}_2^+$,

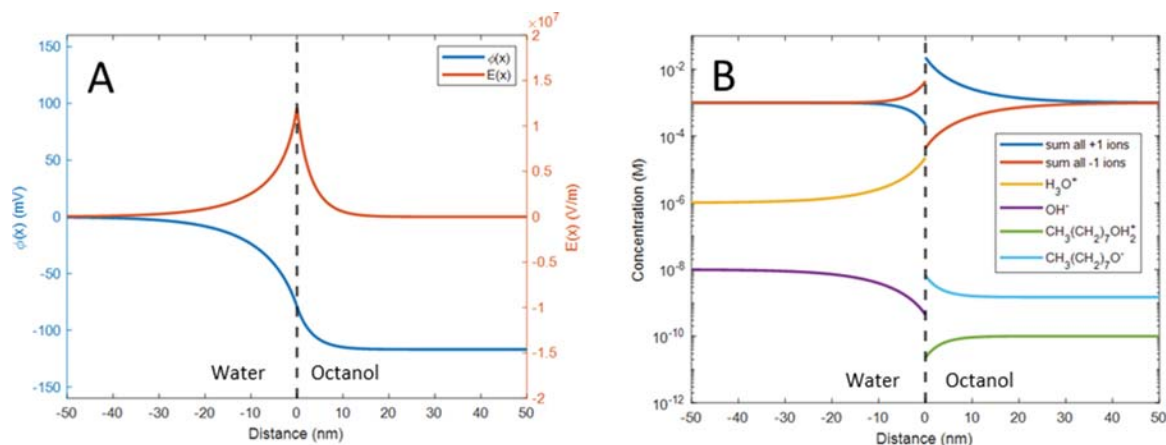


Figure 3. EDLs of a water–octanol interface with pH 6 water at 1 mM ionic strength and pROH₂ 10 octanol at 1 mM ionic strength. (A) Potential (blue) and electric field (orange) of the interface EDLs. (B) Ion gradients of interface EDLs. The surface is located at 0, with negative distances traveling into the water and positive distances traveling into the octanol. The temperature is 20 °C.

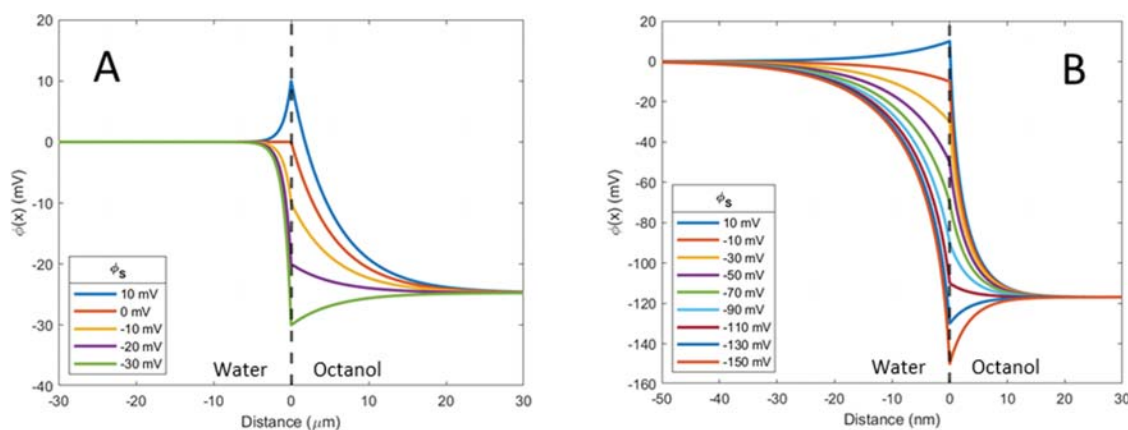


Figure 4. (A) EDL potential as a function of distance from a water–octanol interface of pure octanol and pure water for multiple surface potentials. (B) EDL potential as a function of distance from a water–octanol interface with pH 6 water at 1 mM ionic strength and pROH₂ 10 octanol at 1 mM ionic strength for multiple surface potentials. The interface surface is located at 0 with negative distances traveling into the water and positive distances traveling into the octanol. (A) μm and (B) nm. The temperature is 20 °C.

$\text{CH}_3(\text{CH}_2)_7\text{O}^-$, OH^- , and H_3O^+ at the surface do not correspond to their concentrations in the bulk solutions. To establish chemical equilibria at the surface, they exchange ions locally, with the counterion located in the other solution. The result is that the EDLs on either side of the interface have equal but oppositely signed net charge.

For the one-dimensional case of an infinite plane as the interface, we can graph the electric field and potential within the EDLs using known analytical solutions²¹ if we specify a specific surface potential, ϕ_s . The surface potential is affected by surface charges from surfactant ions at the interface. Figure 2A shows the electric field and potential across a neutral water and neutral octanol interface, with ϕ_s determined such that there are no surface-bound charges. The calculation for this ϕ_s is shown in Note 1 of the Supporting Information. The resulting ϕ_s is dependent on the ionic strengths of the two liquids, the bulk pH of both solutions, and the surface charge density of surfactant ions. Figure 2B shows the ion gradients of the same interface. The pure water–octanol systems shown is slightly oversimplified in that it neglects the pH and ionic strength changes from the dissolution of one solvent into the other, which is discussed later.

The widths of the EDLs, characterized by their Debye lengths, are quite large. This is a result of the extremely low ionic strength of pure water and octanol. Solutions with higher ionic strengths have much shorter Debye lengths, typically in the nanometer range.

We can also look at the one-dimensional case of an infinite plane, water–octanol interface with other species dissolved in the liquids, again with ϕ_s determined such that there are no surface-bound charges. We further restrict the system to only ions of +1 and -1 valence so that we can use the known analytical solutions to a one-dimensional EDL.²¹ Figure 3 shows the case of 1 mM ionic strength water buffered at a pH of 6 and 1 mM ionic strength octanol buffered at a pROH₂ of 10. These are the values for the ionic strength and pH equivalent in both liquids after the system has come to equilibrium. Due to partition functions of unspecified species in the liquids, these are not necessarily the values of those of the liquids prior to forming the interface. The results shown in Figure 3 are good for any system of buffers in the liquids that result in a 1 mM ionic strength aqueous solution buffered at a pH of 6 and a 1 mM ionic strength octanol solution buffered at a pROH₂ of 10 upon reaching equilibrium at the water–octanol interface surface. The final chemical equilibrium values

include any ionic strength and pH changes caused by the dissolution of small amounts of one solvent into the other. So long as measured values of the two bulk solvents on either side of the interface at equilibrium are used, effects of the two solvents dissolving into each other will be automatically included in estimating the potential difference between the bulk solutions.

The thinner EDLs in Figure 3 compared to Figure 2 result from the increased ionic strength at 1 mM versus the low ionic strength of the pure liquids. The use of eq 17 shows a potential difference of -117 mV between the octanol and water bulk solutions.

INDEPENDENCE FROM SURFACE POTENTIAL AND IONIC STRENGTH

So far, we have graphed only systems with no surfactant ions. In practice, this is quite rare because most surfaces have absorbed ions that give a surface charge density to the surface. These surfactant ions contribute to the surface potential, φ_s . The change in surface potential greatly affects the slope of both the aqueous and alcoholic EDLs. Measurements of φ_s can be difficult to obtain. Fortunately, when deriving the equation for estimating the potential drop across a liquid–liquid interface using the change in protonated species, the surface potential, φ_s , cancels out. Thus, we do not need to know the details of the surface potential to estimate the potential drop and the average electric field strength of the interface.

To help visualize this concept, several graphs of the EDLs for a pure water–octanol interface with neutral bulk octanol ($\text{pH}_2\text{OR} = \text{pOR}$) and neutral bulk water ($\text{pH} = \text{pOH}$) are shown in Figure 4A. Figure 4B shows the case of a +1 or -1 ion restricted system of 1 mM ionic strength water buffered at a pH of 6 and 1 mM ionic strength octanol buffered at a pROH_2 of 10. In both cases, the potential across the two EDLs is shown for several different surface potentials. Despite different surface potentials, the difference in potential from one bulk solution to the other remains unchanged.

Another common factor that affects EDLs is the ionic strength of the liquid. Higher ionic strengths are known to create thinner EDLs.²² Notably, ionic strength is not present in our equation for the potential drop across the interface. A careful distinction needs to be made here. Two systems with the same bulk pH and bulk pROH but using solutions of different ionic strengths will have the same potential drop. This does not mean that increasing the ionic strength of a solution does not change the potential drop because increasing the ionic strength of one solution may change the equilibrium bulk pH and bulk pROH_2 of the system.

ESTIMATED AVERAGE ELECTRIC FIELD STRENGTH

The average electric field strength can be estimated by taking the potential drop, φ_{ROH} , and dividing it by the length of the two EDLs. The Debye length, κ^{-1} , is often used to characterize the length of an EDL. For small potentials, where the potential of the EDL can be approximated as following an exponential decay, the Debye length is the exponential decay parameter.²³ At three times the Debye length, the potential has decayed to about 2% of its value at the surface.²² We use $3\kappa^{-1}$ to approximate the width of each EDL

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 V_T}{2000 F I}} \quad (19)$$

where ϵ_r is the relative permittivity of the solvent, ϵ_0 is the permittivity of free space, F is the Faraday constant, and I is the ionic strength of the solution in M units. Thus,

$$\bar{E} \cong -\frac{(\Delta\varphi)}{3(\kappa_{\text{water}}^{-1} + \kappa_{\text{alcohol}}^{-1})} \quad (20)$$

Making substitutions into eq 20 yields

$$\bar{E} \cong -\frac{2.303 V_T (pK_b + pH - pK_w - p\text{H}_2\text{OR})}{3\sqrt{\frac{\epsilon_0 V_T}{2000 F} \left(\sqrt{\frac{\epsilon_{\text{water}}}{I_{\text{water}}}} + \sqrt{\frac{\epsilon_{\text{alcohol}}}{I_{\text{alcohol}}}} \right)}} \quad (21)$$

We can solve eq 21 for our previous two example cases of water–octanol. The pure water–octanol case has a potential drop of -25 mV, and the Debye lengths of pure water and pure octanol are 964 and 5572 nm, respectively, at 20 °C (from eq 19). Estimating the thickness of the interface as 3 times the combined Debye length (19.6 μm), we estimate an average electric field strength of ~ 1275 V/m across the interface.

For the case of 1 mM ionic strength water solution buffered at a pH of 6 and 1 mM ionic strength octanol solution buffered at a pROH_2 of 10, the potential drop is -117 mV and the water and octanol Debye lengths are 9.64 and 3.46 nm, respectively. Approximating the thickness of the interface as 3 times the combined Debye lengths (39.3 nm), we estimate an average electric field strength of $\sim 3.0 \times 10^6$ V/m across the interface. It is easy to understand how large electric fields can arise at the interface of two liquids in contact.

APPLICATION TO CELL BIOCONDENSATES

A current research area of interest is biocondensates formed from the condensation of proteins inside cells.^{24,25} Each ionic species can have a different partition function between the biocondensate and its surroundings. The resulting buffer system within the biocondensate thus can have a different pH than the surroundings. If a pH difference occurs, it can be used to estimate the change in potential across the surface from outside to inside the biocondensate in a similar fashion to the water–alcohol system. The potential change would indicate that an electric field is present at the biocondensate surface, which may play an important role in the chemical reactivity of biocondensates.

The calculation of the potential difference is slightly different because it involves the same chemical species on both sides of the interface. This simplifies the calculation immensely as both sides of the interface must result in the same H_3O^+ concentration at the surface. Using eq 3, we write two equations for H_3O^+ : one for the interior EDL and one for the exterior EDL at the biocondensate surface.

$$[\text{H}_3\text{O}^+]_S = [\text{H}_3\text{O}^+]_{\text{bulk water}} \exp(-\varphi_S/V_T) \quad (22)$$

$$[\text{H}_3\text{O}^+]_S = [\text{H}_3\text{O}^+]_{\text{biocondensate interior}} \exp(-(\varphi_S - \Delta\varphi)/V_T) \quad (23)$$

Here, $\Delta\varphi$ represents the potential difference measured from the exterior solution to the interior of the biocondensate. Combining eqs 22 and 23 and solving for $\Delta\varphi$ gives

$$\Delta\varphi = -V_T \ln\left(\frac{[\text{H}_3\text{O}^+]_{\text{bulk water}}}{[\text{H}_3\text{O}^+]_{\text{biocondensate interior}}}\right) \quad (24)$$

Once again, φ_s , cancels out of the calculation. Converting to pH values, we find

$$\Delta\phi = 2.303 V_T (pH_{\text{biocondensate interior}} - pH_{\text{bulk water}}) \quad (25)$$

■ IMPORTANT ASSUMPTIONS AND LIMITATIONS

Several approximations are used within this work whose implications should be discussed. First, the Boltzmann distribution of ions comes with its own limitations. What has been presented is based on a continuum model of the ion concentration, thereby failing to capture atomistic effects on the ion distributions. Additionally, the Boltzmann distribution is valid only for the diffuse portion of the EDL. Surfaces with high surface charge may form a Stern layer of desolvated ions at the interface.²⁶ Any change in potential across a Stern layer is not captured in this calculation.

An additional approximation is the neglect of changes in the solvation energy of ions at the surface compared to ions within the solvent. The surface ions participating in the equilibria are in a mixed water–alcohol solvent at the surface. By including them in the Boltzmann distribution, we are approximating them as freely exchanging with the fully solvated ions of the same type in their respective solvents.

Similarly, using K_a and K_b , which represent the reactivity of fully solvated alcohol species, to approximate the alcohol group's reactivity at the surface also neglects the energetic effects of partially solvating the ions. Given that the partial solvation should cause a similar shift in solvation energy for each ionic species, we expect that this should have a minimal effect on the ratio of K_a to K_b , used in eq 10 and thus allows for a reasonable approximation to be made for the surface reactivity.

■ CONCLUSION

We have derived here a simple method for estimating the potential change and average electric field strength across an amphiprotic liquid–liquid interface by measuring the pH and pH equivalent of the two liquids. The independence from surface charge and the use of only a measurement made in the bulk solutions allow easy measurements for the estimation of these values in a variety of applications.

■ ASSOCIATED CONTENT

Data Availability Statement

MATLAB code for the data in Figures 2–4 is available in the Supporting Information as well as on GitHub (at <https://github.com/ChristianChamberlayne/Simple-Estimate-of-the-Potential-Drop-Across-an-Amphiprotic-Liquid-Liquid-Interface.git>). The inputs can be readily modified for alternative chemical systems.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpbc.2c05696>.

Analytical solution to ϕ_S with no surface-bound charges; MATLAB code for the data in Figures 2–4 (PDF)

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Notes

The authors declare no competing financial interest.

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