The time-dependent development of electric double-layers in pure water at metal electrodes: the effect of an applied voltage on the local pH

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Water maintains a pH value of 7 owing to a balance between dissociation into hydronium (H$_3$O$^+$) and hydroxide (OH$^-$) ions and their recombination. An examination is made of the effect of applying voltages from 0.1 to 0.82V on these ions between metal electrodes which act as blocking electrodes. The movement of hydronium ions away from and hydroxide ions towards the anode is followed. This movement results in the formation of an ion double-layer with a steeply rising electric field and a maximum pH of approximately 12. At the cathode, the opposite occurs and the pH reaches a minimum of approximately 1.7. The time constant for double-layer formation is found to increase exponentially with voltage, and the pH at each electrode varies linearly with voltage; thus, the pH can be controlled systematically at each electrode. The dimensions of the double-layers are such that large biomolecules at the electrodes will be immersed in a pH environment close to the extreme values at the electrode. This means that the charge on the molecules may be controlled as they adsorb onto the electrode; this may prove valuable for the operation of biosensors.

Keywords: pH; pure water; double-layer; biosensor

1. Introduction

The formation of double-layers in an electrolyte when electric potentials are applied to metallic electrodes was first proposed by Helmholtz (1879). The concentration of ions and the distribution of potential were first solved as a steady-state problem by Gouy (1910) and Chapman (1913). The time-dependent solution for the formation of a double-layer in an aqueous electrolyte containing extrinsic ions on the other hand has only recently been solved (Morrow et al. 2006). The pH of a solution is an important property, especially when the solution contains molecules for which the charge is pH-dependent, as it is for biological macromolecules. In order to calculate the effect of applied potentials on the pH of a solution, the dissociation of water needs to be included in the analysis. The steady-state problem for the distribution of pH in pure water in the vicinity of

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the cathode has recently been solved using an approximate method (Brüesch & Christen 2004). In view of the importance of applied potentials in sensing processes in solution, especially biological processes at interfaces (Abe et al. 2008), the time-dependent solution is addressed here for electric potential and pH distributions in pure water. As a sensing process using an electrode requires knowledge of the response of the electrode/solution system, then knowledge of the time-dependent current in the external circuit is an important outcome of the calculation.

Pure water is an electrolyte as a result of the spontaneous self-dissociation reaction \( \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \).

The \( \text{H}^+ \) ion is hydrated and becomes the hydronium ion, \( \text{H}_3\text{O}^+ \); the \( \text{H}_3\text{O}^+ \) ion may exist as a complex such as \( \text{H}_5\text{O}_2^+ \) or \( \text{H}_7\text{O}_3^+ \) (Brüesch & Christen 2004). The \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) ion number densities are small (6 × 10^{19} \text{ m}^{-3}) compared with the number density of \( \text{H}_2\text{O} \) molecules (3.32 × 10^{28} \text{ m}^{-3}); however, the \( \text{H}_3\text{O}^+ \) ions have an important function in defining the pH of water.

The properties of pure water near metal electrodes have been studied by Guidelli & Schmickler (2000), Sánchez (2003) and Brüesch & Christen (2004). The electrification of pure water droplets on polymer surfaces during semi-conductor production has been attributed to double-layer effects by Yatsuzuka et al. (1994). However, it appears that there has only been one detailed study of double-layer formation at a cathode in pure water (Brüesch & Christen 2004). The study by Brüesch and Christen involved a steady-state solution at a cathode for one applied voltage.

Previously, a time-dependent formalism was developed to study the double-layer formation in salt (NaCl) solutions and, when run to the steady state, the results were in excellent agreement with the Gouy–Chapman solution of the nonlinear Poisson–Boltzmann equation (Morrow et al. 2006). However, \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) ions arising from dissociation of water were ignored. The calculations described here use the same basic formalism to study pure water; however, extra source terms are used to account for the spontaneous self-dissociation of water into \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) ions and the corresponding recombination of \( \text{H}_3\text{O}^+ \) and \( \text{OH}^- \) ions back into water. The source term reaction rates are balanced so that the equilibrium number densities are such that the pH is equal to the value 7 for pure water.

The calculations for the formation of double-layers in the NaCl involved a complex balance between fluxes of ions drifting in a space–charge-modified electric field and the diffusive ion fluxes owing to the steep ion gradients produced. The calculation for pure water involves similar fluxes; however, the source terms have a considerable modifying effect when ion densities in the double-layer deviate strongly from equilibrium.

Voltages applied to electrodes in solution are an important feature in some designs of biosensors (Abe et al. 2008) and as biosensors often use AC-applied voltages, it is necessary to use time-dependent methods to analyse double-layer formation. The aim of this paper is to fully understand the spatio-temporal formation of double-layers in pure water at both the cathode and the anode without the complicating effects caused by the addition of ions other than those naturally occurring. In order to achieve this, a full solution of the time-dependent dissociation–recombination drift–diffusion problem is undertaken.
2. Theory

In this section, an outline of the continuity equations used to obtain the time-dependent development of double-layers in water is given. The ion and potential distributions are calculated as a function of time after the application of a potential difference between two metal electrodes using only the basic properties of pure water:

— the mobilities and diffusion coefficients of H$_3$O$^+$ and OH$^-$ ions and
— the reactions rates for the spontaneous self-dissociation of water into H$_3$O$^+$ and OH$^-$ ions and the recombination of these ions.

Any approach to solving such time-dependent problems is usefully validated by making detailed comparisons with the Gouy–Chapman steady-state solution of the nonlinear Poisson–Boltzmann equation as described by Morrow et al. (2006).

(a) The continuity equations for time-dependent analysis

In order to obtain time-dependent solutions for the distributions of the ion number densities, the potential and the electric fields, small time-steps must be used to solve the continuity equations for the drift and diffusion of hydronium and hydroxide ions. These equations include terms for the spontaneous dissociation of water into hydronium and hydroxide ions and their subsequent recombination to produce water. In this way, new ion-density distributions are obtained with only slight incremental changes in their values from one time-step to the next. Simultaneously, new electric fields must be obtained by solving Poisson’s equation with the new net charge distribution to give the new ion drift velocities. The continuity equations for hydronium ions and hydroxide ions are

$$
\frac{\partial \rho_{H^+}}{\partial t} = -\frac{\partial}{\partial x}(\rho_{H^+} W_{H^+}) + \frac{\partial}{\partial x} \left( D_{H^+} \frac{\partial \rho_{H^+}}{\partial x} \right) + \alpha_W - \beta W \rho_{H^+} \rho_{OH^-} \tag{2.1}
$$

and

$$
\frac{\partial \rho_{OH^-}}{\partial t} = -\frac{\partial}{\partial x}(\rho_{OH^-} W_{OH^-}) + \frac{\partial}{\partial x} \left( D_{OH^-} \frac{\partial \rho_{OH^-}}{\partial x} \right) + \alpha_W - \beta W \rho_{H^+} \rho_{OH^-}, \tag{2.2}
$$

where $t$ is the time; $x$ is the distance from the anode; $\rho_{H^+}$ and $\rho_{OH^-}$ are the hydronium ion and hydroxide ion number densities, respectively; $W_{H^+}$ and $W_{OH^-}$ are the hydronium ion and hydroxide ion drift velocities, respectively; $D_{H^+}$ and $D_{OH^-}$ are the hydronium ion and hydroxide ion diffusion coefficients, respectively. It is assumed that the transport properties of the ions in solution are determined for constant room temperature (298 K) conditions, giving constant diffusion coefficients, $D$ and ion mobilities, $\mu$, such that $W_{H^+} = \mu_{H^+} E$ and $W_{OH^-} = \mu_{OH^-} E$, where $E$ is the electric field and $\mu_{H^+}$ and $\mu_{OH^-}$ are the hydronium ion and hydroxide ion mobilities, respectively. The coefficient for recombination of hydronium and hydroxide ions to produce water is $\beta_W$, and the rate of dissociation of water into hydronium and hydroxide ions is $\alpha_W$. Here, $\alpha_W$ is assumed to remain constant as the ion concentrations are always negligible in comparison with the concentration of water molecules.
Equations (2.1) and (2.2) are solved simultaneously with Poisson’s equation:

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{e}{\varepsilon_\text{r} \varepsilon_0} (\rho_{\text{H}^+} - \rho_{\text{OH}^-}),$$

(2.3)

where $\varepsilon_\text{r}$ is the relative permittivity, $\varepsilon_0$ is the permittivity of free space, $e$ is the electron charge and $\phi$ is the electric potential.

The electric field, $E$, is then computed using:

$$E = -\frac{\partial \phi}{\partial x},$$

(2.4)

(b) The current in the external circuit

The current, $I$, flowing in the external circuit owing to the movement of ions in the water is given by the equation of Morrow–Sato (Morrow & Sato 1999), which can be simplified for the case of small gaps to give:

$$I = \frac{A}{d} \left( e \int_0^d \left[ \rho_{\text{H}^+} W_{\text{H}^+} - \rho_{\text{OH}^-} W_{\text{OH}^-} + D_{\text{H}^+} \frac{\partial \rho_{\text{H}^+}}{\partial x} - D_{\text{OH}^-} \frac{\partial \rho_{\text{OH}^-}}{\partial x} \right] \, dx + \varepsilon_\text{r} \varepsilon_0 \frac{\partial V_a}{\partial t} \right),$$

(2.5)

where $V_a$ is the applied voltage, $A$ is the cross-sectional area of the electrodes and $d$ is the gap between the electrodes. Small gaps are defined by $A \gg d^2$. The use of the Morrow–Sato equation allows the displacement current to be included to give the true total external current owing to either AC-applied voltages or a voltage impulse applied to a solution.

(c) The pH calculation

We calculate the concentration of hydronium ions and use this to give an approximation to the pH using Sorensen’s original definition of pH (Sorensen 1909): $\text{pH} = -\log_{10}[\text{H}^+]$, where $[\text{H}^+]$ is the concentration of hydronium ions in moles per cubic decimetre (Daintith 2000). The modern definition modifies this pH value using an activity factor, which depends on the nature of the ions in solution as the hydronium activity may be affected by screening. As we are dealing with pure water, the activity of the hydronium is not expected to be modified by the minority hydroxide ions near the cathode, but there may be a modification near the anode. We assume that the temperature of the water is 25°C, so that the pH of pure water in equilibrium is 7.

3. Numerical methods

The numerical method used to solve the continuity equations is an implicit flux-corrected transport method described in detail elsewhere (Morrow & Noye 1989; Steinle & Morrow 1989). For the long calculations required, with approximately $10^9$ time-steps, it is crucial to use a very accurate numerical algorithm. This method has been used for very long calculations in gas discharges for corona (Morrow 1997), streamer (Morrow & Lowke 1997) and lightning...
(Morrow & Blackburn 2002) calculations; it has been shown to introduce negligible numerical dispersion or numerical diffusion with the errors randomizing rather than accumulating.

The time-step for the calculations is limited by the Courant–Friedrics–Levy condition for stability (Roache 1972) given by

$$\Delta t \leq \frac{\Delta x}{W},$$

where $\Delta t$ is the time-step, $\Delta x$ is the mesh size and $W$ is the ion drift velocity. $\Delta t$ must be evaluated after every time-step on the entire mesh and the minimum value used.

A very fine mesh must be used with the minimum $\Delta x = 2\text{nm}$ near the boundary where the electric field and $W$ are large; hence $\Delta t$ is generally small and many time-steps are necessary. Typically, approximately $10^9$ time-steps are used for many of the calculations presented. It is not possible to follow the DC case with an applied voltage of 0.82V to full relaxation as the computer time required becomes prohibitive; eventually, the difference in the charge densities between each species at the boundary exceeds the precision of the computer (even using double precision). However, at lower applied voltages of 0.4V and less, it is possible to follow the calculation until the current is close to zero.

The geometry for the calculation is simply two plane metal electrodes separated by pure water with some external circuit attached to apply the required potentials. (Figure 6 may serve as a diagram of the geometry where the left and right vertical axes represent the electrodes and the strong variation in pH at each electrode can be seen.) The boundary conditions used for the ions at an electrode are non-conducting boundary conditions at each electrode where ions flow to and from the boundary; the ions do not flow across the boundary or emanate from the boundary.

4. Physical data for water

The static dielectric constant of water has been measured by many authors as summarized in Fernández et al. (1995) and does not vary significantly with frequency in the range from 0 to 20MHz; for the calculations presented here $\varepsilon_r = 78.5$ at a temperature $T = 298\text{K}$.

Standard values for hydronium and hydroxide ion mobilities and diffusion coefficients have been used (Adamson 1973; Atkins 1998):

$$\mu_{\text{H}^+} = 36.2 \times 10^{-8} \quad \text{and} \quad \mu_{\text{OH}^-} = 20.5 \times 10^{-8} \text{m}^2\text{V}^{-1}\text{s}^{-1},$$

while

$$D_{\text{H}^+} = 9.31 \times 10^{-9} \quad \text{and} \quad D_{\text{OH}^-} = 5.27 \times 10^{-9} \text{m}^2\text{s}^{-1}.$$  

These values for mobility have recently been verified using capillary electrophoresis techniques (Duso & Chen 2002), and the mobilities and diffusion coefficients are related by the Nernst–Townsend equation (Huxley & Crompton 1974): $D/\mu = kT/e$, at a temperature $T = 298\text{K}$, where $k$ is Boltzmann’s constant.

Electric double-layers in pure water

The recombination coefficient ($\beta_W$) has been measured for pure water by Ertle & Gerischer (1961) (see also De Maeyer & Kustin 1963); they obtained $\beta_W = 2.32 \times 10^{-16} \text{ m}^3 \text{ s}^{-1}$. We assume that $\beta_W$ is not modified by changes in pH, i.e. the hydronium ion concentration, over the range that applies in the calculations. A suitable value for $\alpha_W$ can be derived by considering that for pH = 7 at equilibrium $\alpha_W = \beta_W \rho_{H^+} \rho_{OH^-}$ and $\rho_{H^+} = \rho_{OH^-} = 6.022 \times 10^{19} \text{ m}^{-3}$, giving $\alpha_W = 8.41 \times 10^{23} \text{ m}^{-3} \text{ s}^{-1}$.

The computational mesh varies with position and it is defined in these calculations with an initial spacing at each electrode of $dx_{j+1/2} = 2.0 \text{ nm}$. For these calculations, where two electrodes are considered, the mesh expands exponentially from one electrode to the centre of the solution then contracts exponentially to the other electrode; 50 mesh points are placed over a gap of 500 $\mu\text{m}$ between electrodes. The anode is set at $x = 0 \mu\text{m}$ and the cathode at $x = 500 \mu\text{m}$.

The potential is applied to the anode and the cathode is at 0 V. In order to make a comparison with the theoretical results of Brüesch & Christen (2004), a voltage of 0.82 V is applied initially; however, an equilibrium is not reached at this voltage for a finite number of calculations. However, by applying voltages of 0.4, 0.3, 0.2 and 0.1 V, equilibrium solutions can be examined.

5. Results

(a) Current decay

With an applied voltage of 0.82 V, the current obtained as a function of time is shown as the upper curve of figure 1. The current has an initial value of $7.33 \times 10^{-7} \text{ A}$ and initially decays rapidly but then decays much more slowly and does not reach its equilibrium value of close to zero even after 4 s and greater than $10^9$ time-steps. If the applied voltage is reduced to 0.4 V, then a relatively low current
is reached after 3 s, with much faster current decay as the voltage is reduced to 0.3, 0.2 and then 0.1 V.

(b) The conductivity of pure water

The initial current represents the current that flows in the absence of ion double-layers at the electrodes and is driven by a uniform field. This initial current can therefore be used to calculate the conductivity of pure water. The conductivity value obtained is independent of the applied voltage as expected as constant mobility and diffusion coefficients are used and no space–charge effects are active initially. The initial current was used to calculate the conductivity of pure water; the value $\sigma = 5.68 \, \mu\text{S m}^{-1}$ was obtained. This agrees closely with the generally accepted value for deionized water: $\sigma = 5.5 \, \mu\text{S m}^{-1}$ (Pashley et al. 2005). Note that Pashley et al. (2005) obtained a considerably higher value for the conductivity of degassed water. However, the ion mobilities and diffusion coefficients used in the calculations presented here are those appropriate for deionized water (not degassed water); therefore, the value for conductivity should be close to the generally accepted value for pure but not degassed water.

(c) Current decay times

The decay curve for the current is more complex than a simple exponential curve; however, it is convenient to define the decay time ($\tau$) as the time for the current to decay to $1/e$ of its initial value. Figure 2 shows the log of the decay time as a function of the applied voltage. This figure shows a curve for an approximate fit to the decay time dependence on the applied voltage ($V$) provided by the empirical equation:

$$\tau \approx 1.5 \times 10^{-2} \exp(5 \, V) \, \text{s.}$$  \hspace{1cm} (5.1)
Electric double-layers in pure water

Figure 3. Number densities of hydronium ions (H$_3$O$^+$) (line with plus symbols) and hydroxide ions (OH$^-$) (line with circles) (a) near the anode and (b) near the cathode in pure water evaluated for the case when 0.4 V is applied for a time of 3 s.

(d) Charge and field distributions

Results are presented for the solution obtained when 0.4 V is applied for 3 s. This case is chosen because the current has relaxed close to zero and the ion double-layers are fully formed. Figure 3a,b shows the hydronium and hydroxide ion-density distributions at the anode and the cathode, respectively. At the anode (figure 3a), the positive hydronium ions are depleted down to a density of approximately $10^{16}$ m$^{-3}$ as they are driven away from the positive charges on the anode. Their numbers only return to the equilibrium value (defined by a pH of 7; approx. $6 \times 10^{10}$ m$^{-3}$) at a distance of 5 µm. In contrast, the hydroxide ions are drawn to the anode and their density rises from their equilibrium value at 5 µm
Figure 4. Net charge number density distributions (a) near the anode and (b) near the cathode in pure water, evaluated for the case when 0.4 V is applied for a time of 3 s.

from the anode and reaches a maximum value of approximately $10^{23} \, \text{m}^{-3}$ at the anode. At the cathode (figure 3b), the opposite occurs with the hydronium ions reaching a maximum of approximately $10^{23} \, \text{m}^{-3}$ and the hydroxide ions depleted to a density of approximately $10^{16} \, \text{m}^{-3}$.

The net charge density is negative at the anode (figure 4a) and is positive at the cathode (figure 4b).

These charges give rise to a steeply varying electric field at the anode with a negative slope (figure 5a), and at the cathode with a positive slope (figure 5b). After a distance of 3 μm from both electrodes, the electric field is low and tending to zero (figure 5a,b).
Electric double-layers in pure water

Figure 5. Electric field distribution (a) near the anode and (b) near the cathode in pure water evaluated for the case when 0.4 V is applied for a time of 3 s.

(e) Distribution of pH

The pH variation across the gap between electrodes can be computed from the hydronium ion distribution as shown in figure 6. Over most of the gap, the pH is held at a value of 7 by the strong and balanced source terms for dissociation and recombination; only at the electrodes can the high electric fields of the ion double-layers disturb this equilibrium. The depletion of hydronium ions at the anode causes the pH to rise to a value of 10.5, whereas at the cathode, the accumulation of hydronium ions causes the pH to fall to a value of 3.5. The pH distributions close to the anode and the cathode (shown in figure 7a,b) indicate that the pH is considerably disturbed from the equilibrium value within a distance of 1 μm from each electrode.

As biomolecules of interest have diameters of approximately 10 nm, it is useful to analyse the pH variation within 20 nm of each electrode (as shown...
Figure 6. The pH distribution over the entire gap between electrodes in pure water, evaluated for the case when 0.4 V is applied for a time of 3 s.

Figure 7. The pH distribution (a) near the anode and (b) near the cathode in pure water, evaluated for the case when 0.4 V is applied for a time of 3 s.

Electric double-layers in pure water

Figure 8. The pH distribution within a distance of 20 nm from (a) the anode and (b) the cathode in pure water, evaluated for the case when 0.4 V is applied for a time of 3 s. The pH departs substantially from 7 and is approximately constant over dimensions on the scale of a biomolecule.

in figure 8a, b). A biomolecule with a diameter of 10 nm close to the anode would be enveloped in a solution of pH close to 10.5, and close to the cathode it would be enveloped in a solution of pH close to 3.5.

Figure 9 shows the effect of a variation in the applied voltage on the pH near the anode and the cathode. At the anode (figure 9a), the pH rises linearly with the applied voltage and can be defined with good precision by the equation:

\[ \text{pH} = 7 + 8.73 \ V, \]  \hspace{1cm} (5.2)

where \( V \) is the applied voltage.

Similarly, at the cathode (figure 9b), the pH decreases linearly and may be described by the equation:

\[ \text{pH} = 7 - 8.73 \ V. \]  \hspace{1cm} (5.3)
Figure 9. The points show the effect of variation of the applied voltage on the pH at (a) the anode and (b) the cathode in pure water, evaluated for the case when 0.4 V is applied for a time of 3 s, close to equilibrium. The line is the fit provided by the empirical equations (5.2) for (a) and (5.3) for (b).

(f) Comparison with the time-independent results of Brüesch & Christen (2004)

The results presented above are for a relatively relaxed solution after 3 s with an applied voltage of 0.4 V. Unfortunately, the only theoretical results available to compare with the results presented here are the analytical equilibrium results of Brüesch & Christen (2004); they use a higher applied voltage equivalent to 0.82 V for the case presented here. As has been discussed above, it is impractical to continue using an applied voltage of 0.82 V to calculate beyond 4 s using more than $10^9$ time-steps. Nevertheless, our non-equilibrium solution after 4 s is compared with the calculations of Brüesch and Christen in figure 10. Surprisingly, the results agree very well with the equilibrium results of Brüesch and Christen except those very close to the cathode.
Figure 10. The present computed pH distribution close to the cathode in pure water (dashed curve) for an applied voltage of 0.82 V applied for 4 s (>10⁹ time-steps) compared with the equilibrium calculations of Brüesch & Christen (2004), (points represented as plus symbols).

6. Discussion

The decay of the current after the voltage has been applied is not exponential and depends on complex interactions and the movements of charges. For example, diffusion competes with ion drift, and the source terms compete to maintain a pH of 7, while space–charges modify the electric field. When the voltage is first applied, the electric field penetrates the solution and ions begin to move; this constitutes the initial current. At each electrode, charges move either towards the electrode or away from it revealing a net charge that raises the electric field, while in the bulk of the water away from the electrodes, the electric field falls. Eventually, all the voltage is dropped across the two ion double-layers that are in equilibrium, and the electric field in the bulk of the water is virtually zero; the current goes to zero.

The higher the voltage, the more ions must move to create the ion double-layers; thus, the decay time for the current increases rapidly with voltage. These results can be compared with previous work with NaCl solutions (Morrow et al. 2006); an empirical equation for the relaxation time for that case was obtained as follows:

\[ \tau \approx 0.128 M^{-0.517} \exp(92 V^2) \mu s, \]

where \( \tau \) is the relaxation time, \( M \) is the molarity and \( V \) is the applied voltage. Applying this equation for the case of pure water presented here does not give the correct decay times. An exact agreement cannot be expected because (i) the equation is an empirical one; (ii) the ion densities are many orders of magnitude smaller; (iii) the ion properties are quite different; and (iv) there are very strong sink and source terms active. However, equation (6.1) does predict
the trend of the results seen with a much more rapid decay in the current for a modest reduction of the voltage. The empirical equation developed in this paper (equation (5.1)) may be a useful guide for future results.

Surprisingly, for conditions close to equilibrium, the pH at the anode rises linearly with the voltage, and the pH at the cathode falls linearly with the voltage. It is not at all clear why this is the case. However, this relationship can be very useful in estimating the effects of any given applied voltage on the pH at the electrodes.

The ion densities at the centre of the bulk of the water in the absence of a perturbing electric field are kept tightly in balance and equal to approximately $6 \times 10^{19} \text{m}^{-3}$ to maintain the pH at 7. After a voltage has been applied and the current flowing in the circuit is close to zero (indicating that the ion double-layers are fully formed), then the ion densities closer than 2 $\mu\text{m}$ from the electrodes begin to diverge from their equilibrium values and eventually differ by seven orders of magnitude at each electrode. The net charge produced by this ion-density difference near each electrode produces a very steeply rising electric field at each electrode.

The pH is constant at 7 over most of the gap during the example studied in detail (with an applied voltage of 0.4 V); however, it rises to 10.5 at the anode, falls to 3.5 at the cathode and the disturbance in the pH value extends out 2 $\mu\text{m}$ from each electrode. A most interesting result is that on the scale of biomolecules (10 nm), the pH is almost constant at >10 at the anode, and <4 at the cathode. Protein denaturation with pH change is a well-known phenomenon (see Scopes (1994), or Lehninger (1978)). This is because changing the net charge on a protein changes the forces holding a protein in a particular shape and the protein may uncoil or fold in a different manner. This means that both the charge on biomolecules such as proteins and their molecular configuration may be greatly changed at each electrode compared with their values in the bulk of the water.

The agreement between the results presented here and those of Brüesch & Christen (2004) is very good and may improve if the calculations are driven further to give a circuit current closer to zero. However, the ion double-layer structure is rapidly set up and changes minimally as the current reduces; for example, with an applied voltage of 0.4 V, the result after 1 s is very similar to that after 3 s. The divergence of the results presented here for calculations very close to the cathode from those of Brüesch and Christen is probably a result of the fact that the calculations have not reached equilibrium and charges are still moving to achieve a higher net charge at the cathode.

No published experimental results have been found with which to compare the calculations presented. While it is hard to imagine making pH and ion concentration measurements in the region where strong variations occur close to the electrode, it should be possible to measure the current decay times as a function of the applied voltage.

The results presented in this paper have been obtained using an extraordinary number of time-steps, approximately $10^9$. This is because of the requirement for a very fine mesh size of 2 nm in a region where the electric field is very high in order to obtain stable results at each electrode. The very high electric field (and hence drift velocity) and small mesh size at each electrode mean that a very small time-step may be taken as defined by the Courant–Friedrics–Levy condition...
for stability (Roache 1972). For example, with an applied voltage of 0.4 V, after 3 s and $5 \times 10^8$ time-steps, the time-step used was 3.8 ns. Such long calculations are possible only when the extremely accurate implicit flux-corrected transport algorithm is used, as discussed in §1.

7. Conclusions

This work presents the first solution of the full time-dependent dissociation–recombination drift–diffusion problem in pure water when an electric potential difference is applied between metallic electrodes.

The main results are as follows:

— The calculated position dependencies of ion densities and pH near the cathode some seconds after the application of the voltage approach those of the steady-state solution of Brüesch & Christen (2004).
— The value of the conductivity of pure water obtained from the initial current response to an applied voltage agrees well with the accepted value for the conductivity of deionized water.
— The maximum or minimum pH at each electrode varies linearly with the applied voltage.
— The relaxation time for the current in the external circuit varies approximately exponentially with the applied voltage.
— The maximum electric field at each electrode at equilibrium is very high; it is of the order of $1.5 \text{MV m}^{-1}$ for an applied potential of 0.4 V.

The pH remains locked at pH 7 in the bulk of the water away from the electrodes, but at the anode the pH rises to 10.5 and at the cathode falls to 3.5. On the scale of biomolecules of interest (10 nm), the pH is greater than 10 at the anode and less than 4 at the cathode over distances of the order of 30 nm. This has significant consequences for the net charge on biomolecules and their configuration near the electrodes when a voltage is applied. The results have direct relevance to biosensors that use the adsorption of molecules onto electrodes. The large changes in pH that accompany even small applied voltages will have significant impacts on the state of the adsorbed molecules.

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