ORIGINAL PAPER

The electroneutrality approximation in electrochemistry

**Edmund J. F. Dickinson · Juan G. Limon-Petersen ·
Richard G. Compton**

Edmund J. F. Dickinson

Richard G. Compton

Juan G. Limon-Petersen

For the special issue "Electrochemistry: Past, Present and Future".

E. J. F. Dickinson · J. G. Limon-Petersen ·
R. G. Compton (✉)
Physical and Theoretical Chemistry Laboratory,
Department of Chemistry, University of Oxford,
South Parks Road, Oxford, OX1 3QZ, UK
e-mail: richard.compton@chem.ox.ac.uk

Abstract The electroneutrality approximation assumes that charge separation is impossible in electrolytic solutions. It has a long and successful history dating back to 1889 and may be justified because of the small absolute values for the permittivities of typical solvents. Dimensional analysis shows that the approximation becomes invalid only at nanosecond and nanometre scales. Recent work, however, has taken advantage of the capabilities of modern numerical simulation in order to relax this approximation, with concomitant advantages such as avoiding paradoxes and permitting a clear and consistent 'physical picture' to describe charge dynamics in solution. These new theoretical techniques have been applied to liquid junction potentials and weakly supported voltammetry, with strong experimental corroboration for the latter. So long as dynamic processes are being studied, for which analytical solutions are unavailable in any case, numerical simulation is shown to render electroneutrality unnecessary as an *a priori* assumption.

Introduction

The electroneutrality approximation

Mass transport in the absence of convection but in the presence of an electric field is described by the Nernst–Planck equation:

$$\mathbf{J}_i = -D_i \left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla \phi \right) \tag{1}$$

where for species i, $\mathbf{J}_i$ is its flux vector, D_i is its diffusion coefficient, C_i is its concentration and z_i is its charge. F is the Faraday constant, R is the gas constant, and T is temperature. ϕ is the electrical potential, such that the electric field may be expressed as $-\nabla\phi$. Often the Nernst–Planck equation is considered together with an expression for conservation of mass:

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot \mathbf{J}_i = D_i \nabla \cdot \left(\nabla C_i + \frac{z_i F}{RT} C_i \nabla \phi \right) \tag{2}$$

For systems involving n different species, the set of n equations of the form of Eq. 2 contains $(n + 1)$ unknowns, i.e. the n concentrations C_i and the potential ϕ. Therefore, an additional relation is required to solve this set of equations. A very common choice is the electroneutrality approximation, which states that:

$$\sum_i z_i C_i = 0 \tag{3}$$

that is, there is no charge separation anywhere in solution and so neutrality is maintained everywhere. In the following discussion, we shall explain the origin of this approximation and assess its past use, before considering to what extent electroneutrality remains an applicable approximation for electrochemical problems, in light of recent theoretical and experimental developments.

Origin of the electroneutrality approximation

When charge separation occurs in electrochemistry, Coulombic forces influence the transport of ionic species. To describe mass transport, it is necessary to correlate the induced migration in terms of an electric field with the degree of charge separation in solution. Gauss's Law, one of Maxwell's equations, provides the necessary field formulation in classical electrodynamics:

$$\nabla^2 \phi + \frac{\rho}{\epsilon_s \epsilon_0} = 0 \tag{4}$$

where ρ is the charge density ($\mathrm{C\,m^{-3}}$), ϵ_s is the relative permittivity of the medium, and ϵ_0 is the permittivity of free space.

If the only charge carriers are dissociated ions, the charge density is related to the number densities of these ions:

$$\rho = e \sum_i z_i n_i = F \sum_i z_i C_i \tag{5}$$

where in addition to the definitions above, n_i is the number density of the ion i, and e is the charge on an electron. Hence:

$$\nabla^2 \phi + \frac{F}{\epsilon_s \epsilon_0} \sum_i z_i C_i = 0 \tag{6}$$

This is commonly called the Poisson equation and is the fundamental relation between electric field and charge separation for an electrolytic solution.

Dimensional analysis of the Poisson equation leads us to certain conclusions. Firstly, we normalise potential by the 'thermal volt' RT/F and concentration by the bulk concentration of electrolyte C^*:

$$\theta = \frac{F}{RT} \phi \tag{7}$$

$$c_i = \frac{C_i}{C^*} \tag{8}$$

$$\nabla^2 \theta + \frac{F^2 C^*}{RT \epsilon_s \epsilon_0} \sum_i z_i c_i = 0 \tag{9}$$

and multiplying through by the collection of constants:

$$2r_D^2 \nabla^2 \theta + \sum_i z_i c_i = 0 \tag{10}$$

where r_D is a characteristic parameter with units of length, commonly referred to as the Debye length:

$$r_D = \sqrt{\frac{RT \epsilon_s \epsilon_0}{2F^2 C^*}} \tag{11}$$

The Debye length indicates the length over which separated charge, and hence electric fields, are screened in an electrolytic solution. For a given degree of charge separation, the extent over which the electric field can vary, and hence over which $\nabla^2 \theta$ can take a large value, is limited by the Debye length. If the Debye length is vanishing on all significant length scales of the system we are considering, we can approximate $r_D \approx 0$, and hence:

$$\sum_i z_i c_i = 0 \tag{12}$$

which is equivalent to Eq. 3, the electroneutrality condition. Since the Debye length is typically of the order

of nanometres in electrochemical systems, this would appear to be a strong approximation.

The inherent paradox in the electroneutrality approximation

The first use of the electroneutrality approximation was by Walther Nernst in 1889 [1], in his consideration of electromotive forces in electrolyte solutions. He introduced it without justification, stating:

> In that within the solutions, no free electricity [*sic*][1] can persist (at least not in any quantity such that its total amount would be remotely comparable to the fixed + and − electricity on the ions), so the condition
>
> $$p'_1 + p'_2 + \ldots = p''_1 + p''_2 + \ldots$$
>
> must be fulfilled.
> – Walther Nernst, May 1889[2]

Max Planck employed the electroneutrality approximation in order to find the steady-state potential difference across a liquid junction in which two solutions of different concentrations are left to freely diffuse into one another [2]. In the course of this work, he highlighted its dangers:

> The action of electrostatic forces was accounted for by Nernst, via the assumption that absolutely no free electricity [*sic*] may arise within the solution; hence these forces may indeed be ascertained. This assumption admittedly corresponds to the laws of electrostatics to a good approximation, and also suffices for the objective pursued by Nernst; but it would only be exactly accurate if the charges of the ions, as measured electrostatically, were infinitely large. As the ions indeed have very large, but nevertheless finite, electrostatic charges, it follows that before electrical forces can come into action, as a rule a finite and determinable amount of free electricity [*sic*] must have been established in the solution.
> – Max Planck, December 1889[3]

On the grounds of the vanishing value of ϵ_0, however, Planck persuaded himself that the 'free electricity', that is, charge separation, is equally vanishing, and hence electroneutrality is an acceptable approximation which may be advocated for its utility in finding mathematical solutions to problems in the theory of electrolytic solutions. Already by May of 1890, 5 months after the paragraph above was submitted, Planck was sufficiently confident in the usefulness of the approximation that he introduced it in his more general work on liquid junction potentials without any further caveat, merely stating it as fact established by his previous work [3].

Planck was strictly correct in his criticism, however: despite its widespread use, the electroneutrality condition suffers from a fundamental inherent paradox which is not often acknowledged. In solving the Nernst–Planck equations, we are trying to determine the effect of the electric field, which only arises due to Coulombic forces and hence only arises in the presence of a net charge separation. Yet, to determine the electric field, we have made the approximation of zero charge separation—what, then, is the cause of the electric field? In effect, the electric field can take any value it pleases in order that electroneutrality is maintained. Coulombic attractions are hence arbitrarily strong, such that any charge separation is damped *instantly* by an arbitrary migration of opposite charge. The electric field is not constrained in any way to satisfy Maxwell's equations.

In the face of such a paradox, it is (very!) surprising that the electroneutrality approximation can be so successful. We shall demonstrate that for most systems it fails only at very short timescales (compared with the Debye time $t_D = r_D^2 / D$, where D is a characteristic diffusion coefficient for the electrolyte), where the finite mobility of ions prevents the instantaneous passage of charge, or at very short space scales (compared with the Debye length) where the approximation of screening of charge separation over an infinitesimal distance is no longer accurate.

Electroneutrality for liquid junctions

Historical background

The liquid junction potential problem in electrochemistry motivated the earliest use of the electroneutrality approximation. Experimentally, the system under consideration arises when two solutions of unequal concentration of electrolyte, or of different composition altogether, are brought into contact. The inequality between different rates of diffusion for different ions induces a charge separation and hence an electric field,

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[1] The [*sic*] is used to indicate antiquated terminology while maintaining a faithful translation. "Free electricity" is taken to mean "free charge density" in a modern translation, but in the originals the word(s) "(freie) Elektrizität" are used consistently in place of "Ladung" or "Ladungsdichte".

[2] Author's own translation from the original, pp 133–134. The p'_i refer to osmotic pressures of cations and the p''_i refer to osmotic pressures of anions. We infer that by "fixed electricity", Nernst means that $\sum_i z_i c_i \ll \sum_i |z_i| c_i$.

[3] Author's own translation from the original, p 163.

which balances transport rates until a constant potential difference is observed. The initial work of Nernst [1] and Planck [3] was followed by the development of a simpler equation for the liquid junction potential by Henderson [4], who followed the majority of Planck's arguments. These include a finite boundary layer between the solutions, which is electroneutral and at steady state.

Doubt has long been cast on the meaning of these results. In 1930, Edward Guggenheim wrote 'The physical conditions corresponding to the Planck formula have not generally been understood' [5] and identified the exclusion of boundary layers in the theory of a 'free' liquid junction as corresponding more closely to experimental reality. The mathematical tools for dealing with such free liquid junctions were developed by Hickman [6], who argued that electroneutrality is the long time asymptote to a complete description of the behaviour, but on this occasion the implications of the results for the dynamic behaviour of liquid junctions were not discussed. This work was followed up by Jackson who clearly described the long time behaviour and critically assessed the use of electroneutrality [7].

Recent work [8, 9] has demonstrated that liquid junction potentials may not correctly be associated with a steady state but rather are dynamic (non-equilibrium) properties, which are not electroneutral, thus resolving the paradox identified above of a potential difference occurring in the absence of charge separation.

Dynamic theory

The most recent arguments, by Dickinson et al., were as follows, in brief [9]. Let us suppose two adjoining solutions which are rapidly allowed to freely diffuse into one another. If a cation and anion have different diffusion coefficients and are both subject to a concentration gradient, their rates of diffusion are initially unequal. This engenders a charge separation and consequently an electric field. To attain a condition of equilibrium (equal concentrations everywhere, and hence no concentration or charge gradients), if there has been a net transfer of charge across the junction at short time, there must be some transfer of charge in the opposite direction at long time, before equilibrium can be recovered. Therefore, the system will be electroneutral at equilibrium, but if an infinite supply of bulk solution is available on either side of the junction, this equilibrium will not occur at finite time. The system therefore discharges at a rate proportional to continuing diffusion, but also the junction region

where electroneutrality is not obeyed expands at the same rate. Therefore, the quantity of charge separated decreases as the distance of its separation increases, yielding a constant potential difference even though the system is not at steady state and not electroneutral.

The use of modern simulation techniques, in addition to traditional mathematical analysis, was vital in the determination and confirmation of these arguments; electroneutrality was not assumed *a priori* in the simulation and so charge separation effects could be considered. The simulation procedure was to solve the Nernst–Planck–Poisson equations (Eqs. 2 and 6) in normalised space and time coordinates (with respect to the Debye length and Debye time), from an initial condition of concentrations described by step functions. The outer boundaries were set to bulk concentration at a distance of $x = \pm 6\sqrt{Dt_{max}}$, which is equivalent to the provision of an infinite quantity of bulk solution. The discretisation of these equations led to a set of non-linear simultaneous equations for the discretised variables at each time step, which were solved using the iterative Newton–Raphson method, with details of the numerical methods being provided in the Supporting Information [9]. Both potential difference and electric field data were inferred directly from the simulation results.

The liquid junction potential and maximum system electric field are shown in [9] at Fig. 1 for an example
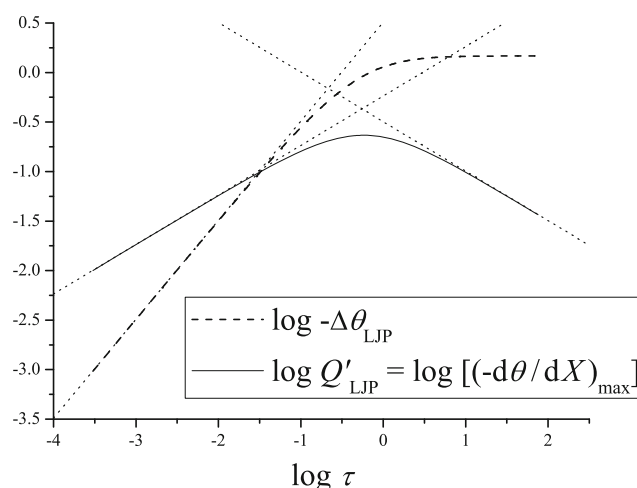
Fig. 1 Dynamic behaviour of the liquid junction potential, $\Delta\theta_{LJP}$, and degree of charge separation, Q'_{LJP}, in a liquid junction in which 0.1 M HCl is allowed to freely diffuse into 0.01 M HCl. Both axes have been normalised, with $\tau = t/2t_D$ (linearly proportional) and $X = x/\sqrt{2}r_D$. θ is defined as in the main text. Reprinted with permission from Dickinson et al. [9]. Copyright 2010 American Chemical Society

system, in which a solution of 0.1 M HCl is allowed to freely diffuse into a solution of 0.01 M HCl. The latter variable is representative of the quantity of charge separation in the system, due to Gauss's Law. The more rapid diffusion of H^+ to the left induces a negative liquid junction potential. The key features of this graph are the evolution of the liquid junction potential at a rate initially $\propto t$, as the charge separation evolves $\propto t^{\frac{1}{2}}$. The assumption of zero migrational feedback onto the mass transport can be applied to predict the $t \to 0$ asymptotes, which the simulation fits exactly; the evolution of the charge separation and the potential difference is clearly entirely due to the separation of charge.

As the electric field develops, it acts to slow the mass transport of protons and to accelerate the mass transport of Cl^- ions, thus slowing the development of charge separation and, at length, reversing it. A concentration profile and potential profile are shown in [9] at the time of maximum charge separation; it is clear that the position of electroneutrality, the 'junction position', diffuses to the left along with the ions. As the system tends back to equilibrium, the transport of Cl^- across this plane is faster than that of H^+ such that electroneutrality is slowly recovered at long time. The time dependence of the continuing diffusion of both ions causes the charge separation to decay $\propto t^{\frac{1}{2}}$ while the region of separated charge, i.e. the diffusion layer, grows $\propto t^{\frac{1}{2}}$, and so the potential difference measured across the junction tends to a constant.

Again, the $t \to \infty$ asymptotes are entirely predictable from the mathematical work of Hickman [6], confirming the accuracy of the simulation, and the implicit 'physical picture' of this work is confirmed with great clarity due to the presentation of large quantities of data. Additionally, the use of simulation techniques allows the identification of exact time and space scales over which electroneutrality is closely obeyed. In typical liquid junction systems, the maximum charge separation occurs at around one Debye time after contact between the solutions.

While exact results are only available for the complete system without electroneutrality in certain asymptotes and for the simplified Type 1 junction with a concentration gradient for a single cation and anion, numerical solution is constrained only by simulation runtime in terms of the complexity of the system. Therefore, complicated four-species systems have been simulated [10], confirming that the dynamic theory presented above applies to all cases. In addition, phenomena of theoretical interest, and perhaps practical

utility, can be determined, such as multi-layer liquid junctions in which multiple layers of opposite charge arise dynamically in the presence of more than three different ionic species. Furthermore, quantitative deviations due to the electroneutrality approximation can be assessed, by comparing the Henderson equation to the more complete simulation model.

The incorporation of a partially permeable membrane allows the formation of a double layer in which charge remains separated at steady state which is very close to the membrane, either instead of or in addition to a diffusional liquid junction of the dynamic type discussed above. In either case, simulation reveals that electroneutrality is not obeyed across a range of around three Debye lengths [11] (see Fig. 2). This is in good agreement with the dimensional analysis presented above and leads to deviations from the Donnan or Henderson equations; evidently an analysis based on the electroneutrality approximation would fail to predict such effects.

Discussion

We note that a particular advantage of finite difference simulation is that the Poisson equation is scarcely more complicated to implement than the electroneutrality condition and the use of the latter does not particularly
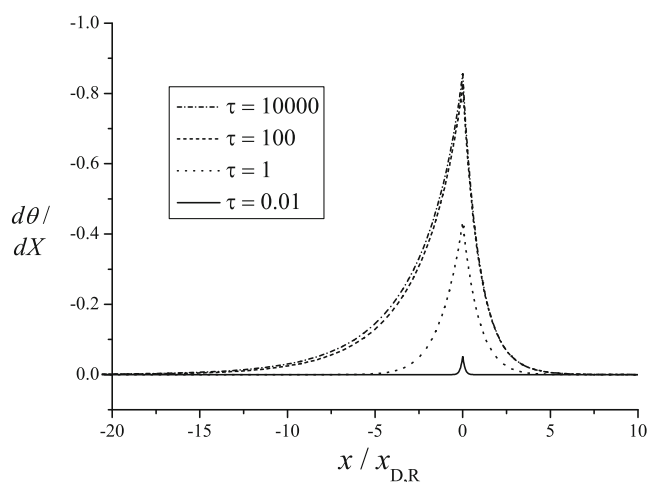
Fig. 2 The developing electric field (region of charge separation) for steady-state double layers either side of a membrane in an AX|AX system where the ratio of concentrations in $C_R^*/C_L^* = 10$ and the membrane is impermeable to X^-, simulated using the Poisson equation in full. Both axes have been normalised, with $\tau = t/2t_{D,R}$ and $X = x/\sqrt{2}r_{D,R}$, with R indicating to the right of the membrane. Reprinted with permission from Ward et al. [11]. Copyright 2010 American Chemical Society

aid the stability of a simulation, so electroneutrality confers no particular advantages. When calculated in full by dynamic simulation using the Poisson equation, the predicted magnitudes of most liquid junction potentials differ from Henderson's work only by a small amount [10], as may be expected considering the strength of the electroneutrality approximation for long times after solution contact.

The development of the topic of liquid junctions suggests that although electroneutrality facilitates mathematical analysis and may give correct results for certain observables, other methods of theoretical investigation exist, which are not simplified by electroneutrality. By using simulation techniques in order to incorporate the Poisson equation in full, a potential difference is attributable to the quantity and distribution of separated charge. Hence, the simulation studies avoid paradox and hence have an epistemological advantage; physical conclusions drawn from simulation data recorded dynamically are more physically meaningful and have permitted the revision of arguably outdated 'physical pictures' such as equilibrated boundary layers.

Electroneutrality in voltammetry

Introduction

Another major use of electroneutrality, especially in the last 25 years, has been to facilitate the theoretical study of weakly supported chronoamperometry and voltammetry. In the absence of sufficient supporting electrolyte, normally added deliberately to improve solution conductivity, voltammetric methods can no longer be treated using a diffusion-only theory due to the presence of electric fields in the system. In particular, the prediction of the magnitude of ohmic drop and the contribution of migration to the observed current have been problems of considerable theoretical and experimental interest.

We note that non-Faradaic current due to the capacitance of the double layer at the surface of a charged electrode is a widely observed phenomenon in voltammetric experiments. Since this process is entirely due to charge separation, it cannot admit analysis via electroneutrality. A range of other approximations have been applied, including the Debye–Falkenhagen approximation which applies when charge separation is sufficiently small that the Nernst–Planck equations may be linearised. A review of charging processes has been presented by Bazant et al. [12], in which it is made clear that in the linear regime the characteristic timescale of capacitive charging is a mixed timescale between the diffusive timescale associated with the mean mobility

of the ions, and the Debye time itself. The resulting double layer extends over a few Debye lengths and therefore the charge applied to the electrode causes solution electroneutrality to be violated only within a small spatial range, as expected from the Poisson equation.

Historical background

Analytical results for *steady-state* voltammetric currents at low support have been reported by a number of authors [13–18], with Myland and Oldham providing the most general results in this theme of investigation [19, 20]. Common to these studies is the use of the electroneutrality approximation and the additional exclusion of the role of the specific structure of the double layer. These results concern ideal spherical or cylindrical geometries. The application of the Nernst or Butler–Volmer equation to describe the electron transfer is standard; this is assumed to take place at some plane arbitrarily close to the outer edge of the double layer, where electroneutrality is maintained. Additionally, dynamic problems, and more complex steady-state problems, have sometimes been approached using numerical simulation together with the electroneutrality approximation [21–26]. The field has been reviewed by Ciszkowska et al. [27] and by Bond [28].

These studies were able to quantify the two principal effects which arise when voltammetry is performed in media of low ionic strength. The first of these is an 'ohmic drop', i.e. a shifting of voltammetric features to higher overpotentials due to the decreased conductivity of the solution, and the second is the contribution of migration to the incident flux of the electroactive species. Both result from the introduction of a net charge into the solution due to the passage of Faradaic current, which in the absence of sufficient supporting electrolyte cannot be rapidly screened. Interestingly, depending on the relative signs of the change of charge in solution due to electrolysis and the charge on the electroactive species, the effect of migration may be repulsive or attractive. For example, electrodeposition of a cation will make the diffusion layer more negative and elevate limiting current by attracting cations to the surface. Of course, both effects occur entirely due to an uncompensated charge separation in the diffusion layer, and so the explanation of either using electroneutrality is paradoxical, if nonetheless effective.

Alternative approaches

Oldham et al. reviewed the suitability of the electroneutrality approximation for weakly supported steady-state

voltammetry [29] by developing exact expressions for the steady states under two limiting cases, which confirmed the general suitability for electroneutrality when the electrode is larger than nanoscale. The limitations of electroneutrality for nanoelectrodes were discussed by Smith et al., considering the inaccuracy of the approximation where the diffusion layer approaches the scale of the Debye length [30]. A number of approaches have followed in which different models for the double layer, of varying sophistication, have been introduced [31–35]. In many of these works, we note the use of numerical simulation in order to approach the Nernst–Planck–Poisson equation set without approximation, in order to study systems with complex boundary conditions or under transient conditions.

Streeter et al. [36] reviewed the problem of chronoamperometry and introduced a so-called 'zero-field' approximation, in which the detailed structure of the double layer is not considered and simply its infinitesimal size, compared with the diffusion layer, is used to constrain a condition of zero enclosed charge within the plane of electron transfer. This provides a boundary condition with which the Nernst–Planck–Poisson equation can be solved in full; the results presented demonstrated better agreement with a 'full' model assuming a detailed structure for the double layer [33] than did electroneutrality, although both approaches were accurate at experimentally significant times. The zero-field approximation has recently been critically examined, [37] confirming that it, like electroneutrality, is unsuitable at nanoelectrodes where the double layer may be significant in size compared with the diffusion layer.

The zero-field approximation has been successfully applied to model a range of chronoamperometry and cyclic voltammetry experiments at microelectrodes and macroelectrodes, performed in the Compton research group [38–44]. The timescales of these experiments tend to greatly exceed the Debye time, and the electrode is much larger than the Debye length, even with small concentrations of supporting electrolyte. It has been observed that the results differ minimally from those that would result from an electroneutrality approximation, as would be expected for these conditions, although electroneutrality has not been assumed *a priori*. Interestingly, this is the case even under 'extreme' conditions such as the stripping of preconcentrated cadmium from a mercury drop in the total absence of supporting electrolyte, except for the cadmium salt solution [43]. In this case charge is injected very rapidly into solution, but nonetheless the voltammetric currents are, to a very strong approximation, controlled by the maintenance of electroneutrality in the diffusion layer (see Fig. 3). A major conclusion of this work was the much greater demands for 'full support' in cyclic voltammetry during stripping experiments where rapid charge injection into solution is the norm.

Another example of 'extreme' conditions is the electrolysis of a charged redox active ion in the total absence of supporting electrolyte. Therefore, electroneutrality can only be maintained by migration of the counter-ion. This situation was discussed theoretically at steady state using the electroneutrality approximation, by Oldham [19]. Recently, this problem has been approached dynamically, using chronoamperometry and cyclic voltammetry together with quantitative modelling using the Poisson equation and the zero-field approximation [42, 45]. The results show very little discrepancy with Oldham's results (at steady state); those discrepancies that occur can be attributed to a steady state not in fact being achieved on the experimental timescale. Numerical simulation indicates that except at very short time or distance, electroneutrality is obeyed.

As an example, a typical fit of an experimental cyclic voltammogram at trace support is presented at Fig. 4; the presence of ionic impurities in the reactant required the modelling of a trace of inert electrolyte. Furthermore, an example simulation using the Poisson equation with the zero-field approximation is shown for the case with a total absence of added supporting electrolyte at Fig. 5, together with the equivalent result using the electroneutrality approximation. It is clear
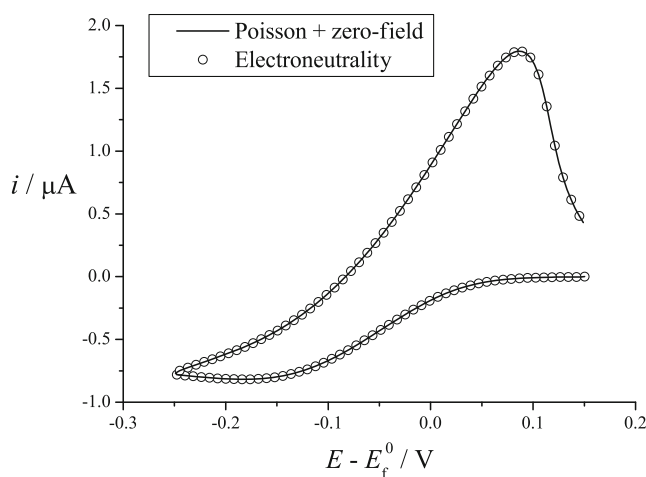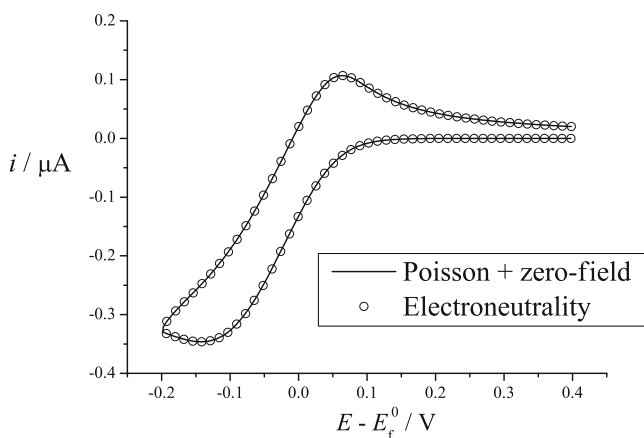

Fig. 3 A comparison of simulated cyclic voltammograms for the formation of a thallium amalgam at a 45 μm mercury hemisphere by reduction of a 5 mM aqueous thallium nitrate solution, and the subsequent stripping of thallium, in the absence of additional supporting electrolyte and at a scan rate of 200 mV s^{-1}. The electroneutrality and zero-field approximations give equivalent results
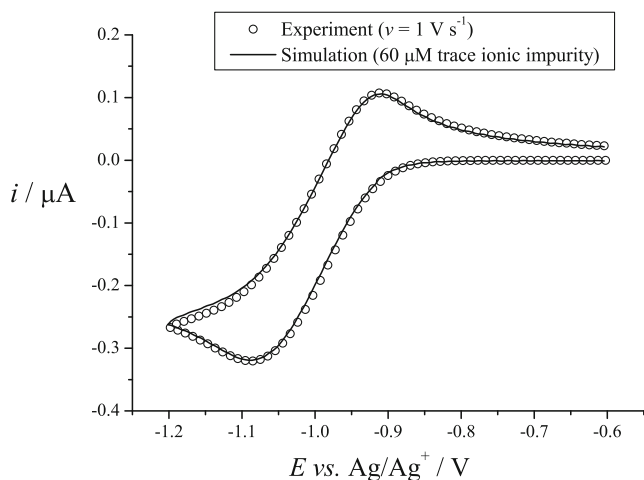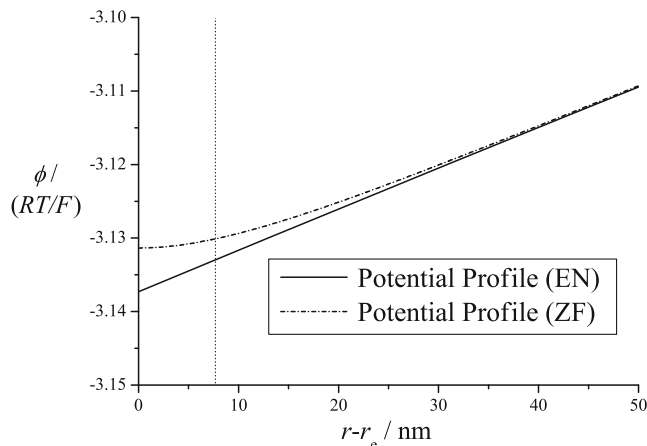
Fig. 4 Experimental voltammetry for the reduction of unsupported 3 mM cobaltocenium hexafluorophosphate in acetonitrile on a 25 μm radius mercury hemisphere, compared with simulation using the Poisson equation and the zero-field approximation. Adapted from Limon-Petersen et al. [45], Fig. 5, p. 140, with permission. Copyright Elsevier (2010)


Fig. 6 A comparison of simulated potential profiles at the forward peak current, for the reduction of unsupported 3 mM cobaltocenium hexafluorophosphate in acetonitrile on a 25 μm radius mercury hemisphere, showing the region in which the predicted potential profile differs between the electroneutrality and zero-field approximations. The *vertical dotted line* marks one unit Debye length from the electrode surface

that the voltammetry is effectively indistinguishable, principally because the strength of the electroneutrality approximation means that the electric field, and hence the concentration profiles, differs only within a few Debye lengths of the electrode surface (Fig. 6).

The use of numerical solution, however, permits the modelling of *dynamic* experiments across the full range of timescales, and hence better determination of experimental parameters such as diffusion coefficients and kinetic parameters as well as improved mechanis-

Fig. 5 A comparison of simulated cyclic voltammograms for the reduction of unsupported 3 mM cobaltocenium hexafluorophosphate in acetonitrile on a 25 μm radius mercury hemisphere, showing that the electroneutrality and zero-field approximations give equivalent results

tic insight. For instance, the numerical simulation of dynamic experiments allowed modelling of an investigation in which the comproportionation of anthraquinone with its dianion was shown to proceed at a diffusionally controlled rate in acetonitrile solution [44], according to the principles set out at steady state by Norton et al. [46].

The investigation compared fully supported and weakly supported voltammetry: under weak support a marked decrease in the transport-controlled current for the second reduction wave was observed (Fig. 7). Since this corresponds to the contribution of repulsive migration to the transport of an anion into a negatively charged diffusion layer, this shows that transport of the radical anion is rate-limiting and therefore comproportionation occurs rapidly. The difference in current is not consistent with transport-controlled reduction of anthraquinone at the surface, since the neutral molecule is unaffected by the presence of an electric field.

We note that steady-state investigation and analysis via electroneutrality could have attained the same conclusions; the elucidation of active comproportionation pathways in the reduction of fullerenes by Kowski et al. is an excellent example [47]. However, the availability of numerical simulation for the analysis of dynamic voltammetry allows the use of different scan rates to investigate the relative rates of different chemical and diffusional processes, and in any case is voltammetric best practice. What is more, once numerical simulation is adopted, the principal virtue of the electroneutrality
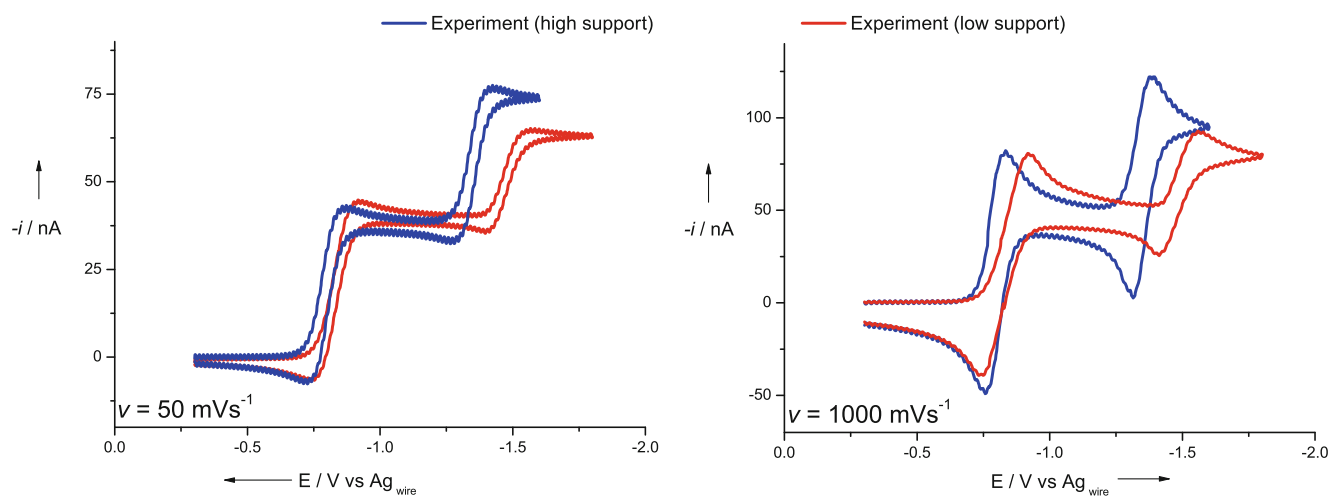
Fig. 7 Experimental voltammetry for the two-electron reduction of anthraquinone in acetonitrile, with full and trace supporting electrolyte and at two different scan rates. Reproduced with permission from Belding et al. [44]. Copyright (2010) Wiley-VCH Verlag GmbH & Co. KGaA

approximation is lost since its implementation is not significantly less complex than a more complete model in which deviations from ideal electroneutrality may also be assessed.

Conclusions

The electroneutrality approximation amounts to the conclusion that insufficient Gibbs free energy is available from diffusion or chemical reaction to separate charge in an electrolytic medium over a long distance or for a long time. In practice, 'long' means with respect to the Debye scale, which is of the order of nanometres and nanoseconds, and therefore charge separation rarely impacts on an experiment and may be treated as absent to a good approximation. This is borne out by detailed theoretical and experimental observation, both for liquid junction systems and for voltammetry under weak support.

The major advantage conferred by the electroneutrality approximation is that it greatly facilitates analytical solution of the Nernst–Planck equations. This still cannot be accomplished for many problems, however, especially if dynamic solution is desired. Modern experiments are typically analysed instead using numerical simulation, especially since this widens the scope of feasible investigations. Our experience is that the electroneutrality approximation does not make numerical simulation more straightforward or more stable, except in certain special cases such as at steady state, or where one species is neutral and hence does not

migrate, or where all species may be assumed to have equal diffusion coefficients [14]. Therefore, it becomes unnecessary as an *a priori* assumption, although it is not in significant error compared with simulation using the full Poisson equation, as expected given the strength of the approximation.

The avoidance of electroneutrality prevents the introduction of troubling paradoxes wherein a potential difference occurs in solution without any accompanying charge separation. Therefore, more complete physical interpretations are available for simulations without electroneutrality. We expect this useful and insightful but now perhaps superfluous approximation to steadily cease to be a cornerstone of the analysis of coupled diffusion and migration in electrochemistry. By avoiding its use, wider possibilities may be opened for the future, such as the study of short time and space scales or research into greater subtleties of charge dynamics or weakly supported electrochemistry.

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