Electrochemical analysis in charge-transfer science: The devil in the details

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Abstract
It is easy to carry out electrochemical analysis. It is demanding, however, to do it right, as inherent challenges, emerging from details in the data collection and the result interpretation, frequently present themselves. In pertinence to electron–donor–acceptor interactions, herein, we focus on voltammetrically obtained electrochemical potentials and their immense utility for extracting important characteristics of molecular analytes. Recommendations how to address key pending challenges, based on recent developments in electroanalytical and charge-transfer science, accompany the discussions on undesired impacts from irreversibility of oxidation and reduction, supporting electrolytes, choices of reference, liquid junctions, and ‘nonideality’ of molecular shapes. As the wide implications of charge transfer are indisputable, using the tools at our disposal for improving the reliability of electroanalysis is crucial for advancing modern science and engineering.

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Introduction
Heterogeneous charge transfer (CT) is the principal drive for electrochemical transformations. At the same time, electrochemical analysis is of utmost importance for evaluating the energetics of CT processes, such as electron transfer and hole transfer (HT). In particular, the electrochemical potentials of a donor and an acceptor are crucial for estimating the thermodynamic driving force ($-\Delta G^{(0)}$) of CT between them [1].

Along with optical excitation energy, $\epsilon_{00}$, the reduction potentials of the acceptor ($E_{A,\text{red}}^{(0)}$) and of the oxidized donor ($E_{D,\text{ox}}^{(0)}$) define $-\Delta G^{(0)}$ of photoinduced CT, as the Rehm–Weller equation implements [2,3]:

$$\Delta G^{(0)}_{\text{PCT}}(\epsilon) = F \left( E_{D,\text{ox}}^{(0)} - E_{A,\text{red}}^{(0)} \right) - \epsilon_{00} + \Delta G_{\text{chem}}(\epsilon, \epsilon_{D,\text{ox}}, \epsilon_{A,\text{red}}) + W(\epsilon)$$

(1a)

It is not to be confused with the Rehm–Weller equation that describes an empirical relationship between CT rate constants and driving forces that do not reveal Marcus inverted behavior [2,4].

The last term, $W$, accounts for the Coulombic interaction between the donor and the acceptor that, in this case, are non-radical species with initial charges $x$ and $y$, respectively, separated at center-to-center distance $R_{DA}$ [3]:

$$W(\epsilon) = \frac{n^{(y-x-n)}q^2}{4\pi \epsilon_0 \epsilon_{DA}}$$

(1b)

The Born solvation term corrects for the interactions of the donor and the acceptor with the media, which for transferring $n$ electrons is [3]:

$$W(\epsilon) = \frac{n^{(y-x-n)}q^2}{4\pi \epsilon_0 \epsilon_{DA}}$$
Herein, we introduce a concise overview of the electroanalytical techniques yield can prove quite misleading for CT analysis. The broad accessibility to cyclic voltammetry (CV), along with the ease of CV measurements, has made CV the principal experimental technique for obtaining electrochemical potentials [5–9]. As facile as CV and other voltammetry measurements are, inherent systematic errors in interpreting the potentials that electroanalytical techniques yield can prove quite misleading for CT analysis.

The zero-to-zero energy, \( \varepsilon_{00} \), or optical excitation energy, correlates with the difference between the LUMO and the HOMO of the photoexcited species. Upon excitation of the donor, therefore, \( F \left( E_{D}^{(0)} \right| [D] \varepsilon_{D}) - E_{A}^{(0)} \right| [A] \varepsilon_{A}) \) \( - \varepsilon_{00} \) represents the energy difference between the LUMO of the acceptor and the LUMO of the donor, and eq. (1a) yields the driving force of photoinduced ET, \( \Delta G_{\text{PET}}(0) \) [1,12,13]. For electrically excited acceptor, on the other hand, \( F \left( E_{D}^{(0)} \right| [D] \varepsilon_{D}) - E_{A}^{(0)} \right| [A] \varepsilon_{A}) \) \( - \varepsilon_{00} \) correlates with the energy difference between the HOMO of the acceptor and the HOMO of the donor,
and eq. (1a) estimates the driving force of photoinduced HT, \(-\Delta G_{\text{HT}}^{(0)}\) [1,12,13].

Removing \(\varepsilon_{00}\) from eq. (1a) allows for evaluation of the driving force for CT between a donor and an acceptor, when both are in their ground electronic states [1]. It proves immensely important for estimating the driving forces of each of the discreet CT steps in long-range electron hopping from reduced species \(D^-\) to the LUMO of \(A\):

\[
\Delta G_{\text{ET}}^{(0)}(\varepsilon) = F\left( E_{D}^{(0)}(\varepsilon_D) - E_{A}^{(0)}(\varepsilon_A) \right)
+ \Delta G_S(\varepsilon_D, \varepsilon_A) + W(\varepsilon) \tag{2a}
\]

and hole hopping from oxidized species \(A^+\) to the HOMO of \(D\):

\[
\Delta G_{\text{HT}}^{(0)}(\varepsilon) = F\left( E_{D}^{(0)}(\varepsilon_D) - E_{A}^{(0)}(\varepsilon_A) \right)
+ \Delta G_S(\varepsilon_D, \varepsilon_A) + W(\varepsilon) \tag{2b}
\]

As conveniently illustrative as these MO ways of thinking are, the correlations between the electrochemical potentials and the energy levels of the frontier orbitals warrant a great deal of caution. Strictly speaking, electrochemical potentials represent energy differences between the reduced and oxidized states. Similarly, \(\varepsilon_{00}\) represents the energy of transitions between ground and excited states. That is, the electrochemical and spectroscopic measurements yield energy differences between different states rather than between different frontier orbitals. While this consideration unveils

Figure 1

Cyclic voltammograms with the characteristic potentials designated. Cyclic voltammograms showing (a–c) reversible oxidation of 4-fluoro-5-(piperidin-N-yl)anthranilamide (Fpi) and (d–f) irreversible oxidation of 4-(piperidin-N-yl)anthranilamide (4Pip). Samples are dissolved in \(\text{CH}_2\text{Cl}_2\) in the presence of 50 mM \(\text{N}((\text{n-C}_4\text{H}_9)_4\text{PF}_6\), as reported in the study reported by Larsen-Clinton et al. [15]. The voltammograms illustrate the following: (a,d) the anodic, \(I_c\), Ohmic, \(I_O\), and Faradaic, and \(I_f\) currents (b,e) the anodic, \(E_a\), cathodic, \(E_c\), and half-wave, \(E^{(1/2)}\), potentials, along with the peak, \(E^{(p)}\), and edge, \(E^{(e)}\), potentials; and (c,f) comparison of the inflection, \(E^{(i)}\) and half-peak potentials, \(E^{(p/2)}\), with \(E^{(1/2)}\). The values of \(E^{(i)}\) are obtained from the second derivatives of the voltammograms, that is, at the potentials where \(\frac{d^2V}{dt^2} = 0\), whereas \(\frac{dE}{dt} = \text{constant}\).
shortcomings of the Koopmans’ theorem, it actually validates the use of electrochemical potentials for analyzing the thermodynamics of CT as eqs. (1) and (2) implement.

**Estimating electrochemical potentials when samples “misbehave”**

Standard electrochemical potentials, \( E^{(0)} \), as extensively obtained from CV measurements, provide key characteristics of the electronic properties of donors and acceptors. Using the average between the anodic and cathodic potentials, i.e., the half-wave potential, \( E^{(1/2)} \), has become an accepted representation of \( E^{(0)} \). Values of \( E^{(1/2)} \) are only attainable, however, when oxidation and reduction are reversible or at least, partially reversible [5,14].

When irreversible behavior prevails, it is popular to report peak potentials, \( E^{(p)} \), or edge potentials, \( E^{(e)} \), as estimates of \( E^{(0)} \) (Figure 1a,b,d,e). As cyclic voltammograms of reversible processes reveal, however, \( E^{(p)} \) inherently overestimates \( E^{(1/2)} \) of oxidation and underestimates \( E^{(1/2)} \) of reduction (Figure 1b) [5]. Similarly, \( E^{(e)} \) underestimates \( E^{(1/2)} \) of oxidation, and overestimates \( E^{(1/2)} \) of reduction (Figure 1b) [5].

A few years ago, we introduced the utility of the potentials at the first inflection points \( (E^{(0)}) \) on the anodic and cathodic waves of, respectively, irreversible oxidation and reduction, as estimates for \( E^{(1/2)} \) [16,17]. Actually, in pulse polarography, \( E^{(1/2)} \) is defined as the potential at the half-height currents, \( i^{(1/2)} \), of the sigmoid voltammograms (corrected for the Ohmic slopes), i.e., \( E^{(1/2)} = E_{i^{(1/2)}} \) where \( i^{(1/2)} = i_{\text{max}} - i_{\text{min}} \) and for reversible behavior, \( E^{(1/2)} = E(\partial^2i/\partial E^2 = 0) = E^{(0)} \). Recent analysis shows that these inflection potentials, \( E^{(0)} \), indeed, offer the best representations of \( E^{(1/2)} \) (Figure 1c) [5]. The half-peak potentials, \( E^{(1/2)} \), represent another good estimator for \( E^{(0)} \) from irreversible voltammograms [6,18]. The estimation of \( E^{(1/2)} \) values, however, depends on the current/voltage baseline and the peak values. Hence, \( E^{(1/2)} \) cannot hold too well for complex voltammographic waves when they appear broad with multiple peaks or when the capacitance and ohmic currents are comparable to the Faradaic signals (Figure 1a,d) [5]. Thus, \( E^{(0)} \) conduces to be a better representation of \( E^{(1/2)} \) than \( E^{(1/2)} \) (Figure 1c,f).

**To be or not to be … an electrolyte**

The answer is ‘to be.’ Supporting electrolytes of ions, which are inactive within the electrochemical windows of the analyses, are essential for sufficiently high conductance of sample solutions in nonionic liquids. High sample resistance increases the Ohmic currents and affects the working electrode (WE) polarization, causing deviations of \( E^{(1/2)} \) from \( E^{(0)} \) (Figure 1a,d) [3,7].

Supporting electrolytes affect \( \varepsilon_D \) and \( \varepsilon_A \), especially for solutions in low-polarity solvents and requires extra care for estimating the CT driving forces (eq. (1) and (2)) [3,19]. Therefore, we extrapolate the reduction potentials for neat solvents, i.e., \( E^{(1/2)} \) for \( C_D = 0 \), from the dependence of \( E^{(1/2)} \) on \( C_D \) (Figure 2a) [3,16,20–22]. This approach allows \( \varepsilon_D \) and \( \varepsilon_A \) to adopt well-defined published values for the used solvents, rather than the electrolyte solutions, improving the reliability of the thermodynamic CT analysis [23,24].

**What makes reference electrodes trustworthy?**

On their own, values of potentials are not truly useful. Conversely, differences between potentials (measured under identical conditions) and potentials reported against reproducibly reliable references are crucially important for science and engineering [25].

Reliable reference electrodes (REs) provide the baseline for comparing results from different measurements. In setups with three and more electrodes [26–28], the voltage differences between REs and the WEs quantify the potentials that drive the electrochemical transformations of interest. Therefore, a RE has to maintain a stable potential during measurements. The high impedance of REs keeps the currents through them negligibly minute and prevents detectable voltage drops. The counter electrodes serve as sinks for the current through WEs.

To ensure reproducibility, REs are usually compartmentalized heterogeneous systems connected with the electrochemical cells via liquid junctions and electrolyte bridges. Inherent physical and chemical characteristics of redox couples are fundamental for designing reliable REs. Redox couples of metal electrodes, M, and their cations \( M^{z+} \), in electrolytes saturated with counterions, \( X^- \), where \( MX_z \) has immensely low solubility, are an excellent choices for reliable REs. The presence of solid \( MX_z \) in \( X^- \)-saturates solutions ensures the constant activity of \( M^{z+} \) in the liquid phase, \( a_{M^{z+}} \), which depends on the MX-solubility product, \( K_{sp} = a_{M^{z+}} a_{X^-}^{z-} \). Maintaining a constant level of \( a_{X^-} \) is key for reproducibly stable REs, the potentials of which depend on \( K_{sp}(MX_z) \) and the standard electrode potential of M, \( E^{(0)}_{M^{z+}|M^-} \). Saturated calomel electrode (SCE) and silver/silver chloride (Ag/AgCl) electrode are the best example of such REs that have become standards for reporting electrochemical potentials vs. them [25].
Broadening of electrochemical applications places demands on shifting to organic-based references and decreasing the sizes of all electrodes. Encompassing a high-impedance connection via a single metal wire, pseudo-reference electrodes (PREs) have proven invaluable for miniaturizing the electrochemical setups. The potentials of PREs, however, strongly depend on their surrounding environment. It warrants careful calibration of PREs with internal standards, and reproduction of at least some of the measurements against a well-characterized RE.

For organic samples, ferrocenium/ferrocene, $\text{Fc}^+|\text{Fc}$, pair is the most widely used standard. The immense stability of the ferrocenium ion ensures that ferrocene undergoes reversible or quasi reversible oxidation in a broad variety of electrolyte solutions at experimentally accessible potentials [3,5]. The immense utility of ferrocene for calibrating electrochemical setups has led to the use of $\text{Fc}^+|\text{Fc}$ as a reference. Reporting electrochemical potentials vs. $\text{Fc}^+|\text{Fc}$, however, is fundamentally wrong. The $\text{Fc}^+$ reduction potential strongly depends on the electrolyte composition [3]. That is, $\text{Fc}^+|\text{Fc}$ potential does not have the invariance of an RE. Therefore, while ferrocene is one of the best internal standards, reporting an electrochemical potential vs. $\text{Fc}^+|\text{Fc}$ indubitably warrants the disclosure of $\text{Fc}^+$ reduction potential measured against an RE under the exact same conditions.

The hidden menace of liquid junctions

Liquid junctions (LJs) and electrolyte bridges provide electrical contacts between solutions in different compartments of electrochemical setups, while preventing cross-contamination. Ion transport across an LJ, along with solvent differences, produces LJ electrical potentials ($E_{LJ}$) [29,30]. The measured voltage difference between the WE and the RE, thus, encompasses the potential across the surface of the WE, needed for the analysis, along with the $E_{LJ}$ values of the LJs between the two electrodes.

The ion diffusion across LJs, driven by concentration gradients, usually contributes only a few mV to $E_{LJ}$, which is one-to-two orders of magnitude smaller than the contribution from the diffusion induced by differences in chemical potential [29]. Also, the contributions of the ion transport to $E_{LJ}$ are inversely proportional to the ion charge [29]. Therefore, supporting electrolytes of multi-charged ions with a small propensity for transport through the LJs offers a means for decreasing the undesired $E_{LJ}$.

The contributions of the solvent differences to $E_{LJ}$ vary widely, e.g., 40 and 100 mV for $\text{H}_2\text{O}|\text{CH}_3\text{CN}$ and $\text{H}_2\text{O}|\text{CHCl}_3$.
DMF junctions, respectively [29]. Placing immiscible solvents across a junction can induce not only a huge potential drop, but also a complete shutdown of the electrical connection. Therefore, employing electrolyte bridges with two or more LJs while keeping solvent miscibility in mind, e.g., water|CH$_3$CN|CH$_2$Cl$_2$, eliminates the enormous $E_{LJ}$ that a single junction between immiscible solvents may produce, e.g., water|CH$_2$Cl$_2$.

**Size matters ... in an inverse manner**

While the donor and acceptor radii, $r_D$ and $r_A$, are key for CT analysis (eq. (1c)), most redox species are not spherical. Computed generalized Born radii, $r_{GB}$, which account for the spatial distribution of the partial charges in redox species of any shape, offer an excellent representation of $r_D$ and $r_A$ [19,31]. Conversely, electrochemistry provides an experimental means for estimating effective radii, $r_{eff}$, of redox moieties, also, regardless their shapes [16,19]. Both, $r_{GB}$ and $r_{eff}$, represent radii of spherical ions with homogeneously distributed charges that experience the same solvation energy as the analyzed non-spherical species [19].

The dependence of reduction potentials on medium polarity provides information about $r_{eff}$. Specifically, $r_{eff}$ is inversely proportional to the slopes of linear fits of $E^{(1/2)}$ vs. $\varepsilon^{-1}$, i.e., $r_{eff} = (8\pi F \varepsilon_0 \text{slope})^{-1}$ (Figure 2b). This inverse relationship between potentials and the radii, however, compromises the reliability of $r_{eff}$ estimates for large redox species. For $r_{eff}$ exceeding 10 Å, the difference between the reduction potentials for electrochemically feasible polar and non-polar solvents drops under about 0.1 V (Figure 3).

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**Figure 3**

Polarity dependence of reduction potentials. Variations of the polarity dependence of the reduction potentials of oxidized donors on their effective radii, $r_{eff}$, for $n = 1$ and $x = 0$ (eq. (1)).

**Figure 4**

Polarity dependence of the potential differences for the donor-acceptor case presented in Figure 2. (a) Dependence of the potential differences on the concentration of the supporting electrolyte, $C_{ui}$, showing the extrapolations for neat solvents, that is, for $C_{ui} = 0$. (b) Dependence of the potential differences, extrapolated for $C_{ui} = 0$, on the solvent polarity, expressed as the inverse static dielectric constant, along with the estimated sum of inverse radii, $S_{1/r}$ (eq. (3b)).
As important as \( r_A \) and \( r_D \) are, it is their inverse values, \( r_A^{-1} \) and \( r_D^{-1} \), that CT analysis implements (eq. (1c)). As we showed, when it is possible to measure the reduction potentials of the acceptor and the oxidized donor for the same media, i.e., \( \Delta E_A = \Delta E_D = \Delta E \), the separate values for \( r_A \) and \( r_D \) become redundant, as a rearrangement of eq. (1) reveals for \( n = 1 \) and \( x = y = 0 \) [12]:

\[
\Delta G_{CT}^{(0)}(\varepsilon) = F\Delta E^{(0)}(\varepsilon) - r_0 + W(\varepsilon) \tag{3a}
\]

\[
\Delta E^{(0)}(\varepsilon) = \frac{q^2}{8\pi F\varepsilon_0} S_{1/r} \left( \frac{1}{\varepsilon} \right) \tag{3b}
\]

where \( \Delta E^{(0)}(\varepsilon) = \left( E^{(0)}_{D+1}(\varepsilon) - E^{(0)}_{A-1}(\varepsilon) \right) \) and \( S_{1/r} = r_A^{-1} + r_D^{-1} \).

The polarity dependence of \( \Delta E^{(1/2)} \) produces the sum of inverse radii, \( S_{1/r} \) (Figure 4). Not only \( S_{1/r} \) is essential for implementing such simplified driving-force calculations (eq. (3)), but also employing \( E^{(1/2)}_{D+1} \) and \( E^{(1/2)}_{A-1} \) from measurements, using the same electrolyte solutions, eliminates from \( \Delta E^{(1/2)} \) the systematic errors from the liquid-junction potentials. In addition to improving the precision of obtaining \( S_{1/r} \), in comparison with that for attaining \( r_D \) and \( r_A \) for large species, the implementation of \( S_{1/r} \) extends beyond the CT thermodynamics. Outer-sphere, or medium, reorganization energy, \( \lambda_m \), is directly proportional to \( S_{1/r} \) [12]:

\[
\lambda_m = \frac{\gamma q^2 q^2}{8\pi F\varepsilon_0} \left( \frac{1}{2} S_{1/r} \right) \tag{4}
\]

The calculations of \( \lambda_m \) employ a model of Born solvation originating from orientational and nuclear/vibrational polarization, as implemented by the Pekar factor, \( \gamma = n_m^{-2} - \varepsilon_m^{-1} \) [1,13,23]. Therefore, \( S_{1/r} \) is an excellent representation of the sum of the inverse radii in eq. (4).

After a Born-solvation analysis of electrochemical potentials produces \( S_{1/r} \) (Figure 4b).

**Conclusions**

As an intricate part of charge-transfer science, the importance of electrochemical analysis cannot be overstated. Energy science, photoredox- and electrocatalysis, biomedical sensor development, environmental engineering and (opts)electronics are some of the areas that are strongly contingent on CT, and place demands for high-fidelity electrochemistry. Without losing sight of the big picture, therefore, paying attention to details, when gathering, implementing, and interpreting electrochemical results, is essential for advancing this broad range of areas of science and engineering.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this publication.

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**Current Opinion in Electrochemistry** 2022, 31:100862

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