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Eliminating the Bias from Liquid-Junction Potential for Charge-Transfer Analysis

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Liquid junctions in electrochemical cells introduce potentials that can strongly affect measurements. Such liquid-junction potential errors can exceed 100 mV. In the analysis of charge-transfer thermodynamics, error differences of 100 mV can have substantial impact on the interpretations. Discussion herein outlines an approach for eliminating the effects of liquid-junction potentials from charge-transfer analysis.

Introduction

Charge transfer (CT) and charge transport (CTr) drive life on Earth and ensure our modern ways of living possible.[1] Electrochemical analysis is essential for the design and characterization of CT systems.[2,3] Specifically, the reduction potentials of the electron acceptor, $E^{(1/2)}_{A|A^{\bullet-}}$, and the oxidized electron donor, $E^{(1/2)}_{D^{\bullet+}|D}$, which cyclic voltammetry (CV) produces, are intricate for estimating CT driving forces, $-\Delta G^{(0)}$.[2,4]

Light-driven processes, such as photoinduced charge transfer (PCT), are key for harvesting solar energy and converting it into a utilizable form like in photosynthesis and photovoltaic devices.[5-7] In addition to the electrochemical potentials, the thermodynamic analysis of PCT requires prior knowledge of the zero-to-zero energy, $\mathcal{E}_{00}$, of the donor or the acceptor, estimated from steady-state optical spectroscopy.[8] Frequently, the conditions of electrochemical and spectroscopic measurements are different, i.e., employing media with different polarity.[9,10] Electrochemical potentials and optical transitions depend on the polarity of the solvating media. Usually, estimating the Born solvation energy, ΔG_S, allows correcting for such polarity differences.[9]

Even with solvation-energy corrections, two challenges remain pending. First, the liquid-junction potentials (E_{LJ}) introduced in the electrochemical cells by using high-precision reference electrodes, such as SCE and AgCl|Ag, introduce bias in the measurements.[11] Second, the CT analysis employing electrochemically measured potentials assumes a prior knowledge of the polarity of the species during oxidation and reduction at the electrode surface.[12,13] Usually, the bulk polarity of the solvent or the electrolyte solution is associated with the measured reduction potentials. At the surface of polarized working electrodes, however, the electric field immobilizes the media within the double layer where the redox species are characterized. Such immobilization, known as "electrofreeze" results in lowering of the static dielectric constant that the redox species experience.[12]

This transaction discusses an approach for eliminating the E_{LJ} bias error from the measured potentials for CT analysis.

Results and Discussion

An increase in medium polarity stabilizes charged species. Therefore, it induces a positive shift in $E^{(1/2)}_{\mathrm{A|A^{\bullet-}}}$ and a negative shift in $E^{(1/2)}_{\mathrm{D^{\bullet+}|D}}$, for non-charged donors and acceptors. The difference between these potentials accounts for the energy level of the CT state when estimating -$\Delta G^{(0)}$. Indeed, E_{LJ} indices the same bias regardless if CV probes oxidation or reduction. Therefore, E_{LJ} does not affect the potential difference, $\Delta E = E^{(1/2)}_{\mathrm{D^{\bullet+}|D}} - E^{(1/2)}_{\mathrm{A|A^{\bullet-}}}$. This consideration allows rewriting the equation for PCT driving force as follow:[11]

$$\Delta G_{\mathrm{PCT}}{}^{(0)}(\varepsilon) = F\,\Delta E^{(1/2)}(\varepsilon_{\mathrm{E}}) - \mathcal{E}_{00}(\varepsilon) + \Delta G_S(\varepsilon, \varepsilon_{\mathrm{E}}) + W(\varepsilon) \qquad [1]$$

Where ε_{E} is the dielectric constant of the media for the electrochemical analysis, and ε – of the media for the spectroscopy and PCT studies; W is the Coulombic term accounting for the electrostatic interaction between the donor and the acceptor; and F is the Faraday constant.[9,14] In this analysis, it is important to ensure that the measurements of $E^{(1/2)}_{\mathrm{D^{\bullet+}|D}}$ and $E^{(1/2)}_{\mathrm{A|A^{\bullet-}}}$ are conducted in the same electrochemical cell and under identical solvent conditions.

The Born-solvation term, ΔG_S, accounts for the interactions of the donor and acceptor with the solvating media:[9,14]

$$\Delta G_S(\varepsilon, \varepsilon_{\mathrm{E}}) = \frac{q_e{}^2}{8\,\pi\,\varepsilon_0}\,S_{1/r}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{\mathrm{E}}}\right) \qquad [2]$$

Where q_e is the elementary charge; ε_0 is the dielectric vacuum permittivity; and $S_{1/r}$ depends on the radii of the donor and the acceptor, r_{D} and r_{A}, the initial charges of the donor and the acceptor, z_{D} and z_{A}, and the number of transferred electrons, n_e:[2,11]

$$S_{1/r} = (2\,z_{\mathrm{D}} + n_e)\frac{1}{r_{\mathrm{D}}} - (2\,z_{\mathrm{A}} - n_e)\frac{1}{r_{\mathrm{A}}} \qquad [3]$$

Using eq. 1, along with 2 and 3, allows estimating CT thermodynamic driving forces without the systematic errors that E_{LJ} introduces in the interpretation of the measurements.

Conclusions

CV measurements are easy to carry out, but their interpretation warrants a great degree of caution. The outlined analysis illustrates eliminating the errors that liquid junctions in electrochemical cells introduce. Nevertheless, understanding the media at the electrode surface is as important for drawing valid conclusions. Such medium effects become especially pronounced when lowering the solvent polarity for redox species with small size.

References

1. J. B. Derr, J. Tamayo, J. A. Clark, M. Morales, M. F. Mayther, E. M. Espinoza, K. Rybicka-Jasinska and V. I. Vullev, *Phys. Chem. Chem. Phys.*, **22**, 21583 (2020).
2. O. O'Mari and V. I. Vullev, *Curr. Opin. Electrochem.*, **31**, 100862 (2022).
3. D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).
4. E. M. Espinoza, J. A. Clark, J. Soliman, J. B. Derr, M. Morales and V. I. Vullev, *J. Electrochem. Soc.*, **166**, H3175 (2019).
5. J. A. Clark, R. Orłowski, J. B. Derr, E. M. Espinoza, D. T. Gryko and V. I. Vullev, *Photosynth. Res.* (2021).
6. H. Lu, D. Bao, M. Penchev, M. Ghazinejad, V. I. Vullev, C. S. Ozkan and M. Ozkan, *Adv. Sci. Lett.*, **3**, 101 (2010).
7. V. I. Vullev and G. Jones, II, *Res. Chem. Intermed.*, **28**, 795 (2002).
8. K. Rybicka-Jasińska and V. I. Vullev, *Charge Transfer & Organic Photoelectrochemistry*, American Chemical Society (2023).
9. D. Bao, B. Millare, W. Xia, B. G. Steyer, A. A. Gerasimenko, A. Ferreira, A. Contreras and V. I. Vullev, *J. Phys. Chem. A*, **113**, 1259 (2009).
10. G. Jones, II and V. I. Vullev, *J. Phys. Chem. A*, **106**, 8213 (2002).
11. R. Orłowski, J. A. Clark, J. B. Derr, E. M. Espinoza, M. F. Mayther, O. Staszewska-Krajewska, J. R. Winkler, H. Jędrzejewska, A. Szumna, H. B. Gray, V. I. Vullev and D. T. Gryko, *Proc. Natl. Acad. Sci. U. S. A.*, **118**, e2026462118 (2021).
12. M. F. Mayther, O. O'Mari, P. Flacke, D. Bhatt, S. Andrews and V. I. Vullev, *J. Phys. Chem. B*, **127**, 1443 (2023).
13. O. O'Mari and V. I. Vullev, *Molecules*, **28**, 4360 (2023).
14. D. Bao, S. Ramu, A. Contreras, S. Upadhyayula, J. M. Vasquez, G. Beran and V. I. Vullev, *J. Phys. Chem. B*, **114**, 14467 (2010).