REVIEW

Half a century of electrochemistry, mainly in non-aqueous electrolytes (a personal view)

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Abstract This article covers activities of about half a century of an electrochemist. This time period covers the days from homemade apparatus and self-developed simulation to commercially available instrumentation with software. Electrochemical research in non-aqueous media and single-ion transfer properties of cations are mentioned. Standard electrochemical reaction rates are critically discussed.

Keywords Electrochemistry in non-aqueous solvents · Reference redox systems · Single-ion transfer properties · Electrode kinetics

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Introduction

This part covers activities as an electrochemist in Vienna (Austria), Baton Rouge (LA, USA), Midland (MI, USA), Vienna again (Austria), Linz (Austria), and a few days in retirement. As such, a description must be personal, citations of publications of the author dominate, but citations of the original papers are given in the respective literature.

Vienna (1963–1966)

Having had a lecture and a laboratory course in electrochemistry, my first real contact came during my diploma thesis in 1963 at the Technical University Vienna (then the Technische Hochschule Wien, THW). My diploma thesis covered the polarographic investigation of nitrogen oxides in dimethyl sulfoxide [1]. My direct supervisor was Dr. Gerhard Schöber who, some time after I finished my doctorate thesis, left the University. The head of the Institute of Inorganic and General Chemistry at the THW then was Prof. Dr. Viktor Gutmann. Gutmann's research interest in those days centered on non-aqueous solvents and the solvent effect on thermodynamic and kinetic properties in non-aqueous systems [2]. Donor–acceptor interactions were to account for interactions between the solutes (ions) and the solvents.

After some preliminary studies in non-aqueous solvents, electrochemical research in the 1960s of the last century moved into systems other than water [3]. Prof. I. M. Kolthoff (Izaak Maurits Kolthoff, 1894–1993) and his research group (especially Dr. J.F. Coetzee, later Professor in Pittsburgh) started systematic studies in acetonitrile [4]. Vienna chose dimethyl sulfoxide as non-aqueous solvent [5]. A German company (Union Rheinische Braunkohlen

Kraftstoff A. G.) got dimethyl sulfoxide as a side product in the cellulose production (Kraft pulping) and gave it away for free to Universities in the hope that some use for this solvent may be found.

Note that dimethyl sulfoxide later was used in medicine and when I interviewed several companies in the USA in the late 1960s, the most frequently asked question was whether I had any medical problems working with dimethyl sulfoxide.

Those were the days of the self-fabricated two-electrode system. The working electrode was preferentially the dropping mercury electrode. The second electrode served both as a counter electrode and a reference electrode. Reference electrodes in those days were mainly based on the aqueous calomel electrode with a large area of approximately 70 cm^2 for the mercury pool to reduce the current density and thus maintain a constant potential. Special emphasis was placed on the design of the junction between the aqueous (saturated calomel) electrode and the non-aqueous electrolyte. I remember we used a very fine sintered glass disc in which we entered a sodium silicate (water glass) solution followed by precipitation of amorphous silicon dioxide by concentrated hydrochloric acid. To ensure that no mass transport was possible through this separator an iron(III) chloride solution was placed inside the measuring cell and an ammonium rhodanide (NH$_4$SCN) solution in a beaker. No red color due to Fe(SCN)$_3$ was to appear in the ammonium rhodanide solution.

The water content in the solvent was considered very crucial and Karl-Fischer titrations were carried out in freshly distilled solvents. Glovebox techniques were employed in the preparation of the electrolyte. Tetraalkylammonium salts (mainly tetraethylammonium perchlorate) served as supporting electrolyte.

The resistance of such a two-electrode arrangement was large, and potential data had to be manually corrected for the contribution of internal resistance (*IR* drop). This was done by measuring the minimal resistance of the arrangement, just before the falling of the mercury drop, with an ac-resistance measuring device. From the minimal resistance, the average resistance was calculated, the current was obtained from the polarogram and each potential data point was corrected for the *IR* drop.

Lanthanoides [6] and later the actinoids [7] were studied. The cations of this group are well suited for research in non-aqueous electrolytes as electrochemical studies in water will result in "hydrogen waves."

Later research was directed towards finding reversible (on the time scale of the experiment) redox reactions to learn about solvent effects on electrode potentials (then mainly polarographic half-wave potentials). Purification of the solvent became very important. Polarographically active impurities yield waves even on a millimolar level. Polarographically inactive impurities could only be detected at a high level by gas chromatography. Traces of such impurities may go undetected. The salts of the depolarizer had to be water free.

Later on, we used also oscillopolarography [8], a technique developed in Prague by the Heyrovský group. This technique did not receive wide attention and was swallowed soon by cyclic voltammetry. In November and December 1965 as well as in June and July 1966, I had the opportunity to work in the Polarographic Institute (then Vlašska 9) in Prague with Drs. J. Mašek and A. Rusina. The Nobel laureate Prof. Jaroslav Heyrovský was still around, although in poor health. The change in leadership was going on. Finally, Prof. A.A. Vlček became the successor and head of the institute. My visit in 1966 ended with the second congress on polarography in Prague where I also saw Prof. I. M. Kolthoff.

The years in America (1966–1973)

In October 1966, I started a post-doctoral fellowship under Prof. Joel Selbin at the Louisiana State University in Baton Rouge. My electrochemical assignment was the preparation of a solution containing a uranium(V) species for spectroscopic studies. Those were the days of ligand field theory and the question arose whether the outermost electron in U^{5+} was a *d* electron or an *f* electron. UO_2^{2+} undergoes a reversible one-electron reduction in dimethyl sulfoxide [9] but UO_2^+ is extremely sensible to oxidation and even in inert atmosphere it disproportionates. A controlled potential reduction by "large-scale" electrolysis (mercury electrode area, 12 cm^2) followed by a quick visible-near infrared spectroscopy was performed to obtain a U(V) solution [9, 10].

In 1967, I participated in the Spring Scientific Meeting of the American Chemical Society in Miami Beach. After a lecture by Prof. R.A. Marcus I listened to a lively discussion between Profs. Marcus and Bockris. I understood practically nothing and little did I know that I shall eventually be at odds with the Marcus theory some 40 years later.

In 1969, I joined the Dow Chemical Company in the Inorganic and Electrochemical research Laboratory in Midland, Michigan. Dow was then and still is the largest producer of chlorine and sodium hydroxide solutions in the world. So I learned what a large electrode really is. The laboratory director was then Dr. Robert D. Blue, an original, who was an excellent electrochemist. His claim to fame was the "Blue clips" which allowed a pseudo bipolar arrangement of diaphragm cells. My direct supervisor was Dr. James J. Leddy, who taught me a lot about industrial electrochemistry and guided my

transition from academic research into the world of industrial electrochemistry.

Coming from the academe into the industrial world, many things were to be learned by a young electrochemist. The chemical industry, as an industry in general, is money-oriented. Industrial researchers will not enter the world of publications and very rarely will be granted patents. Scientists, thus, disappear from the research world, but fighting for savings of a few cents per ton of product on established electrochemical processes, fully covered by patents or expired patents.

Industrial electrochemistry suffers from the two-dimensionality of reaction zones in electrochemistry. Processes occur at electrodes, which generally make capital investment high. Industrial electrochemistry processes are thus only applied if there is no alternative. Besides the production of alkali and alkaline earth metal (magnesium), only the production of aluminum is of importance. All these processes employ molten salt electrolytes. This statement may include the fabrication of fluorine. Zinc, copper, in some cases, and the chlorine–alkali production are the only electrolytic processes of importance in aqueous systems. Other than that, electrochemical processes are limited to mainly electroplating (metal finishing) and to primary as well as secondary cells (batteries).

Most of the chlorine produced goes into chlorination of organic compounds. This means that for each mole of chlorine 1 mol of HCl is produced. Thus, my first assignment was to develop an electrochemical way to recover chlorine from HCl [11].

As electrolytically produced hydrogen in those days had practically no value, I developed a chlorine-alkali cell where the cathode would be a fuel cell type allowing the reaction of air (oxygen) at the electrode to produce water instead of hydrogen. Thus, a hybrid electrolysis cell was created (hybrid cell as the cathode actually functioned as a fuel cell while chlorine is electrolytically produced at the anode) [12]. Such an arrangement lowers the electrode potential at the cathode, thus reducing the overall cell voltage and the consumption of electric energy.

For the chlorine–alkali industry the late 1960s and early 1970s of the last century were exciting and demanding days. The Minimata problem affected the chlorine-caustic production via amalgam cells [13]. An old-fashioned process to produce acetaldehyde from acetylene and water via a mercury salt acting as catalyst in Minimata in Japan triggered serious health problems of the occupants in the area [14]. In consequence, mercury had rough times in industrial processes such as the amalgam technology to fabricate chlorine and caustic soda. This was no problem for Dow, as this company had its strong technological basis in the diaphragm process, but soon environmental and health issues were addressed at asbestos. This started to cause problems also for diaphragm cells using asbestos as a diaphragm.

The Minimata problem and the follow-up discussion resulted in (unjustified) banning mercury use for all purposes, including research in some countries thus also affecting academic and analytical research. This causes serious problems to electrochemistry as the dropping or stationary mercury electrode is well established both experimentally and theoretically. Polarography, defined as electrochemistry on the dropping mercury electrode, which had contributed so much to the development of electrochemistry in the first half of the twentieth century began to disappear from the research activities in many countries. Mercury in the hands of experienced chemists following proper safety rules does not pose any health problem, but allows continuation of interesting electrochemical research [15].

In 1966, Henri Beer got a patent for a dimensionally stable electrode by doping a titanium electrode with rhenium and/or rhodium oxides [16]. Thus, a very strong competition for the anode material graphite appeared. The scientific community also took notice of this, and research papers on modified electrodes were published. At about the same time, DuPont began with the large-scale production and marketing of the fully fluorinated ion-exchange membrane named Nafion®, which would hold up as an ion-exchange membrane in a chlorine-caustic cell [17]. Both effects finally led to the commercial design of the membrane cell (nickel as cathode, a Nafion® membrane and a dimensionally stable anode), which now is standard in countries, which prohibit mercury and/or asbestos in chlorine–alkali cells. The new membrane also allowed revisiting the zinc–bromine battery (secondary cell) [18]. Despite strong efforts by many research institutions, however, the zinc–bromine cell never reached the market. According to insiders, the problem is the dendrite formation of zinc during recharging, which poses greater troubles than the storage of bromine. Now the so-called lithium-ion battery seems to cover the future battery market.

Adjusting the pH to 6.4 in blood plasma should allow electrophoretic separation of γ-globulins and albumin, another industrial research topic of mine [19].

In 1973, I participated in the Gordon Research Conference on Electrochemistry in California. I also had some function, most probably secretary, of the Midland chapter of the Electrochemical Society (USA). In that function, I also arranged a visit of Prof. Bockris in Midland, but I left for Vienna before Prof. Bockris visited Midland.

Organic electrochemistry was intensively studied in the 1950s and 1960s of the last century. Many processes looked very promising for industrial processes. The Baizer (Manuel M. Baizer, 1914–1988) process for the dimer-

ization of acrylonitrile to adipodinitrile (1,4-dicyanobutan) was applied on an industrial level [20] and seemed promising for other large-scale industrial processes, but the enthusiasm for organic industrial electrochemistry soon faded away.

Vienna again (1973–1979)

In 1973, I returned to the Technical University in Vienna to continue scientific electrochemical research as a group leader for electrochemistry in non-aqueous solvents. During those years, the late Prof. Alan J. Parker came to Vienna as a visiting professor. He was one of the leading personalities in single-ion transfer properties. One of techniques he used was of electrochemical in nature, namely the suppression of the liquid junction potential between two non-aqueous electrolytes by a bridge filled with 0.1 mol dm^{-3} solutions of tetraethylammonium picrate [21]. He aroused my interest in single-ion transfer properties but also in solvents which would donate via a sulfur atom in the molecule. Together with Drs. Karl Danksagmüller and Peter Rechberger and later in Linz with Mag G. Kraml and Drs. S. Sperker and W. Mayrhofer, investigations in N,N-dimethylthioformamide, N-methylthiopyrrolidone(2), and 2,2′-thiodiethanol were performed [22–30].

In 1975, a congress of the International Society of Electrochemistry co-organized by Prof. Gutmann (with Prof. Nelly Konopik) on electrochemistry in non-aqueous system, took place in Baden near Vienna. This was probably the highlight and the beginning of the end of systematic research in electrochemistry in non-aqueous systems. I remember a few of the plenary speakers: Profs. A.J. Parker, Roger Parsons, and Lev I. Krishtalik.

The years as a member of Commission I.3 (electrochemistry) of the International Union of Pure and Applied Electrochemistry

In 1977, the Ciba Foundation offered a scholarship to participate as an observer in the Warsaw General Assembly of the International Union of Pure and Applied Chemistry (IUPAC). I was selected and chose to be an observer in Commission I.3 (electrochemistry). In 1977 in Warsaw, it was then that I met Prof. Norbert Ibl for the first and only time. At my second participation in 1983 in Leuven, I learned that he had died. Soon after the Leuven meeting, Prof. Jaroslav Kůta, a fatherly friend, a quiet, modest, and excellent electrochemist left us forever. In Lynby (Denmark) in 1985, I became a titular member of Commission I.3 (electrochemistry), being in the same Commission with Profs. Allen J. Bard, Roger Parsons, and Sergio Trasatti. In 1985, I became secretary of Commission I.3 under the chairmanship of Prof. Katsumi Niki. From 1987 until 1991,

I was chairman of the commission. The most important contributions from my side were the IUPAC paper "Recommendations on Reporting Electrode Potentials in Nonaqueous Solvents" [31–34], a paper which so far was cited more than 600 times. Other activities covered the papers on the "Polarographic Half-wave Potentials of Cations in Nonaqueous Solvents" [35, 36] and on "Nomenclature, Symbols and Definitions in Electrochemical Engineering" [37, 38] and participation of the second edition of the IUPAC handbook: *Quantities, Units and Symbols in Physical Chemistry* [39] which especially in the "Electrochemistry" chapter endured long discussions. There were also lively discussions in those days on the definition of pH, with strong contributions from Prof. Roger Bates and on single-ion transfer properties (a project carried out under the guidance of Commission V.5 (Electroanalytical Chemistry)) between Prof. Yizhak Marcus and the author.

Still being an IUPAC fellow, I feel that the importance of IUPAC seems to have decreased. Reasons for this may be (in the opinion of the author) the lack of general topics which need international agreement and the fall of the so-called iron curtain. IUPAC general assemblies were, for a long time, one of the very few ways to meet and to discuss with selected colleagues from the socialistic (communistic) countries.

Electrochemistry at the Johannes Kepler University in Linz (Austria)

In 1979, I followed a call as professor for chemical and mechanical technology at the Johannes Kepler University Linz (Austria). Electrochemical research became a sideline of the research activities of the Institute for Chemical Technology of Inorganic Materials. However, polarographic and cyclovoltammetric studies continued with the help of interested students (e.g. Dr. F. Hörzenberger) and with colleagues from Poland (Prof. Andrzej Lewandowski, Poznań; Prof. Marek Orlik, Warsaw) and the Czech republic (Dozent Libuše Kišova, Prof. Jaro Komenda, Brno). Dozent Kišova was one of the very few persons to work with both Prof. Heyrovský and Prof. Frumkin. Firstly, emphasis was placed on continuing studies of polarographically reversible redox reaction of cations (Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Tl$^+$, Cu$^+$, Cu^{2+}, Cd^{2+}, Pb^{2+}, etc.) and potentiometric measurements of the Ag| Ag$^+$ electrode in non-aqueous electrolytes [40–42], using the reference redox system *bis*(biphenyl)chromium(I)|(0). Employing the extra-thermodynamic assumption of the solvent independence of the reference redox system, Gibbs single-ion transfer values for these cations were calculated and compared with data derived from solubility studies (tetraphenylarsonium tetraphenylborate assump-

tion) and values from potentiometric studies (assumption of a negligible liquid junction potential) [40].

Measurement in a non-isothermal cell allowed the estimation of the temperature dependence of polarographically reversible electrode processes [43] and thus the calculation of transfer entropies. In combination with the Gibbs energies of transfer, the calculation of single-ion enthalpies of transfer from solely electrochemical measurements into solvents and solvent mixtures became possible [44, 45]. Studies in solvent mixtures led to information on selective interaction (selective solvation) of different cations in mixtures [45].

A statistical analysis (together with Dr. M. Auinger) [46, 47] of the single-ion Gibbs energies of transfer and in up to 40 non-aqueous solvents referred to the above-mentioned reference redox system showed that the potentials are affected by different ion–solvent interactions based on chemical bonding between the donor sites in the solvent molecules and the respective cation (ion) [48]. Electrostatic interactions as claimed by the Born [49] theory and its extensions did not account for the solvent-induced shift of the half-wave potentials upon the nature of the solvent.

After having learned about the ion–solvent interaction from (polarographically) reversible electrode processes, it became of interest to learn about solvent effects on electrode reaction rates. Especially the contributions of Dozent Libuše Kišova and Profs. Jaro Komenda and M. Orlik were decisive in studies of electrode kinetics [50–54]. At least two independent methods were chosen to obtain data for the electrode kinetics of the one-electron reduction of Eu^{3+}. One technique was *ac*-polarography followed by analysis with both Randles plots and by the Sluyters procedure. The other technique was based on cyclic voltammetry together with computer simulation of the voltammograms to obtain the standard reaction rate constants. A special cell and apparatus was developed for this purpose [51]. The program for the computer simulation was the work of Prof. M. Orlik [55]. While we were able to obtain standard reaction rate constants by different, independent techniques, which agreed within experimental error, much to our surprise we learned that standard electrode reaction rate constants are also influenced by the concentration and the nature of the supporting electrolyte. Thus, we learned that standard electrode reaction rates are a function of the nature of the electrolyte, not only of the solvent. Correction via the Frumkin theory [56] did not result in standard reaction rate constants which were independent of the electrolyte concentration.

Two famous electrochemists, Prof. Petr Zuman (Clarkson University, USA) and Prof. Andrzej Lasia (Université de Sherbrooke, Canada), were guest professors in Linz. Prof. Zbigniew Galus (Warsaw, Poland) was a frequent guest in Linz as the author was in Warsaw.

Summary of some of the results

Solvent effects on reversible redox potentials

The electrode potentials of reversible electrode processes of cations were found to be affected by ion–solvent interactions (chemical bonding) between the donor sites of the solvent molecules and the respective cations. Such research was carried out in more than 40 solvents of quite different chemical composition (not only homologous series). It became apparent that such interactions not only follow classification schemes established for complex chemistry [57, 58], but also that previous schemes are too crude to account for the subtleties of ion–(cation)–solvent interactions [48]. The focus on cations is due to the many reversible redox processes found for mono and divalent monoatomic cations in aqueous and many non-aqueous systems. No comparable anion redox couples were found. Thus, all of this research is somewhat cation-oriented.

Reference redox systems

Reference redox systems should eliminate the problem of liquid junction potentials between the electrode potentials measured at the working electrode and the reference electrode. Liquid junction potentials are transport properties and thus neither reproducible nor thermodynamic values. The systems ferrocenium ion|ferrocene and *bis*(biphenyl) chromium(I)|(0) were recommended to be used in non-aqueous systems [31–34]. While ferrocene is commercially available, *bis*(biphenyl)chromium(I) salts have to be prepared in the respective laboratory by a somewhat tedious method. Thus, ferrocene is generally preferred. "Improvements" by substituted ferrocene does not generally change the situation of reference redox system. Any electrode potential of a redox couple "reversible" in all electrolytes studied in the same electrolyte will yield thermodynamic data and may serve as reference redox system, but an unnecessary flurry of reference redox systems will not allow meaningful compilation of electrochemical data in different electrolytes.

Literature indicates that the ferrocenium ion|ferrocene redox couple as possible reference system for ionic liquids suffers from poor solubility in several ionic liquids. Therefore, the research group of Prof. Alan M. Bond (Clayton, Australia) proposes cobaltocenium ion|cobaltocene as a possible internal potential standard for electrode potential measurements in ionic liquids [59].

A thorough study for the systems ferrocenium ion| ferrocene, *bis*(biphenyl)chromium(I)|(0) cobaltocenium ion|cobaltocene [60] varying the electrode material in the ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate

may show a way to resolve the problem of reference redox systems in ionic liquids.

Single-ion transfer properties of cations

Single-ion transfer properties are extra-thermodynamic propensities and require an extra-thermodynamic assumption. Electrode (half-wave potentials) of reversible electrode processes may be converted into single-ion Gibbs energies of transfer via the assumption of a solvent-independent redox couple (e. g., *bis*(biphenyl)chromium (I)|(0) system) [31–34]. Such data is now available in up to 40 solvents of quite different composition [48]. Electrochemical measurements of the temperature dependence of reversible electrode processes allow calculation of transfer entropies and thus a complete set of data ($\Delta_t G^o$, $T\Delta_t S^o$, $\Delta_t H^o$) may be derived. Such data can be compared with values obtained from (non-electrochemical) solution chemistry via solubility products and calorimetric studies. Agreement between values obtained from electrochemistry and solution chemistry using different assumptions may offer a data set which can be used in the description of solvent effects on thermodynamic and kinetically controlled processes in different media.

The "universal" scale of standard redox potentials

A universal scale of standard redox potentials is an old dream of electrochemists. Just as single-ion transfer properties, the universal scale of standard electrode potentials is based on extra-thermodynamic assumptions. Currently, such data are obtained from either solubility studies or from electrochemical measurements [61].

Electrode kinetics

Electrode kinetics is probably the most unfulfilled and poorly understood area in electrochemistry. Generally, only one technique is employed and kinetic data are rarely verified by a second technique. Thus, even the apparently simple electrode process of the oxidation of ferrocene in acetonitrile varies from 0.02 to 220 cm s^{-1} albeit in different supporting electrolytes [62], but although an effect of the nature and the concentration of the supporting electrolyte on standard reaction rate constants were reported [54], four orders of magnitude are more than one might expect. Electrolyte properties which may affect the standard reaction rate constants are not yet fully understood (also generally lacking such as simple physicochemical properties, e. g., electrolyte densities, viscosities, etc.). From the data available at present, it seems that a separation of solvent contributions to the electrode kinetics is not possible. Both the nature and the concentration of the supporting electrolyte influence electrode kinetics.

Solved and unresolved problems in electrochemistry (in view of the author)

This chapter is not too easy to write as one may easily get the impression of "sour grapes" (cognitive dissonance) of a retired researcher. Anyhow there is a try:

Three topics, namely the solvent effect of reversible electrode processes, single-ion transfer properties derived from electrochemical measurements and from chemical studies in solution, as well as the universal scale of standard redox potentials may be considered closed. Research grants in these research areas are very unlikely. However, there is a wealth of information in the publications concerning these topics, which may be used by researchers. Unfortunately, such usage requires some fundamental understanding of both chemistry and electrochemistry, not generally present in a researcher working with purchased equipment and software. The background and the concepts of the software are only understood by the creators of the software, but the concepts used in the software reflect itself in the analysis of the data. Very few people write their own software and design their own apparatus. Thus, an intimate understanding of the physicochemical situation is absent.

The interest in electrochemistry in room temperature ionic liquids awoke the problem of reporting redox potentials anew. A possible approach to solve this problem has been published [60].

Impact factor of the journal and citation indices become very important, but they tend to channel research into mainstreaming of topics temporarily in vogue. Researchers try to publish papers with very little, if any scientific content in journals with high-impact factors. They really try to piecemeal their research results making it difficult for the scientific public to understand the meaning and the results of such research. No continuous research on one topic to clear issues once and for all is possible. At best, one or two solvents in the homologous series are investigated, but that is already an optimum. Peer review, while necessary, is not without problems. Referees are human beings, with all their drawbacks. They like to be cited and praised, but never criticized. Referees are usually experts in the field, well familiar with traditional concepts, and rather hesitant to accept papers with new ideas. Criticism of old data (maybe data from the referee) is not always appreciated. Strategically placed research grants also channel research effort in proper directions, as most Universities struggle for funds.

Profs. John O'M. Bockris and Amulya K.N. Reddy complain in their excellent book *Modern Electrochemistry* that the Nernst hiatus long prevented proper treatment of electrode kinetics [63]. This is surely true, but do we have a dielectric hiatus in electrochemistry nowadays? Ion–solvent interactions are still treated with the Born model and its extensions, although more advanced concepts of treating

ion–solvent interaction on a molecular level (as chemical interactions) are available.

The Frumkin correction for the influence of the supporting electrolyte on standard reaction rate constants is basically electrostatic, and the Marcus equation [64] for estimation of standard reaction rate constants relies strongly on dielectric properties. As correlations with the exponential term of the Marcus equation were not successful, solvent properties were introduced into the pre-exponential factor, but maybe a fresh approach to electrode kinetics could be helpful.

Even the composition of the double layer between the electrode and the surrounding solution is based on electrostatic considerations, but what do we really know about how the electron transfer between a solvated ion and the electrode occurs?

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