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Corrected Marcus plots

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Abstract The advantages of corrected Marcus plots as compared to the more traditional corrected Tafel plots are discussed and illustrated by the treatment of experimental data. The procedures are proposed to avoid the uncertainties of EDL correction and to estimate the reliable values of transmission coefficient and total reorganization energy. Special emphasis is placed on the diagnostics of activationless reactions in frames of the same method.

Introduction

The electron transfer at charged interface is a complex process affected by several interrelated phenomena, namely (1) electrode-reactant electron coupling, (2) solvent and intermolecular reorganization, and (3) the specific state/concentration of the reacting specie in the reaction zone, and especially at the closest approach. The theory of elementary act [1] operates with a limited number of parameters and predicts the dependence of the reaction rate i on overvoltage η , taking into account the phenomena (1) and (2). Both i and η are experimentally available quantities, but the comparison of i , η -polarization curves with theory fails if the phenomena

(3) are not properly addressed. These phenomena discussed traditionally in terms of ‘electric double layer’ (EDL) are extremely sensitive to the electrode charge density σ . Unfortunately nobody can separate the effects of η and σ without involving certain models.

A brilliant idea of the Frumkin correction [2, 3] provides a general approach to this separation. It has been combined more or less successfully with a simplified linear $\log i$, η relations derived from the phenomenological Broensted-like consideration of activation energy. What we are presenting below is the development of this idea with the use of more solid theoretical background. The major novelty of this paper lies not in its original experimental part (it is illustrative), and not in computational part too (it provides supplementary information), but in demonstrating a general approach to construction of a link between theory and experiment.

This is our pleasure to dedicate this paper to Professor Mikhail A. Vorotyntsev, who is unexcelled in his art of constructing such links. Following his usual style in the area we try to do our best to apply theory from the very beginning, i.e., in the course of experimental data treatment. We should also stress that Professor Vorotyntsev is deeply implicated in the topic under discussion, as he had pioneered the problem of transfer coefficient versus overvoltage dependence in electrochemical reactions (and in particular predicted activationless ET) [4–8]. He also contributed to elucidation of numerous EDL problems [9, 10].

The analysis presented below rests on the famous Marcus quadratic formula for activation energy [11], and this is the reason for our choice of this title. We try to demonstrate that such an approach is more general and can cover also a number of “beyond Marcus” phenomena.

Dedicated to Professor M.A. Vorotyntsev on the occasion of his 60th birthday.

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Why the corrected Tafel plots do not suit us

The idea of corrected Tafel plots (CTP) [12, 13] was put forward on the basis of a combination of general equation for ET rate (current density i):

$$i = \chi \exp\left(-\frac{\Delta G^\ddagger}{RT}\right), \quad (1)$$

and Broensted-like formula for activation energy ΔG^\ddagger

$$\Delta G^\ddagger = \alpha F(\eta - \psi_1) + z_0 F \psi_1, \quad (2)$$

where η is overvoltage, z_0 is the charge of reacting specie, ψ_1 is the potential in the point of localization of this specie, α is the transfer coefficient (it turns to be simply a fitting parameter), and χ is preexponential factor (for a fixed reactant concentration; it can be considered as a sort of phenomenological rate constant). This means that when replotting i versus η experimental curve in the following coordinates

$$\left(\ln i + \frac{z_0 F}{RT} \psi_1\right) \text{ versus } (\eta - \psi_1), \quad (3)$$

one can get $\ln \chi$ and α from the intersect and slope, respectively.

The charge of reactant can be affected by various equilibria in the solution bulk. In general both the size and initial charge of reactant determine its location and trends of ion pairing as well as a deviation of the work terms from values predicted for hypothetical point charge in the point of ψ_1 potential. It is practically impossible to separate these effects in terms of z_0 and ψ_1 parameters. Therefore, despite of a more clear meaning (as compared to χ and α) both z_0 and ψ_1 are not completely defined. Dealing with the systems with one sort of reacting specie one can clarify z_0 before constructing CTP, by considering the sections of current versus supporting electrolyte concentration c at constant electrode charge [14]. Unfortunately this technique fails to work for more complex systems with parallel ET to (from) several reacting species of various charges (see Refs. [15–18] for details).

In any case it is impossible to get the reliable values of three or four parameters when constructing CTP from one set of experimental data¹. A single degree of freedom available in the course of this construction is to vary ψ_1 (assuming possible dependence of the location of an effective point charge on the reactant size). The criteria to judge about the validity of ψ_1 choice are (1) CTP linearity and (2) coincidence of CTP for various solution compositions. Criterion (1) is doubtful, as there are no physical reasons for $\alpha = \text{const}$ in an arbitrary range of overvoltage η . Criterion (2) is sometimes difficult to apply because of experimental problems (rather narrow interval of ionic strength giving a possibility to overcome the mass transport limitations, parallel discharge of additives, etc.). Additional complication for (2) is the uncertainty of the available models of potential distribution in the vicinity of charged interface.

¹The attempts to consider two types of experiments, namely the dependence on c and on metal nature (see [19] for example) result in additional problems which are not specially discussed in this paper. The most important complications follow from the χ dependence on metal nature [20] as well as from the specific adsorption of reactants, usually ignored in CTP construction

The latter problem is argued to be rather general and cannot be solved in the framework of any ET theory. Its complicating (sometimes misleading) effect can be minimized by using an approximate potential distribution near the interface in combination with a real charge distribution in the reactants and product ('molecular psi-prime effect') [21, 22]. A crucial point in estimating the reasonability of this approach is just the existence of criteria to separate realistic and senseless model configurations of the reaction zone. We should stress that a search for disagreements is sometimes more important than finding of agreement (the latter might always be apparent). A curious historical fact confirming this statement is a target of CTP construction in the original paper of Delahay and coworkers [12], who proposed the CTP procedure in its most widely used form. Their target setting was not to determine kinetic parameters from CTP but to discover the deviations and to consider their possible reasons. In [12], the deviations for multi-charged cations were explained qualitatively in terms of local electrostatic interactions, still actual general problem. Another sort of deviations found in concurrently published Ref. [13] initiated the longstanding studies of cationic catalysis.

Frumkin correction as combined with the Marcus theory

The Marcus theory of heterogeneous electron transfer [1] clearly demonstrates that the transfer coefficient α is overpotential dependent. The Marcus equation for the activation energy to be substituted in Eq. 1 can be presented in its initial version (valid for diabatic reactions and parabolic reaction terms) as follows:

$$\Delta G^\ddagger = w_o + \frac{(\lambda_R + \Delta G)^2}{4\lambda_R}, \quad (4)$$

$$\Delta G = F\eta + w_r - w_o, \quad (5)$$

where $\lambda_R = \lambda_{in} + \lambda_s$ is the total reorganization energy (consisting of inner- (in) and outersphere (s) components), and ΔG is reaction Gibbs energy which depends on overvoltage η and the work terms for oxidized and reduced forms (w_o and w_r , respectively, see below for more details about these terms).

The right-hand quadratic term in Eq. 4 can be linearly expanded for any narrow ΔG interval,

$$\Delta G^\ddagger \approx w_o + \alpha \Delta G + \frac{\lambda_R}{4}. \quad (6)$$

Equation 5 corresponds to Tafel-like i versus η dependence if w_o and w_r are low or overvoltage independent. The slope $d\eta/d\log i$ is proportional to the transfer coefficient, and the latter quantity depends on ΔG :

$$\alpha = \frac{1}{2} + \frac{\Delta G}{2\lambda_R}. \quad (7)$$

Assuming that the work terms are of purely electrostatic nature, and the reactant/product species can be represented as conducting spheres, the work terms are written in the conventional form,

$$w_o = Fz_o\psi_1; w_R = F(z_o - 1)\psi_1; w_R - w_o = F\psi_1, \quad (8)$$

By combining Eqs. 1, 4, 5, and 8, we obtain the following relation first discussed in our papers [23, 24]:

$$\sqrt{2.3RT(\log(\chi) - \log(i)) - Fz_o\psi_1} = \frac{F(\eta - \psi_1)}{2\sqrt{\lambda_R}} + \frac{\sqrt{\lambda_R}}{2}. \quad (9)$$

It is valid in the normal Marcus region and predicts the linearity of plots constructed in coordinates (corrected Marcus plots, CMP)

$$\sqrt{2.3RT(\log(\chi) - \log(i)) - Fz_o\psi_1} \text{ versus } (\eta - \psi_1), \quad (10)$$

where three parameters are involved. The preexponential term χ has a meaning different from the meaning of that in (3) coordinates. This quantity is now determined by the reactant concentration, electronic transmission coefficient κ_e , effective frequency factor ω_{eff} , and reaction volume. As two latter quantities are of well-known order, and concentration is exactly known, χ in (10) is governed mostly by κ_e . The electronic transmission coefficient and λ_R values extracted from experimental data can be compared with those calculated on the basis of different models (see, e.g., [24, 25]). The third parameter (ψ_1) remains the same as in (3).

Fitting parameter α does not simply disappear when going from (3) to (10), but a solid linearity criterion appears instead of it. Moreover, due to the dependence of both terms in the right-hand part of Eq. 9 on λ_R , the second sensitive and exact criterion can be employed: the values of λ_R calculated from the intersect and the slope of resulting linear plots (10) must coincide.

To demonstrate how sensitive is the suggested procedure and what is the degree of accuracy and unambiguity of the λ_R , χ , and ψ_1 determination, we need an appropriate model process demonstrating the advantages and complications of new procedure. The choice of such a process is discussed in the next Section.

Problem of experimental measurements of ET rate at ‘mid’ overvoltages

The majority of electrode reactions can be observed in a narrow region of low overvoltages (0–0.2 V, very rarely up to 0.5 V, see a brief review in [22]) because of the subsequent mass transport limitations. If reorganization energy has an order of 1 eV, Eq. 7 predicts no serious deviations from linearity, and the criterion of linearity of (10) is less informative. This does not mean that CMP procedure will not work for these processes, but for initial test we are looking for wider region with more significant deviations of α from 1/2.

The uniquely wide regions of available overvoltages are known for a group of reactions taking place under strong electrostatic repulsion (which increases with overvoltage), namely cations electrooxidation at a positively charged surface and anions electroreduction at a negatively charged surface [26]. For the latter ($\text{S}_2\text{O}_8^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{Fe}(\text{CN})_4^{3-}$, MnO_4^-), the mass transport limitations are absent or can be corrected in a wide range of overvoltages exceeding 1 V. From the first glance it gives the best chance to observe α versus η dependence. However, for the majority of mentioned reactants these wide regions start already at high (1 or even 2 V) overvoltage. The preceding region of lower η finds itself at positive electrode charges, i.e., in the absence of repulsion. Therefore, the reduction is fast, and ET is screened by diffusion.

The Marcus equations are formally valid at $F\eta/\lambda_R < 1$. More exactly, some deviations are predicted already at $F\eta/\lambda_R < 0.8$ (at the vicinity of activationless region) [5–7]. The most well-known reactions of anions at high overvoltages at negatively charged surfaces are found to be more or less activationless [27].

We are dealing below with the example of relatively simple ET reaction which is possible to observe in a ‘‘mid-width’’ overvoltage region, namely the reduction of cerium(IV)- decatungstate anion $[\text{H}_2\text{CeW}_{10}\text{O}_{36}]^{6-}$ (denoted below as CeW_{10}). The experimental data were presented recently in Ref. [28]. The molecular structure shown in Fig. 1 demonstrates a central Ce(IV) atom surrounded by two pentatungstate ligands. Positions of protons are conditional, but their preferential bonding with oxygens surrounding central atom agrees with general trends of chemistry of heteropolyoxometalates [29] (this protons are ‘nonacidic’, i.e., do not dissociate in the total pH range of anion stability). The reduction of Ce(IV) to Ce(III) starts at potentials more than 1 V exceeding the potential of tungstate ligand reduction. The current decrease induced by repulsion starts at the potential of zero charge, when the overvoltage amounts to ca. 0.6 V. At pH ~ 6 , the reactant is still stable and simultaneously the reduction of ligand starts at rather negative potentials (the overvoltage for Ce(IV/III) system close to 1.1 V).

Reactant molecular characterization and molecular psi-prime effect

The ab initio quantum chemical calculations were performed at the SCF level using the *Gaussian* 03 program suite [30]. The valence electronic shell of the Ce, W, O, and H atoms was treated by a basic set of DZ quality (31G), while the effect of inner electrons was included in the effective core potential (CEP) [31]. The unrestricted formalism was employed to describe the open-shell system in the reduced state.

The atomic charges (see Table 1) were calculated using the ChelpG method [32], which provides the best fit for the molecular potential. An external electric field

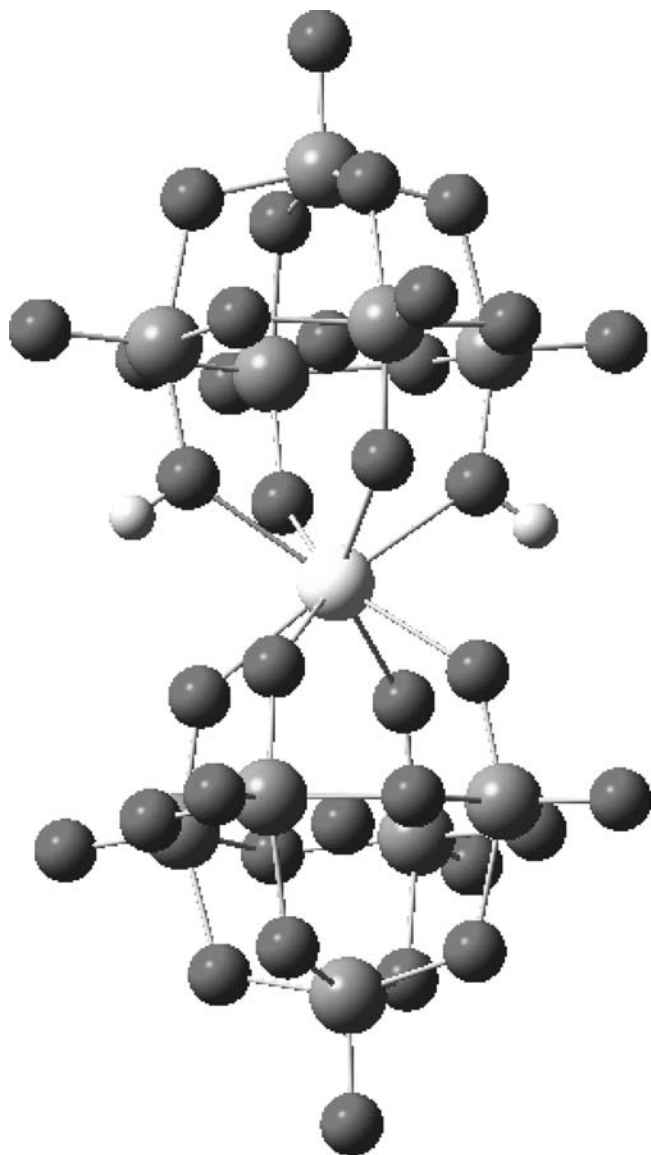


Fig. 1 View of the $[\text{H}_2\text{CeW}_{10}\text{O}_{36}]^{6-}$ molecular structure

induced by six positive point charges positioned symmetrically around CeW_{10} was involved in the model calculations in order to compensate high values of the negative charges of heteropolyanion. Since even a restricted geometry optimization of such molecular systems is extremely demanding from the view point of computer resources, we employed the pertinent geometrical coordinates obtained from the XRD data for the sodium salts [33, 34].²

²The O-H bond length and the H-O-Ce valence angle were chosen to be 0.96 Å and 112.4 grad, respectively. Several versions of oxygen atoms bonded with the protons were tested, and the version imaged in Fig. 1 was concluded to be the most probable (total energy is ca. 40 kJ mol⁻¹ lower than for any other versions)

The large molecular size of the reactant (comparable with Debye length if solution is not too dilute) forces take into account the real atomic charge distribution for the realistic choice of work term [22]. The sensitivity of resulting work term to the values of atomic charges is not very high (the deviation of 0.1 does not change the result noticeably). Under these circumstances, there is no necessity to consider such effects as the decrease of dielectric permittivity in the reactant cavity [22], so the reactant is considered simply as a set of point charges in solution. Even under such a crude approximation the result seems to be more realistic than for a single point charge or homogeneously charged sphere usually considered for classical Frumkin correction.

The Gouy-Chapman formula [26] was addressed to describe the potential distribution along the normal to the interface

$$\psi_1(x) = \frac{4RT}{F} \operatorname{arctanh} \left[\tanh \left(\frac{F\psi_0}{4RT} \right) \exp(-\kappa x) \right], \quad (11)$$

where x is the distance between point charge and the outer Helmholtz plane (OHP), the subscript 0 corresponds to OHP potential, and κ is the reciprocal Debye length. An effective psi-prime potential was computed as follows [22]:

$$w_o = F \sum_{i=1}^n z_i \psi(x_i), \psi_{\text{eff}} = \frac{1}{z_o} \sum_{i=1}^n z_i \psi(x_i). \quad (12)$$

As a multicharged anion can hardly remain nonassociated in solution even at 10 mM concentration of supporting sodium acetate, we estimated the degree of association using ion-selective sodium electrode.³ Our data are satisfactorily in agreement with the predominant existence of $\text{Na}_4[\text{H}_2\text{CeW}_{10}\text{O}_{36}]^{2-}$ associated species, which are considered below as the reactants. No additional association is assumed for reduced form. The atomic charges of sodium cations are assumed to be +1, as only a negligible charge transfer was observed in our test quantum chemical calculations.

The procedure of CMP construction

The reaction zone was considered according to the scheme given in Fig. 2. Four sodium cations were assumed to be located in couples, attached to two ligands. The value of ψ_1 in (II) was varied indirectly by scanning r_1 and r_2 distances (see Fig. 2). The sets of r_1 and r_2 were considered for various Ce-OHP distances r and two orientations (vertical, imaged in Fig. 2, and horizontal, with the same assumptions about possible cations localization).⁴ Therefore, various combinations of r , r_1 ,

³These experiments will be presented in detail in a separate communication.

⁴We distinguish r , the distance corresponding to the location of atoms in a real reacting specie and x , the model distance related to a hypothetical point charge (Eq. 11).

Table 1 Typical values of atomic charges (elementary charge units) for oxidized and reduced $[\text{H}_2\text{CeW}_{10}\text{O}_{36}]^{z-}$ species

	Atomic charges	
	Oxidized form, $z = -6$	Reduced form, $z = -7$
Ce ^a	4.15	3.56
W ^b	2.69–2.90	2.76–2.91
O ^c from the first coordination sphere of Ce	–1.11 (protonated) –(1.20–1.24)	–1.11 (protonated) –(1.13–1.14)
O ^c from ligands, edge	–(0.82–0.99)	–(0.91–1.11)
O ^c from ligands, bridge	–(1.00–1.14)	–(1.06–1.22)
O ^c from ligands, center	–(1.70–1.71)	–(1.63–1.76)
H ^d	0.52	0.51

Symbols used in Fig. 1

- a A large bright sphere
- b Ten atoms, large dark spheres
- c Small dark spheres
- d Small bright spheres

and r_2 became fitting parameters. It does not mean the increase of the number of parameters because only very few sets satisfy the criteria of CMP, so the choice was rather rigid. Moreover, by scanning r , r_1 , and r_2 , we were able to sort out the electrostatic work terms from a very wide range. Even if some details of configuration used for analysis differ from a real configuration, the work terms fall in any case in the interval sorted out, and no any uncertainty appears in the key values of reorganization energy and preexponential factor estimated in such a way.

Figure 3 presents the selection scheme employed for the computational treatment of experimental data [28].

For any series of calculations, the value of χ is initially fixed. Distances r , r_1 , and r_2 are scanned with 0.01–0.05 Å steps, and for each set of distances the effective psi-prime potential was calculated according to Eq. 12. Then it is used for the construction of plot (10), in which linearity is considered as satisfactory if the R-factor is at least 0.99. For rare combinations satisfying this first criterion, the reorganization energy values are computed from two terms in the right-hand part of Eq. 9. The sets of r , r_1 and r_2 were recognized as satisfactory only if two independent λ_R values agree within the accuracy of 3–4% (ca. 5 kJ mol⁻¹). A similar procedure was applied to the next χ value. +

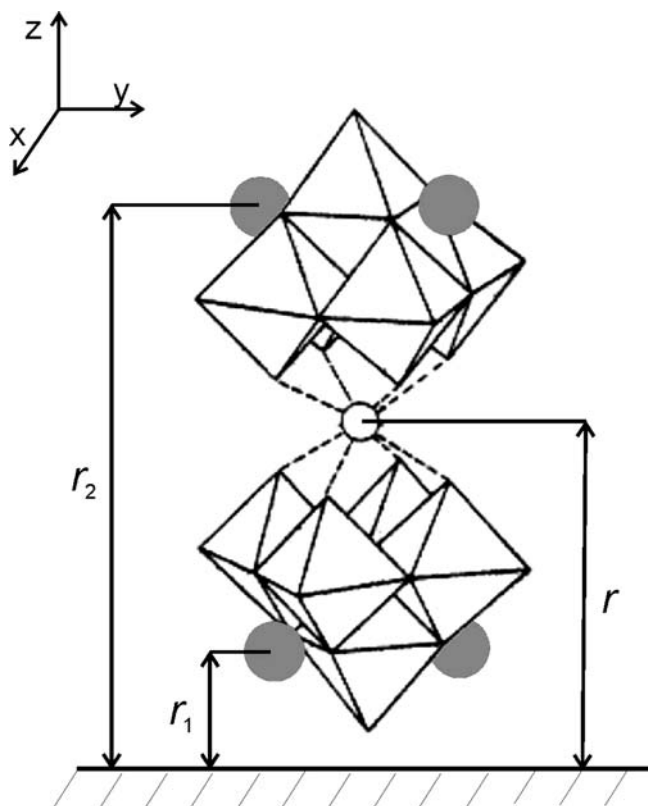


Fig. 2 Schematic representation of the reactant location in respect to the outer Helmholtz plane (*horizontal line at the bottom*). Spheres denote associated sodium cations for which positions are varied in terms of indicated distances

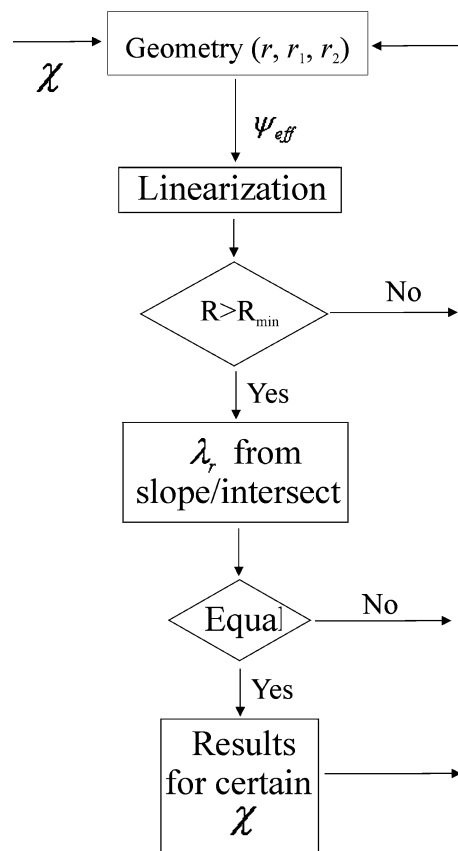


Fig. 3 Schematic representation of the selection procedure

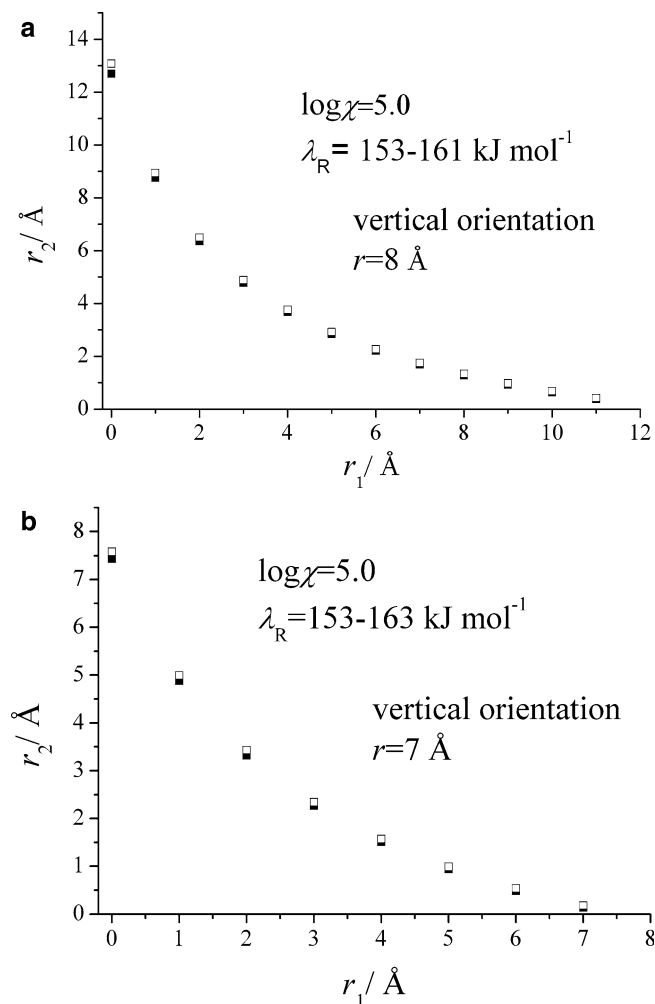


Fig. 4 The examples of sets of geometric parameters satisfying the CMP criteria. *Opened and closed points* correspond to the boundary values of reorganization energy for given r and χ . Experimental data [28] are treated for $c = 10$ mM (acetic buffer) with 1 mM CeW₁₀, dropping mercury electrode

The maximal χ value was estimated⁵. from

$$\chi = Fc \frac{\omega_{\text{eff}}}{2\pi} \delta z \kappa_e \quad (13)$$

assuming $\kappa_e = 1$. For effective frequency $\omega_{\text{eff}}/2\pi = 10^{13} \text{ s}^{-1}$ and reaction volume δz up to 10^{-7} cm , the χ value cannot exceed 10^5 for a given reactant concentration and current densities i in $\mu\text{A cm}^{-2}$. The lower limit of χ is determined by a condition of the real number in the left-hand part of Eq. 9. If a value under square root in (10) becomes negative, this presumes formally to the negative activation energy, which is

⁵Both ω_{eff} and δz upper limits are deliberately higher than the usual values for aqueous solutions, to avoid the underestimate of the upper limit of χ

evidently beyond the Marcus equation. It is demonstrated below that the opposite statement is not correct, i.e., if no linearity is observed for a positive value of this quantity this might point to the activationless behavior.

Another reason for negative values under square root can be neglecting of the specific adsorption terms. A separate communication illustrating this possibility for certain reactions is in preparation; it is aimed at some modification of the method for specifically adsorbed reactants. As for CeW₁₀ considered in this paper, we believe that it does not adsorb on mercury at negative electrode charges, similar to numerous experimentally studied iso- and heteropolytungstates [35].

The both criteria were proven to be extremely sensitive to the set of scanned distances, and for any certain χ a limited number of satisfying distances could be determined with 0.1 Å accuracy. Figure 4 displays the examples of parameter regions selected by these means, and Fig. 5 demonstrates a set of the typical CMP constructed for various χ ($\log\chi = 3.6$ refers to the lowest possible value, when some points for the highest overvoltages start to fall out). It is easy to see that the agreement with both criteria is achieved only in a very narrow range of rather high χ .

For any possible configurations, the total reorganization energy lies in a range of 139–163 kJ mol^{-1} , i.e., the interval is really narrow. There is no pronounced difference of allowable χ , λ_R combinations (Fig. 6a) for vertical and horizontal orientations (segments in Fig. 6a demonstrate the range of λ_R for various geometric parameters at any given χ). The left boundary of the graph in Fig. 6 is related to χ values at which the linearity criteria fail, i.e., we enable (a) to determine χ within the accuracy of one order, (b) to estimate λ_R for any χ within the accuracy of 5 kJ mol^{-1} , and (c) to estimate the region of possible λ_R within the accuracy of 25 kJ mol^{-1} (not exceeding 15–17%). An important test confirming that the treatment remains in frames of introduced model assumptions is calculation of transfer coefficient (Fig. 6b); these quantities approach the limit of Eq. 4 applicability ($\alpha \sim 0.1$) but do not cross it.

Usual CTP constructed for comparison demonstrate no linearity for any possible combinations of z_0 and ψ_1 . It should be stressed that on the basis of CTP procedure, these parameters are mixed to a great extent, i.e., various combinations of z_0 and ψ_1 correspond to various versions of the molecular work terms.

Considering the latter extracted from our analysis, we conclude that for $\psi_1 = \psi_0$ they yield for z_0 a less negative value than -2 . Keeping $z_0 = -2$, the realistic work terms can be obtained at high distances $x = 15\text{--}25 \text{ Å}$ and, therefore, low negative ψ_x (Eq. 11). This means that considering possible CTP is enough to compare, for example, several representative versions with $\psi_1 = \psi_0$ and various $z_0 = -1\text{--}4$ (Fig. 7). It is probably possible to find some intermediate version with the better linearity, but there are hardly any criteria for the choice of

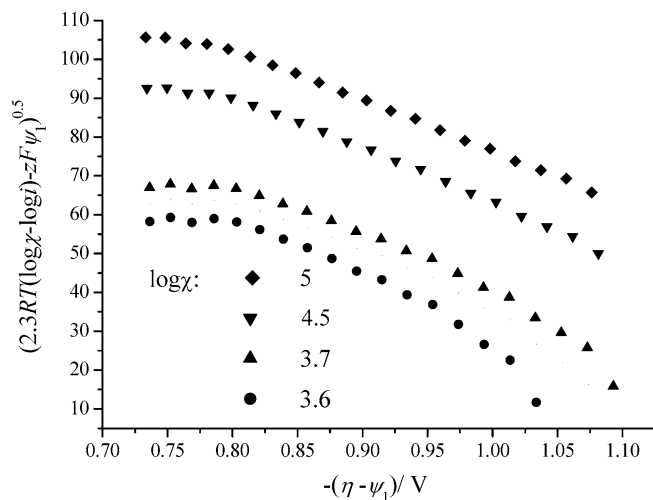


Fig. 5 The examples of CMP for various χ values. For the lowest curve, three points from the right already fall out (*negative quantity under square root*)

this version,⁶ and CTP remains completely spurious, in contrast to CMP.

Are the parameters determined from CMP reasonable?

The solvent and innersphere contributions to the total reorganization energy were independently addressed using a quantum chemical approach. The total energy of CeW₁₀ was scanned in a narrow interval versus the Ce–O bond length which was treated as the innersphere coordinate (see Fig. 8); the possible relaxation of W–O bonds was neglected. It can be seen from figure that the change in the Ce–O bond lengths induced by the electron transfer is rather small ($\approx 0.027\text{\AA}$) and an estimated contribution to the intramolecular reorganization energy does not exceed $\sim 6\text{ kJ mol}^{-1}$. The equilibrium Ce–O distance for the oxidized state was found to be 2.388 \AA which is close to the corresponding values $2.36\text{--}2.37\text{ \AA}$ known from experiment [33]. The experimental data on the reduced CeW₁₀ geometry [34] (less detailed), however, point out to a more noticeable lengthening the Ce–O bonds ($\sim 0.13\text{ \AA}$).⁷ Due to the rather crude character of the model employed, one should stress first of all the main qualitative prediction: a small innersphere contribution to the total reorganization energy.

The solvent outersphere reorganization energy (λ_s) was calculated on the basis of the model of conducting ellipsoids developed by Kharkats [37]. The ellipsoid

⁶All corrected plots under consideration (both CTP and CMP) coincide for experimentally available concentrations of supporting electrolyte (c). However, this criterion is not too sharp, at least for relatively narrow c range. It is not also very sensitive to an assumed configuration of the reaction layer.

⁷Using these data as well as a value of 220 cm^{-1} for the Ce–O vibration frequency in CeW₁₀ [36], a higher estimate of ca. 30 kJ mol^{-1} can be predicted for λ_{in} in frames of the model of harmonic oscillator.

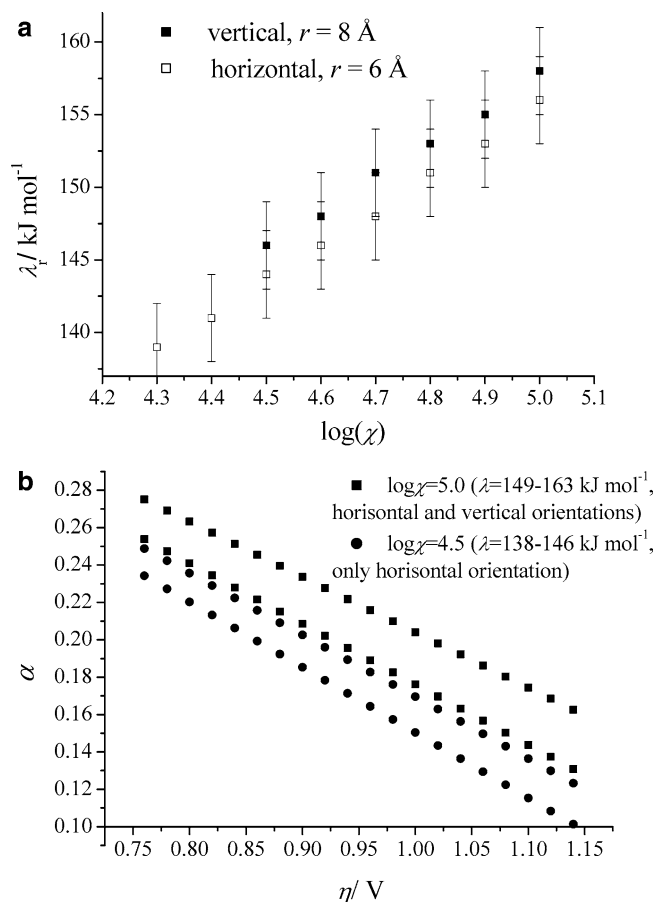


Fig. 6 Possible combinations of parameter values determined from CMP after irrefragable scanning of all geometric parameters (a) and the regions of expected transfer coefficients (b)

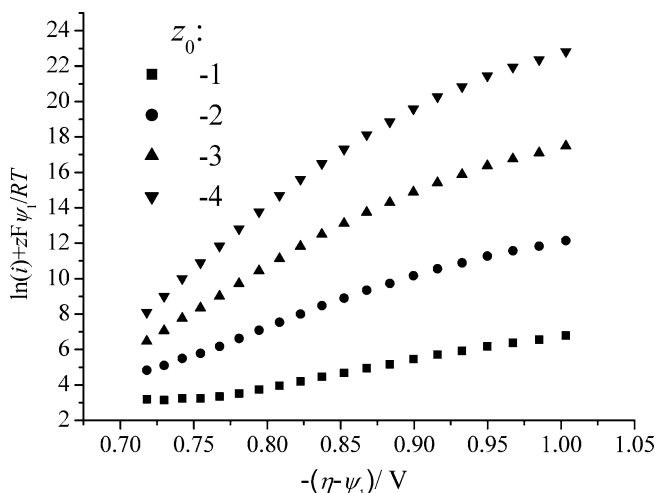


Fig. 7 The CTP constructed from experimental data [28] for $c = 10\text{ mM}$ (acetic buffer) with 1 mM CeW₁₀, dropping mercury electrode. The reactant charge is assumed to be $-4/-1$ (resulting from ionic association with supporting cations)

semiaxes have been estimated as follows: $a = 7.2\text{ \AA}$, $b = c = 4.5\text{ \AA}$. If the axis c is perpendicular to an electrode surface,

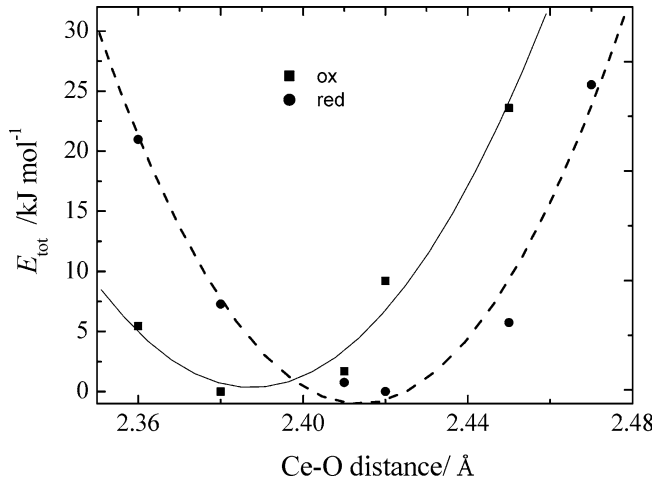


Fig. 8 Total energy of CeW_{10} (reckoned from the minima) in the oxidized (*squares*) and reduced (*circles*) state versus the Ce-O bond length; *solid and dotted lines* are parabolic approximations

$$\lambda_s = Ce_0^2 \left\{ \frac{1}{2r_{\text{eff}}} - \frac{1}{4z} \left(1 - \frac{a^2 + (c_{\text{eff}})^2}{12z^2} \right) \right\}, \quad (14)$$

where $r_{\text{eff}} = \sqrt{a^2 - c^2}/F(\theta, \phi)$ (effective radius of the ellipsoidal figure), and $F(\theta, \phi)$ is the elliptic integral of the first kind with parameters $\theta = \arcsin \sqrt{(a^2 - c^2)/a^2}$ and $\phi = \sqrt{(a^2 - b^2)/a^2 - c^2}$; $c_{\text{eff}} = (b + c)/2$; C is the Pekar factor. In Eq. 14, z is the ellipsoid center-metal surface distance.

If axis c is parallel to the metal surface [36],

$$\lambda_s = Ce_0^2 \left\{ \frac{1}{2r_{\text{eff}}} - \frac{1}{4z} \left(1 + \frac{a^2 + (c_{\text{eff}})^2}{24z^2} \right) \right\}. \quad (15)$$

The solvent reorganization energy versus z is shown in Fig. 9 (a factor of 0.8 was used to correct λ_s to the quantum effects [38]).

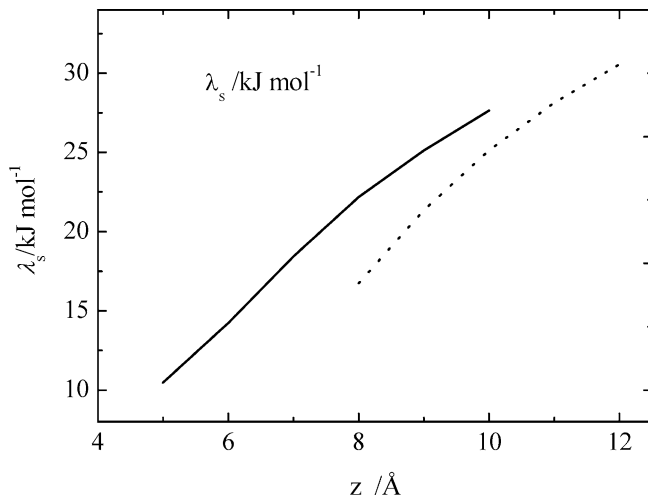


Fig. 9 Solvent reorganization energy computed for two different orientations of CeW_{10} relative to the electrode surface (*horizontal—solid; vertical—dotted*)

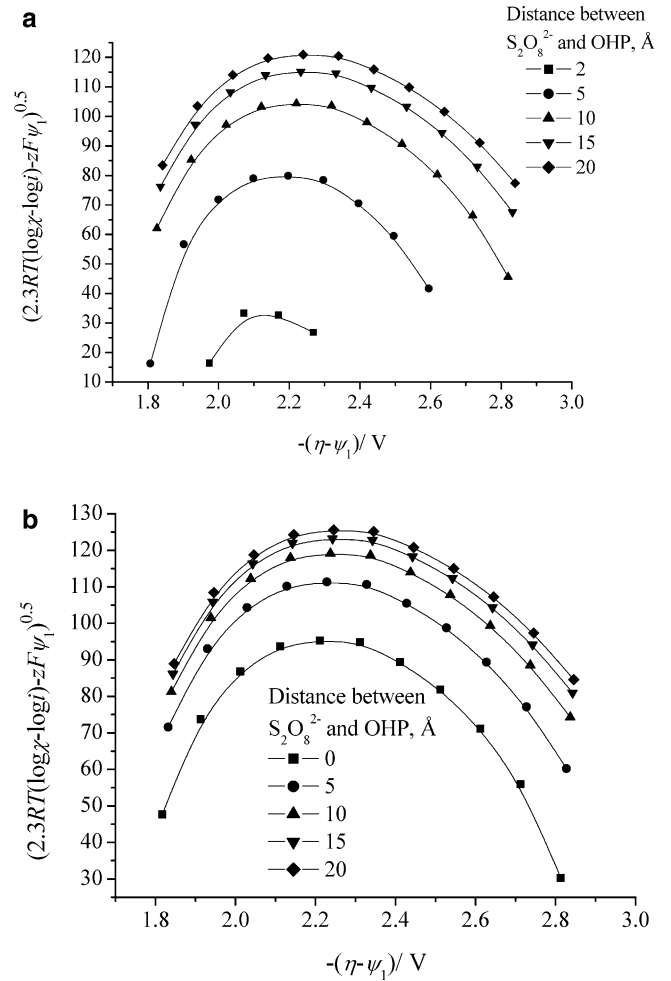
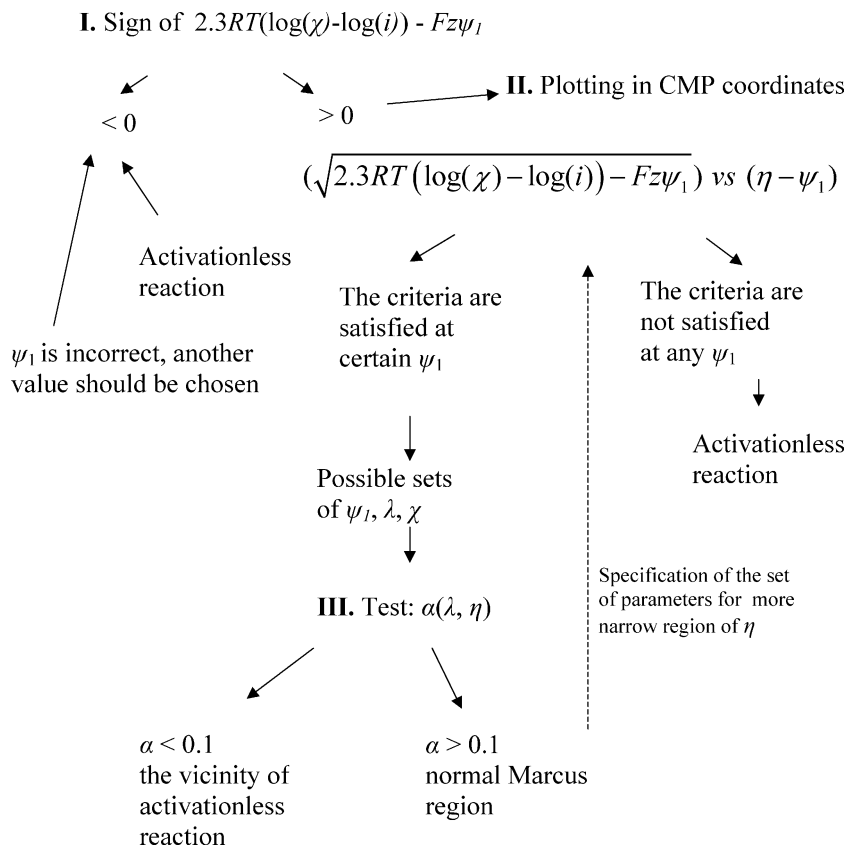


Fig. 10 The examples of peroxodisulfate CMP for $\log \chi = 4$ and various r values. The original data from Refs. [3, 13] are treated. The reduction of bare anion at homogeneously charged interface (**a**) and under conditions of local electrostatic interaction with supporting sodium cation at OHP (**b**) are considered. Molecular details can be found in [27]

The values of z used for the analysis of solvent reorganization can be associated with a sum of the r distances and thickness of the dense part of the double layer (distance between the surface and OHP). For the both orientations, this comparison gives an estimate of $\lambda_s \sim 30 \text{ kJ mol}^{-1}$, i.e., about 20% of the total reorganization energy estimated from the CMP analysis. It looks like the agreement is possible only if the inner-sphere contribution exceeds 100 kJ mol^{-1} , which is possible only if the W-O bonds contribute predominantly to λ_{in} . The problem requires further analysis and is linked to a general problem of the reorganization energy for complex heteropolyanions (see a special section in Ref. [39], p.125).

We do not consider this situation as some dramatic disagreement, but only as an impetus for more rigorous model calculations of the inner-sphere reorganization in future. This should be done in parallel with a search of

Fig. 11 A general scheme of CMP analysis



other model systems for the CMP construction involving more simple reactants and providing an extended comparative analysis with computational data.

Concluding this section, we should comment the values of χ , being at the upper limit for diabatic reactions ($\kappa_e \sim 1$, with the rather high reaction volume assumed without any special reasons). Note that most likely the reaction under discussion is adiabatic. If the resonance splitting in the crossing point of reaction terms exceeds $2kT$, an additional decrease of the activation barrier can occur, and the Marcus formula (4) should be modified. This decrease is affected mostly by the orbital overlap and at certain cases it can depend on the electrode charge [40]. In terms of CMP scheme (10) this modification simply increases the upper limit of χ . By taking some estimates into account for various electrode-reactant systems [40, 41], at least one order increase of χ might be expected. A significant adiabaticity for CeW_{10} reduction on mercury should be also considered as an important prediction of the CMP analysis.

CMP as a test for activationless processes

To illustrate the sensitivity of CMP to the boundaries of applicability of Marcus theory, we present Fig. 10 constructed for the peroxodisulfate reduction on mercury. This reaction presents a classical example of the anion

reduction at the negatively charged electrode surface. Despite it is accompanied by the bond rupture, Eq. 4 can be employed under certain approximations (see in Ref. [27] and Refs therein).

For possible combinations of geometric parameters and χ no linearization was observed. Moreover, the plot in (10) coordinates was nonmonotonous. Situation was similar for both types of interfacial interactions considered earlier in detail in [27], namely for nonlocal and local electrostatic interactions (Fig. 10a and b, respectively). When constructing these Figs, we considered the peroxodisulfate similar to CeW_{10} (Fig. 2); for Fig. 10b, a sodium cation located at OHP was additionally included between the electrode and the reactant.⁸ A trick with the local interaction is helpful in decreasing the number of points fallen out because of the negative values under the square root in the left-hand part of Eq. 9. It could not help, however, in improving the shape of the curve.

The CMP construction for peroxodisulfate remains informative even being unsuccessful: it confirms unambiguously the activationless nature of this reaction in the overvoltage region considered and is helpful in constructing a general scheme of the CMP treatment as a tool for understanding some important features of ET processes (Fig. 11).

⁸This model reflects the Frumkin's qualitative idea of cation bridges [19] specially discussed in Ref. [27]

Conclusions

Surprisingly, in spite of numerous approximations and extremely limited domain of applicability, classical CTP remains very popular. Only their simplicity can be assumed as explanation, the reason for which is really false. The most striking point is by using the CTP linearity (i.e., the condition $\alpha = \text{const}$) as the criterion of true Frumkin correction. When doing it, most of people simply ignore the original remark given in Refs. [3, 13] on the principal CTP uncertainty resulting from impossibility to determine two phenomenological parameters (α and ψ_1) simultaneously.

There is only one possibility to avoid the contradiction of classical CTP linearity and physically grounded Marcus theory, namely to deal with experimental data related to respectively narrow overvoltage region $F\eta/2\lambda_R \ll 1$. As the typical λ_R values are in the range of 100–200 kJ mol⁻¹, one can expect the true linearity of classical CTP for $\Delta\eta < 0.05\text{--}0.1$ V. It is comparable with the width of usual region available for quasireversible reactions under standard convection modes. For the majority of these reactions the available region under discussion starts from zero overvoltage. Usually there are no physical reasons for pronounced α deviations from 0.5 under these circumstances.⁹ Much lower or (rarely) much higher values extracted from CTP cannot only cast doubt on the Frumkin correction, but also point to various specific features of elementary act. There is no chance to understand the physical nature of deviations in frames of CTP.

As we demonstrated above, the CMP procedure gives such a chance. The main reason of its unambiguity is the existence of sharp criteria for separating correct and incorrect versions of electrostatic contributions. The procedure can be generalized in future by substituting traditional psi-prime potential for the work terms. We were dealing with the psi-prime quantity in order to demonstrate that CTP and CMP are allied in respect to electrostatic interactions. The most general approach will consist in introducing potential (electrode-charge)-dependent and -independent components of the work terms as fitting parameters scanned in a wide range. The boundaries of this region should be estimated from the independent analysis of molecular work terms and adsorption energies in order to keep the analysis realistic in terms of the reaction layer configuration. However, since such an approach would look somewhat formal at the first step, we have resorted to a more certain consideration for CeW₁₀.

A generalized approach, making the CMP analysis easier for the electrode processes, accompanied by the specific adsorption, potential-dependent reaction volume, and other complications will be presented in the next communication.

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⁹Deviations are predicted for highly asymmetric innersphere reorganization [42] and dissociative electron transfer [43].

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