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Reliable rate constant determination for heterogeneous electron transfer: CrEDTA$^-$

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Pulse and steady-state photoemission techniques are applied to determine the heterogeneous rate constant of CrEDTA$^-$ reduction on liquid mercury. The resulting value (too high for polarographic determination and available earlier only for amalgamated gold) is important for experimental verification of various predictions of the electron transfer theory.

CrEDTA$^-$ is of interest for basic studies of heterogeneous electron transfer (ET) because of its high stability, convenient value of $Cr^{3+/2+}$ redox potential and the absence of specific adsorption manifestations in the course of reduction on the majority of electrode materials. This reactant was already used to study less common effects of metal[1] and solvent[2,3] nature on ET rate. Further progress depends crucially on the accuracy of experimental ET rate constants.

The heterogeneous reduction of CrEDTA$^-$ in an aqueous medium is rather fast. Correspondingly, the accuracy of rate constants determination by means of traditional electrochemical techniques is limited by pronounced mass transport contributions. The same (or even more heavy) problem arises for the determination of transfer coefficients, as only a narrow potential range is available for extraction of ET rate from mixed currents. This is the reason why classical DC polarography and rotating disc electrode techniques applied earlier[4] require some combination with other techniques. Cyclic voltammetry[2] is even less precise (only anodic/cathodic peak separation of 80 mV is reported in ref. 2, not rate constant). Additional problem is to check whether single electron reduction is really a one-step process. Here we present the data of photoemission techniques,[†] forming a powerful tool to determine ET rate constants for various types of ET, including the processes with a preceding chemical step.[7,8]

The essence of experiments is the photogeneration of solvated electrons (e^-_{aq})

$$CrEDTA^- + e^-_{aq} \xrightarrow{K_a} CrEDTA^{2-} \quad (I)$$

with the subsequent registration of charge (current) related to the oxidation of the product

$$CrEDTA^{2-} - e^-_M \xrightarrow{\chi_a} CrEDTA^-. \quad (II)$$

Signal related to the oxidation of the product resulting from pulse illumination [reaction (II)] was observed at potentials E more positive than –1.3 V. Currents related to the dark reduction of the reactant[4] can be ignored at E more positive than –1.15 V. Under these circumstances (and assuming no reactant adsorption on the basis of previous double layer capacity data[9]), one can use the following equation for the electrode charge *vs.* time dependence after a laser pulse.[10,11]

$$\frac{Q(\tau)}{Q_m} = \frac{\tilde{\chi}\tilde{\gamma}}{\pi}\int_0^{\alpha} \frac{\delta^{-1/2}\tilde{\chi}\tilde{\gamma} - \delta^{-1/2}y + (\tilde{\chi}+\tilde{\gamma})(\alpha-y)^{1/2}}{(\tilde{\chi}^2+y)(\tilde{\gamma}^2+y)[\gamma+(\alpha-y)^{1/2}](1+y/\alpha\Phi)} \frac{e^{-y\tau}}{y}\,dy - \\ -\frac{\alpha\chi\tilde{\gamma}}{\pi}\int_{\alpha}^{\infty} \frac{\gamma y + (\tilde{\chi}+\tilde{\gamma})(\alpha-y)^{1/2} - \delta^{-1/2}\tilde{\chi}\tilde{\gamma}^2}{(\tilde{\chi}^2+y)(\tilde{\gamma}^2+y)(\gamma^2-\alpha+y)[(y/\delta)^{1/2} - (y-\alpha)^{1/2}]} \frac{e^{-y\tau}}{y}\,dy. \quad (1)$$

Equation (1) is presented in terms of the following dimensionless variables: $\tau = t/t_0$, $\alpha = k_a N_a t_0$, $\chi = (\chi_a/D_e)(D_e t_0)^{1/2}$, $\gamma = (D_e t_0)^{1/2}/l_0$, $\delta = D_a/D_e$, $\tilde{\chi} = \chi\delta^{1/2}$, $\tilde{\gamma} = \gamma\delta^{1/2}$, $\Phi = \delta/(1-\delta)$, where $t_0 = 10^{-8}$ s is the laser pulse duration, $l_0 = 2.5\times10^{-7}$ cm is the effective length of solvated electron, k_a is the rate constant of e^-_{aq} capture by acceptor (according to ref. 12, $k_a = 3.0\times10^{10}$ dm^3 mol^{-1} s^{-1}), $N_a = 10$ mM is the acceptor concentration, $D_e = 4.5\times10^{-5}$ cm^2 s^{-1} and D_a are the diffusion coefficients of e^-_{aq} and acceptor, respectively, χ_a is the ET rate constant at a given potential. When α, $\gamma^2 \gg \chi^2$ and τ are high ($t > 10^{-6}$ s, $\tau > 100$), equation (1) can be reduced to[10,11]

$$\frac{Q(\tau)}{Q_m} = \frac{\alpha^{1/2}}{\gamma+\alpha^{1/2}} \frac{1}{\chi(\pi\delta\tau)^{1/2}}. \quad (2)$$

To apply rather cumbersome equation (1) correctly, we first checked the adaptability of reduced equation (2) to our experimental values at $t \to \infty$ (Figure 1). The $Q - t^{-1/2}$ approximation of experimental data according to equation (2) was considered. We found that this simplification is reliable at least for $t > 10^{-6}$ s ($\tau > 100$). The limit corresponds to contribution from solvated electron capture by impurities. These limiting values were used at the next step for the correction of curves fitted by means of equation (1) and compared to experimental charge decays in Figure 1 (solid lines, experimental; dashed, calculated). This analysis assumed $\chi_a \leq 30$ cm s^{-1} and the model parameters $\alpha = 3.0$, $\gamma^2 = 7.2$, $\chi^2 \leq 0.2$ (literature data) for various time intervals. The resulting potential dependence of χ_a, if treated as the Tafel dependence, corresponds to $\beta = 0.23\pm0.13$ (Figure 2). Despite of so low accuracy of β, we can conclude reliably that this value is below 0.5; *i.e.*, the transfer coefficient of the reverse cathodic reaction is above 0.5. The value reported earlier[4] was $\alpha = (1-\beta) = 0.47$, but it was obtained even with a lower accuracy because of unavoidable double layer corrections.

A reason for transfer coefficient deviations from 0.5 at low overvoltages is the asymmetry of inner-sphere reorganisation.[14]

[†] For the majority of experiments, the solution was 10 mM NaCrEDTA + 0.5 M KCl, pH 6.2 was adjusted by 0.01 M acetic buffer. In comparative experiments, 2 mM NaCrEDTA with the same supporting electrolyte was used. Mercury was of 99.9995% purity, N_2O was of 99% purity. All potentials are reported in respect to SCE. The details of devices and photoemission modes can be found in refs. 5 and 6.

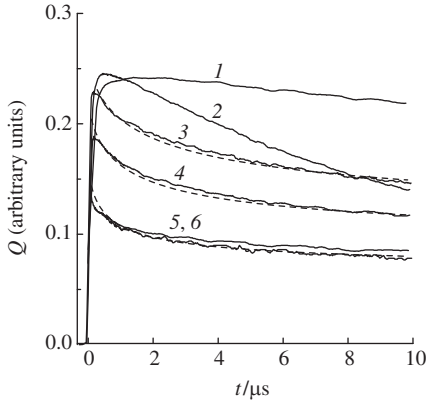

Figure 1 Electrode charge *vs.* time dependence registered after a laser pulse at E (*1*) –1.30, (*2*) –1.25, (*3*) –1.10, (*4*) –1.05, (*5*) –0.95 and (*6*) –0.90 V (solid lines). Dashed lines demonstrate calculated curves corresponding to experimental curves (*3*)–(*6*).

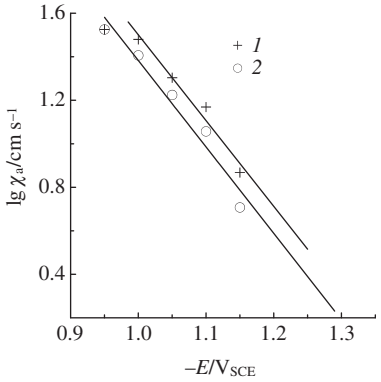

Figure 2 Rate constants at different potentials as determined from the digital simulation and fitting of experimental data using equations (1) and (2). Two different values of D_a were used: (*1*) 3.5×10^{-6} (ref. 4) and (*2*) 6.3×10^{-6} cm^2 s^{-1} (ref. 13).

Just for the type of asymmetry known for CrEDTA$^-$ from quantum chemical analysis,[1,15] $\alpha > 0.5$ is expected.

Typical photocurrent *vs.* potential curves normalized for photocurrent in a 7.7 mM N_2O solution are shown in Figure 3. The half-wave potential is –1.32 V, and this value demonstrates no modulation frequency dependence (a feature is typical of fast ET reactions). We assume that the product CrEDTA^{2-}, resulting from the capture of solvated electrons with the reactant (acceptor) according to reaction (I) tends to oxidize [reaction (II)] at potentials more positive than an equilibrium (or formal) potential, and remains electrochemically inactive at more negative potentials. In N_2O-containing solutions, CrEDTA$^-$ and N_2O compete for the capture of solvated electrons, and the wave

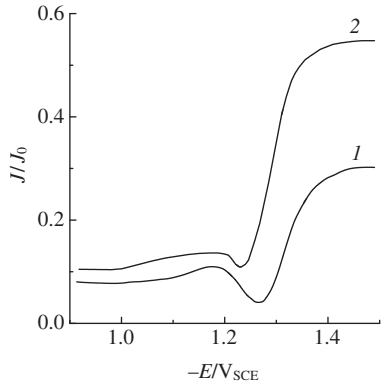

Figure 3 Normalized photocurrent measured in a 0.01 M acetic buffer (pH 6.2) + 0.5 M KCl + NaCrEDTA, (*1*) 2 and (*2*) 10 mM.

decreases with N_2O concentration. The interception of OH radicals by CrEDTA$^-$ can be neglected because of the low rate constant of this process.[12]

Competitive reactions are as follows:

$$N_2O + H_2O + e^-_{aq} \xrightarrow{K_{a0}} N_2 + OH^- + OH^\bullet, \quad \text{(III)}$$

$$OH^\bullet + e^-_M \longrightarrow OH^-, \quad \text{(IV)}$$

and, according to reference data,[12] $K_{a0} = 6\times10^9$ dm^3 mol^{-1} s^{-1}. As $E \geq -1.1$ V, the potential interval corresponds to CrEDTA^{2-} oxidation, and the normalized photocurrent at $E \geq -1.1$ V is determined by electrons captured by N_2O:

$$\frac{J}{J_0} = \frac{K_{a0}N_{a0}}{K_{a0}N_{a0} + K_aN_a} \frac{l_0 + (D_e/K_{a0}N_{a0})^{1/2}}{l_0 + [D_e/(K_{a0}N_{a0} + K_aN_a)]^{1/2}}, \quad (3)$$

where N_{a0} is N_2O concentration (7.7 mM) in solution used for registration of normalization curve $J(E)$ for photoemission current, and N_{a0} is N_2O concentration in the solution under study. This dependence gives a possibility to compute K_a. Figure 4 presents experimental and computed dependences of normalized photocurrent on N_2O concentration for two different CrEDTA$^-$ concentrations. K_a is 1.0×10^{10} dm^3 mol^{-1} s^{-1}, *i.e.*, somewhat lower than the published value[12] of 3.0×10^{10} dm^3 mol^{-1} s^{-1}.

The half-wave potential $E_{1/2} = -1.32$ V agrees well with kinetic measurements at this potential, $Q(t) \approx$ const (Figure 1). From polarography, $E_{1/2} = -(1.22–1.24)$ V. The difference results from the fact that photoelectrochemical experiments take place under the equilibrium of oxidized and reduced reactant species. This equilibrium is shifted when e^-_{aq} are captured, and a portion of oxidized species is transformed into reduced species in the course of fast homogeneous reaction. Interfacial ET is expected to shift the equilibrium towards the opposite side, and under kinetic conditions one should observe oxidation, whereas under steady-state conditions no reduction current should be observed.

ET rate constant at $E = -1.23$ V [$\lg(\chi_{\Phi 0}) = 0.47–0.60$] is even slightly higher than that obtained from rotating disc electrode data[4] for amalgamated gold [$\lg(\chi_{\Phi 0}) \sim 0.22$]. This means that an anomalously high rate of CrEDTA$^-$ reduction on mercury[1,4] (as compared with Cd and Bi) is not an artifact resulting from some mechanistic complications of reduction on amalgam, *i.e.*, in the presence of a strongly adsorbing metal (Au).

To conclude, we applied photoemission techniques for the more precise estimation of kinetic parameters of a model heterogeneous ET reaction. The resulting data were helpful in discovery and more exact confirmation of two important effects, namely, the asymmetry of transfer coefficient and non-electrostatic effect of metal nature on the rate of purely outer-sphere ET. Both effects agree with predictions of the widely understood quantum mechanical theory of ET and contribute to a further development of its predictive scope.

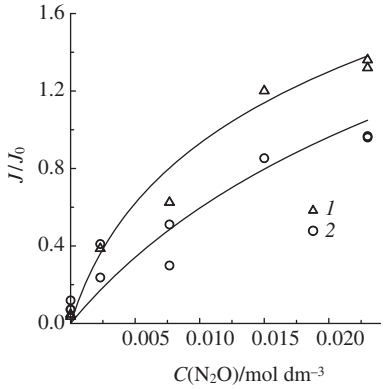

Figure 4 Experimental and computed dependences of normalized photocurrent on N_2O concentration for two different CrEDTA$^-$ concentrations: (*1*) 2 and (*2*) 10 mM.

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