Polarography

Let the k-th reactant M^{z+} is the *depolarizer* ($M^{z+} \; + \; z\,e^- \; = \; M$), a_k^* (c_k^*) and a_M^* (c_M^*) are activities (free concentrations) of the depolarizer and metal, respectively, at the mercury drop electrode surface (i.e. at the interface between solution and amalgam), c_k is the free concentration of the depolarizer in the solution. At each point of the polarographic curve¶ $I \sim E$

$$E = E^0(M^{z+}/M) + \frac{RT}{zF}\ln\frac{a_k^*}{a_M^*} = E^0(M^{z+}/M) + \frac{RT}{zF}\ln\frac{\gamma_k}{\gamma_M} + \frac{RT}{zF}\ln\frac{c_k^*}{c_M^*} = E_0 + \frac{RT}{zF}\ln\frac{c_k^*}{c_M^*} \;,$$

where E_0 is constant, if both ionic strength of the solution and current density (i.e. also γ_k and γ_M) are constant.

If there is only the depolarizer† in the solution, then

$$I = \kappa_k(c_k - c_k^*) = \kappa_M c_M^* \;,$$

$$c_k^* = \frac{\kappa_k c_k - I}{\kappa_k} = \frac{I_\ell - I}{\kappa_k} \;,$$

$$c_M^* = \frac{I}{\kappa_M} \;,$$

$$E = E_0 + \frac{RT}{zF}\ln\frac{\kappa_M}{\kappa_k} + \frac{RT}{zF}\ln\frac{I_\ell - I}{I} \;,$$

$$I = \frac{I_\ell}{2} \;\Rightarrow\; E = E_{1/2} \;,$$

$$E_{1/2} \equiv E_{1/2k} = E_0 + \frac{RT}{zF}\ln\frac{\kappa_M}{\kappa_k} \;.$$

If the solution contains (in addition to the depolarizer) also other reactant(s) (and their complexes), then

$$I = \kappa_k\left(c_k - c_k^*\right) + \sum_{i=1}^{m}\kappa_{n+i}\left(c_{n+i} - c_{n+i}^*\right) = \kappa_M c_M^* \;,$$

$$c_{n+i} = \beta_i\prod_{j=1}^{n} c_j^{q_{ij}} \;.$$

Let

$$c_{n+i}^* = \beta_i\prod_{j=1}^{n} c_j^{*\,q_{ij}} = \beta_i c_k^{*\,q_{ik}}\prod_{\substack{j=1\\ j\neq k}}^{n} c_j^{q_{ij}} \;,$$

i.e. we assume that “fast exchange” is in progress in the solution (all complexes are kinetically labile so that chemical equilibrium is being attained at the mercury drop electrode surface during the electrolysis, i.e. diffusion rate is negligible compared with the rate of all chemical reactions) and that free concentrations of all components, which do not contain the depolarizer§, are the same at the electrode surface as in the solution‡, and let

$$q_{ik} = 0 \;\vee\; q_{ik} = 1 \quad,\quad i = 1,\ldots,m \;,$$

¶ dependence of the current I passing through the solution on the potential E of the mercury drop electrode
† probably as an aqua-complex
§ including inert ions
‡ this assumption can be accepted e.g. if analytical concentration of the ligand is much greater than analytical concentration of the metal

i.e. all complexes containing the depolarizer are mononuclear. Then[1] $(\forall i : q_{ik} \neq 0)$

$$c_{n+i} = \beta_i c_k \prod_{\substack{j=1 \\ j\neq k}}^{n} c_j^{q_{ij}} \ ,$$

$$c^*_{n+i} = \beta_i c^*_k \prod_{\substack{j=1 \\ j\neq k}}^{n} c_j^{q_{ij}} \ ,$$

$$\mathrm{C}_k = c_k + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} c_{n+i} = c_k \left(1 + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} \beta_i \prod_{\substack{j=1 \\ j\neq k}}^{n} c_j^{q_{ij}}\right) \ ,$$

$$\mathrm{C}^*_k = c^*_k + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} c^*_{n+i} = c^*_k \left(1 + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} \beta_i \prod_{\substack{j=1 \\ j\neq k}}^{n} c_j^{q_{ij}}\right) = \frac{\mathrm{C}_k c^*_k}{c_k} \ ,$$

C_k and C^*_k are analytical concentrations of the depolarizer in the solution and at the mercury drop electrode surface, respectively.

$$I = \kappa \left[(c_k - c^*_k) + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} \left(c_{n+i} - c^*_{n+i}\right)\right] = \kappa(\mathrm{C}_k - \mathrm{C}^*_k) \ ,$$

$$\kappa \equiv \kappa(\mathbf{c}, \mathbf{n}, \mathrm{V}, \mathbf{c}\text{'}, \mathbf{q}, \boldsymbol{\beta}) = \left[\kappa_k \left(c_k - c^*_k\right) + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} \kappa_{n+i} \left(c_{n+i} - c^*_{n+i}\right)\right] / (\mathrm{C}_k - \mathrm{C}^*_k) =$$

$$= \left(\kappa_k + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} \kappa_{n+i}\beta_i \prod_{\substack{j=1 \\ j\neq k}}^{n} c_j^{q_{ij}}\right) / \left(1 + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} \beta_i \prod_{\substack{j=1 \\ j\neq k}}^{n} c_j^{q_{ij}}\right) = \left(\kappa_k c_k + \sum_{\substack{i=1 \\ q_{ik}\neq 0}}^{m} \kappa_{n+i} c_{n+i}\right) / \mathrm{C}_k \ ,$$

$$I = \kappa \left(\mathrm{C}_k - \frac{\mathrm{C}_k c^*_k}{c_k}\right) = \kappa \mathrm{C}_k - \kappa \frac{\mathrm{C}_k c^*_k}{c_k} \ ,$$

$$c^*_k = \frac{\kappa \mathrm{C}_k - I}{\kappa} \frac{c_k}{\mathrm{C}_k} = \frac{I_\ell - I}{\kappa} \frac{c_k}{\mathrm{C}_k} \ ,$$

$$c^*_M = \frac{I}{\kappa_M} \ ,$$

$$E = E_0 + \frac{RT}{zF} \ln \frac{\kappa_M}{\kappa} + \frac{RT}{zF} \ln \frac{c_k}{\mathrm{C}_k} + \frac{RT}{zF} \ln \frac{I_\ell - I}{I} \ ,$$

$$I = \frac{I_\ell}{2} \ \Rightarrow \ E = E_{1/2} \ ,$$

$$E_{1/2} = E_0 + \frac{RT}{zF} \ln \frac{\kappa_M}{\kappa} + \frac{RT}{zF} \ln \frac{c_k}{\mathrm{C}_k} \ .$$

From the difference of half-wave potentials of the complexed and "free" depolarizer (at the same ionic strength and current density) it is possible to express analytically¶ the ratio of the free and analytical concentration of the k-th reactant $\frac{c_k}{\mathrm{C}_k}$

$$E_{1/2} - E_{1/2k} = \frac{RT}{zF} \ln \frac{\kappa_k}{\kappa} + \frac{RT}{zF} \ln \frac{c_k}{\mathrm{C}_k} \ ,$$

¶ we must not forget any of the approximations made above

$$\frac{c_k}{\mathrm{C}_k} = \frac{\kappa}{\kappa_k} e^{\frac{zF}{RT}\left(E_{1/2} - E_{1/2k}\right)} \ .$$

I would rather say it once more. The given simple dependence of the ratio of the free and analytical concentration of the k-th reactant $\frac{c_k}{\mathrm{C}_k}$ on the quantities κ, κ_k, $E_{1/2}$, $E_{1/2k}$ was derived on three pivotal assumptions: all complexes are kinetically labile, free concentrations of all components, which do not contain the depolarizer, are the same at the electrode surface as in the solution and all complexes containing the depolarizer are mononuclear. Violation of the first assumption causes the occurrence of several polarographic waves instead of the "average" one. Violation of any of the rest two assumptions lead to much more complicated dependence than the derived one.

For illustration, let us consider that one of the complexes containing the depolarizer is binuclear, e.g.

$$q_{1k} = 2 \quad , \quad q_{ik} = 0 \ \vee \ q_{ik} = 1 \quad , \quad i = 2, \ldots, m \ .$$

Then (the first and second assumption keep valid)

$$c_{n+1} = \beta_1 c_k^2 \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{1j}} \ ,$$

$$c_{n+1}^* = \beta_1 {c_k^*}^2 \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{1j}} \ ,$$

$$\mathrm{C}_k = c_k \left(1 + \beta_1 c_k \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} + \sum_{\substack{i=2 \\ q_{ik} \neq 0}}^{m} \beta_i \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right) \ ,$$

$$\mathrm{C}_k^* = c_k^* \left(1 + \beta_1 c_k^* \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} + \sum_{\substack{i=2 \\ q_{ik} \neq 0}}^{m} \beta_i \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right) = c_k^* \left(\beta_1 c_k^* \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} + \frac{\mathrm{C}_k}{c_k} - \beta_1 c_k \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right) \ ,$$

$$I = \kappa \left[\mathrm{C}_k - c_k^* \left(1 + \beta_1 c_k^* \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} + \sum_{\substack{i=2 \\ q_{ik} \neq 0}}^{m} \beta_i \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right) \right]$$

and c_k^* is evidently the solution of the quadratic equation

$$\kappa \beta_1 {c_k^*}^2 \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} + \kappa c_k^* \left(1 + \sum_{\substack{i=2 \\ q_{ik} \neq 0}}^{m} \beta_i \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right) + I - \kappa \mathrm{C}_k = 0 \ ,$$

$$\kappa \beta_1 {c_k^*}^2 \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} + \kappa c_k^* \left(\frac{\mathrm{C}_k}{c_k} - \beta_1 c_k \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right) + I - \kappa \mathrm{C}_k = 0 \ ,$$

$$c_k^* = \left\{ -\kappa \left(\frac{\mathrm{C}_k}{c_k} - \beta_1 c_k \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right) + \left[\kappa^2 \left(\frac{\mathrm{C}_k}{c_k} - \beta_1 c_k \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \right)^2 - 4\kappa\beta_1 \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} (I - \kappa \mathrm{C}_k) \right]^{\frac{1}{2}} \right\} / 2\kappa\beta_1 \prod_{\substack{j=1 \\ j \neq k}}^{n} c_j^{q_{ij}} \ ,$$

$$c_M^* = \frac{I}{\kappa_M} \ .$$

It would be fond to believe that after substitution for c_k^* and c_M^* in the relation for the potential of the mercury drop electrode E, expression of $E_{1/2}$ and subtraction of $E_{1/2k}$ we get something, that is in whatever way suggestive of the dependence of the ratio of the free and analytical concentration of the k-th reactant $\frac{c_k}{\mathrm{C}_k}$ on the quantities κ, κ_k, $E_{1/2}$, $E_{1/2k}$ (in the case of all complexes mononuclear) derived before.

If we neglect the dependence of the diffusion current constant $\kappa \equiv \kappa(\mathbf{c}, \mathbf{n}, \mathrm{V}, \mathbf{c}', \mathbf{q}, \boldsymbol{\beta})$ on the values of the chemical parameters (variation of diffusion current caused by complexation of the depolarizer is usually small), we can use calibration functions of types -5 and -6 to describe the polarographic data. However, the measured quantity¶ $y = \frac{c_k}{\mathrm{C}_k}$ (or $y = \frac{a_k c_k}{\mathrm{C}_k}$) does not have constant variance, if the measured quantities $E_{1/2}$ and $E_{1/2k}$ have constant variances (variances of the measured quantities κ and κ_k can be neglected considering the slight influence of the values κ and κ_k on the value y). Such a variance must be corrected with non-trivial variance-covariance matrix $\mathbf{V}$. The logarithmic transformation of the measured quantity $y = -\ln \frac{c_k}{\mathrm{C}_k} = -\ln c_k + \ln \mathrm{C}_k$ (or $y = -\ln a_k - \ln c_k + \ln \mathrm{C}_k$), i.e. the use of calibration functions of types $-5ln$ and $-6ln$, is another (and probably better) solution:

1.
$$y = \frac{zF}{RT}\left(E_{1/2k} - E_{1/2}\right) + \ln \frac{\kappa_k}{\kappa} \dagger$$

2.
$$y = \frac{zF}{RT}\left(E_{1/2k} - E_{1/2}\right) - \ln \kappa \quad , \quad \ln a_k = \ln \kappa_k$$

3.
$$y = -\frac{zF}{RT}E_{1/2} + \ln \frac{\kappa_k}{\kappa} \quad , \quad \ln a_k = \frac{zF}{RT}E_{1/2k}$$

4.
$$y = -\frac{zF}{RT}E_{1/2} - \ln \kappa \quad , \quad \ln a_k = \frac{zF}{RT}E_{1/2k} + \ln \kappa_k$$

If we mark the parameter a_k unknown in any of the given cases, its value must be common to several measured values y§. Otherwise there would be more unknown parameters than points.

1. DeFord D. D., Hume D. N., *J. Am. Chem. Soc.* **73** (1951) 5321

¶ random variable

† If a calibration function of type $-5ln$ is used, then $\ln a_k = 0$. If we mark the parameter a_k unknown (with its value common to all measured values y), it can be interpreted by the relation

$$\ln a_k = \frac{zF}{RT}\Delta E_{1/2k} + \Delta \ln \kappa_k \ ,$$

where $\Delta E_{1/2k}$ and $\Delta \ln \kappa_k$ are "corrections" to the measured values $E_{1/2k}$ and $\ln \kappa_k$.

§ e.g. to all measured values y for the given depolarizer M^{z+}