Model Solutions to 3.53 Problem Set 7
(sample problems; not to be submitted as an assignment)

Problem 10.7 For

$$Ti(IV) + e \rightarrow Ti(III)$$

the following experimental conditions are given.

$n = 1$

$C^*_{Ti(IV)} = 3.36$ mM

$T = 25\,°C$

$E_{dc} = E_{1/2} = -0.290$ V vs SCE

$D_O = D_R = 6.6 \times 10^{-6} cm^2/s$

From equation (10.5.25),

$$[\cot\phi]_{E_{1/2}} = 1 + \left(\frac{D_O^{\beta} D_R^{\alpha}}{2}\right)^{1/2} \frac{\omega^{1/2}}{k^o} \qquad (10.5.25)$$

$$= 1 + \sqrt{\frac{D}{2}} \frac{\omega^{1/2}}{k^o} \qquad (1)$$

since $\alpha + \beta = 1$ (footnote 4, page 95; discussion after equation (10.5.25), page 395). A plot of $[\cot\phi]_{E_{1/2}}$ vs $\omega^{1/2}$ will have, from equation (1),

$$slope = \sqrt{\frac{D}{2}} \frac{1}{k^o} \qquad (2)$$

From Figure 10.5.5.

$$slope \approx \frac{4.45}{88 s^{-1/2}} = 5.06 \times 10^{-2} s^{1/2} = \sqrt{\frac{D}{2}} \frac{1}{k^o} \qquad (3)$$

Solving equation (3) for k^o leads to a value of $k^o = 3.6 \times 10^{-2} cm/s$. From equation (10.5.24), at $[\cot\phi]_{max}$,

$$E_{dc} - E_{1/2} = \frac{RT}{F} \ln\frac{\alpha}{\beta} = (0.0257\,V) \ln\frac{\alpha}{\beta} \approx -0.016\,V \text{ at } [\cot\phi]_{max} \qquad (4)$$

Substituting $(1 - \alpha) = \beta$ in equation (4) and algebraic manipulation leads to

$$\frac{\alpha}{1-\alpha} = \exp[-0.6226] = 0.54 \qquad (5)$$

which solves to $\alpha = 0.35$.

Problem 10.8 From equation (10.3.9),

$$\phi = \tan^{-1}\left[\frac{\sigma/\omega^{1/2}}{R_{ct} + \sigma/\omega^{1/2}}\right] \tag{10.3.9}$$

where

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left[\frac{1}{\sqrt{D_O}C_O^*} + \frac{1}{\sqrt{D_R}C_R^*}\right] \tag{10.3.10}$$

$$R_{ct} = \frac{RT}{Fi_0} \tag{10.3.2}$$

$$i_0 = nFAk^0C_O^{*(1-\alpha)}C_R^{*\alpha} \tag{3.4.6}$$

It is given that $k^0 = 2.2 \pm 0.3\ cm/s$, $\alpha = 0.70$, $D_O = 1.02 \times 10^{-5}\ cm^2/s$, $n = 1$, and $T = 295 \pm 2\ K$. For $n = 1$, substitution of equations (10.3.10), (10.3.2), and (3.4.6) into equation (10.3.9) yields

$$\begin{aligned}\phi &= \tan^{-1}\left[\frac{\frac{RT}{n^2F^2A\sqrt{2\omega}}\left[\frac{1}{\sqrt{D_O}C_O^*} + \frac{1}{\sqrt{D_R}C_R^*}\right]}{\frac{RT}{FnFAk^0C_O^{*(1-\alpha)}C_R^{*\alpha}} + \frac{RT}{n^2F^2A\sqrt{2\omega}}\left[\frac{1}{\sqrt{D_O}C_O^*} + \frac{1}{\sqrt{D_R}C_R^*}\right]}\right] \\ &= \tan^{-1}\left[\frac{k^0C_O^{*(1-\alpha)}C_R^{*\alpha}\left[\frac{1}{\sqrt{D_O}C_O^*} + \frac{1}{\sqrt{D_R}C_R^*}\right]}{\sqrt{2\omega} + k^0C_O^{*(1-\alpha)}C_R^{*\alpha}\left[\frac{1}{\sqrt{D_O}C_O^*} + \frac{1}{\sqrt{D_R}C_R^*}\right]}\right]\end{aligned} \tag{1}$$

Let $C_O^* = C_R^* = C^*$ and $D_R = D_O$.

$$\phi = \tan^{-1}\left[\frac{\frac{2k^0}{\sqrt{D_O}}}{\sqrt{2\omega} + \frac{2k^0}{\sqrt{D_O}}}\right] \tag{2}$$

It is given that $k^0 = 2.2 \pm 0.3\ cm/s$, $\alpha = 0.70$, $D_O = 1.02 \times 10^{-5}\ cm^2/s$, and $T = 295 \pm 2\ K$, such that $k^0/\sqrt{D_O} = 688\ s^{-1/2}$. For several decades of ω, ϕ is tabulated below.

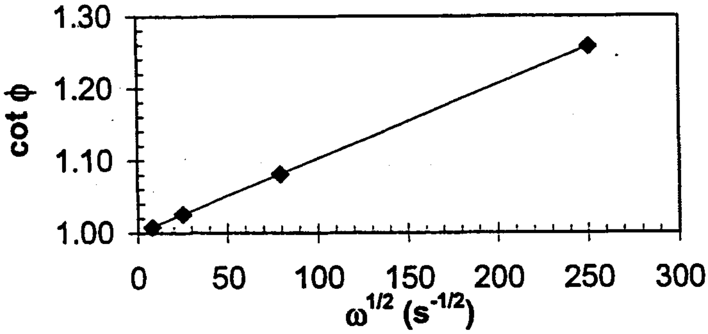
$\omega/2\pi$	ω	$\phi(rad)$	ϕ(deg)	$\omega^{1/2}$	$\cot\phi$
10	62.8	0.7813	44.77	7.93	1.008
100	628	0.7727	44.27	25.07	1.026
1000	6283	0.7463	42.76	79.27	1.081
10000	62831	0.6718	38.49	250.66	1.258

For reversible reactions, $\phi = 45°$. For $k^0 = 2.2 \pm 0.3\ cm/s$, the reaction will be reversible at low frequencies, as is consistent with the data in the table where $\phi \rightarrow 45°$ as ω decreases.

A plot of $\cot\phi = 1/\tan\phi$ versus $\omega^{1/2}$ is shown. Note that $E = E_{1/2} = E^{0'}$ when $D_O = D_R$; then, k^0 is the operative heterogeneous rate. For these conditions, equation (10.5.25) applies, and it simplifies as shown for $D = D_O = D_R$ where $\beta = 1 - \alpha$.

$$[\cot\phi]_{E_{1/2}} = 1 + \left[\frac{D_O^\beta D_R^\alpha}{2}\right]^{1/2} \frac{\omega^{1/2}}{k^0} \tag{10.5.25}$$

$$= 1 + \frac{D^{1/2}}{\sqrt{2}k^0}\omega^{1/2}$$



Regression yields $\cot\phi = 1.03 \times 10^{-3}\omega^{1/2} + 1.0000$. The *slope* $= \sqrt{D/2}/k^0$; for the values here, $\sqrt{D/2}/k^0 = 1.03 \times 10^{-3}\ s^{1/2}$.

Consider Figure 10.3.3, which shows the real and imaginary vectors that define the response for a quasireversible electron transfer. The real vector, measured along the same vector as $\dot{E}_{ac}$ for a phase angle of 0°, is $R_{ct} + \sigma/\omega^{1/2}$. The vector 90° out of phase defines the imaginary term, $\sigma/\omega^{1/2}$. The ratio of these two terms defines $\cot\phi$. From equation (10.3.9),

$$\cot\phi = \omega R_s C_s = \frac{R_{ct} + \sigma/\omega^{1/2}}{\sigma/\omega^{1/2}} \tag{3}$$

Thus, the ratio of a current measurement on the real axis made at 0° displacement with respect to $\dot{E}_{ac}$ and a second current measurement 90° out of phase (quadrature current) will yield $\cot\phi$. Note that this assumes effects from uncompensated solution resistance and double layer charging are negligible.

To make a good measurement of k^0, the frequency must be high enough that the measured value of ϕ must be less than 45°. As above, this condition is favored by higher frequency (faster measurements). Here, frequencies greater than 10 kHz are needed to reduce ϕ by at least one degree. Commercial instrumentation is available that generate frequencies of 20 MHz.