

Evaluation of Uncompensated Solution Resistance for Electrodes with Spherical-Cap Geometry

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Typical custom and commercial hanging mercury drop electrodes have the geometry of a spherical cap formed by the plane of the lower surface of the electrode holder cutting off the top of the drop. To conduct accurate quantitative measurements by voltammetry, it is necessary to be able to account for the effects of solution resistance, R_u . A method of determining the solution resistance is proposed and tested. The method involves making measurements of a test reaction (in this case, oxidation of ferrocene) by cyclic voltammetry at scan rates where resistance effects are important and at more than one concentration. When the data are analyzed by digital simulation, it is found that only one value of R_u will provide adequate matches between simulation and experiment at all concentrations. An approximate equation has been derived that allows calculation of R_u from the dimensions of the spherical-cap electrode and the solution resistivity. The calculated values of R_u for electrodes of three different sizes agreed well with the measured values. Error analysis was performed for a particular measurement, the determination of the standard heterogeneous electron-transfer rate constant, k_s , by cyclic voltammetry, and it was shown that uncertainty in R_u puts an upper limit of about 1 cm/s for the determination of k_s with the hanging mercury drop electrodes used in this study.

When mercury electrodes are employed in electroanalytical measurements, the geometry of the electrode is naturally almost spherical owing to the high surface tension of the mercury–solution interface.¹ For the classical dropping mercury electrode, the radius of the capillary bore is much smaller than the radius of the mercury drop at the end of its life so that the electrode is almost a complete sphere with a small but experimentally significant area at the capillary orifice that is not in contact with the solution. The same can be said of static mercury drop electrodes that typically have a maximum ratio of capillary radius to drop radius of about 1/3. This spherical-cap geometry is depicted in Figure 1A.

Hanging mercury drop electrodes can also be created by supporting a preweighed mercury drop on a support such as that shown in Figure 1B.² Here the radius of the mercury-wettable electrical contact can be comparable to the radius of the drop.

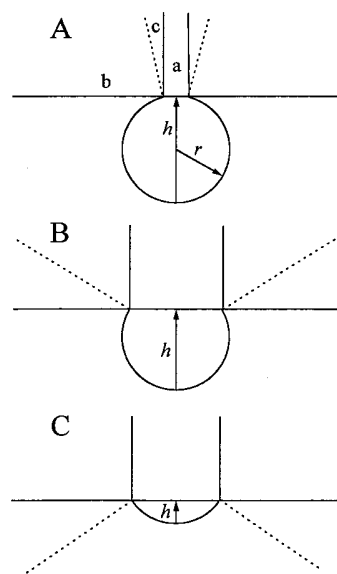


Figure 1. Three different spherical-segment electrodes. h is the height of the segment and r is the radius of curvature. a indicates the mercury thread or other metallic contact, b the insulating holder for the shielded spherical-segment electrode, and c the insulating holder for the unshielded spherical-segment electrode.

Finally, mercury can be supported on a metal microdisk electrode in a quantity sufficient to form a hemisphere or sometimes a still smaller spherical cap as shown in Figure 1C.^{3–5}

Irrespective of the electrode geometry, it is often necessary to compensate or account for the effects of solution resistance when quantitative experiments are carried out by voltammetric techniques. Failure to do so can lead to serious errors in the parameters that are extracted from the data, for example the rate constant of a chemical reaction coupled to electron transfer.⁶ Once the resistance has been evaluated, its effects can be compensated by one of two principal approaches: positive-feedback IR compensation and inclusion of the resistance in the software programs used in analysis of data. The former is a well-developed technique that has been widely used in connection with many voltammetric

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techniques^{7,8} while the latter was not widely practiced until the introduction of advanced software (e.g., DigiSim) that allows inclusion of uncompensated resistance in fitting simulations to experimental cyclic voltammograms.⁹ A useful tactic is to use positive-feedback compensation to correct for a large fraction of the resistance and account for the remainder in the simulations. In any case, significant errors can be encountered if the uncompensated resistance is not accurately known.

In this paper, we will compare methods for the evaluation of the uncompensated solution resistance at hanging mercury drop electrodes and present an improved equation that allows calculation of the resistance from measured dimensions of the spherical-segment electrodes.

EXPERIMENTAL SECTION

Solvent, electrolyte, and reagents were as described in our earlier work.^{10,11} The working electrode was an EG&G Princeton Applied Research (PAR) model 303A static mercury drop electrode equipped with a jacketed cell (PAR), and the reference electrode was a silver reference electrode (AgRE) comprising a silver wire in contact with 0.010 M AgNO₃, 0.10 M Bu₄NPF₆ in acetonitrile. PAR model 273 and 283 potentiostats were used, and electrochemical impedance spectroscopy made use of a PAR model 1025 frequency response detector. All measurements were performed at 298 K.

Simulations were performed with the software package DigiSim (Bioanalytical Systems; Version 3.0). Spherical diffusion geometry was employed with an expanding space factor of 0.5, $r_{0,\min} = 20$, and a step size of 5 mV.

RESULTS AND DISCUSSION

The uncompensated resistance in a cell is that resistance which, when multiplied by the total cell current, gives the difference in potential between the solution at the surface of the working electrode (but outside the electrical double layer) and the solution at the tip of the reference electrode probe. A number of methods have been developed for its measurement. It has long been noted that application of increasing positive-feedback compensation to the point of incipient potentiostat instability will give an approximate value for the resistance, but in practice the method can lead to errors. A second approach, one that has been adopted by some instrument manufacturers, is to apply a small potential step, with amplitude ΔE , in a region of potentials where no faradaic reaction occurs ("double-layer region"), measure the current two or more times after pulse application, and extrapolate back to zero time where the current, I_0 , allows calculation of R_u ($R_u = \Delta E/I_0$).⁸ It has been noted that this technique can also give erroneous results in certain cases.⁸

One can also determine R_u from voltammetric studies of a redox reaction using the electrode and solution of interest. For example, a couple that is known to be reversible can be investigated over the appropriate range of scan rates and positive-

feedback compensation can be applied until the properties of the cyclic voltammograms adhere to the criteria for reversibility: difference between half-peak and peak potentials equaling 56.5 mV, difference between anodic and cathodic peak potentials being about 59 mV (with some dependence on switching potential), and peak potentials that are independent of scan rate (numerical criteria are for a one-electron reaction at 298 K).² However, one must assume that the couple is behaving reversibly under the conditions of the experiment, and potentiostat instability is often encountered as 100% compensation is approached. Wipf and Wightman¹² also used a reversible couple to evaluate uncompensated resistance but did so by applying no electronic compensation and introducing increasing amounts of resistance into a simulation program until a good match was found between the simulations and the experimental voltammograms.

We introduce here an improved procedure for estimating the resistance. In this procedure, studies are conducted by cyclic voltammetry of any redox reaction for which the characteristic potential scale is not a function of concentration, only the current being affected. In other words, in the absence of solution resistance, the position of the voltammogram on the potential axis must not change as the concentration is changed. The reaction can be reversible or irreversible and can include chemical reactions coupled to electron transfer. The only restriction is that such chemical reactions must be first order. To apply the method, a series of voltammograms are recorded with partial positive-feedback resistance compensation at scan rates where the effects of resistance are evident and at two or more concentrations. When digital simulations are fit to the data, it will be found that a singular value of residual uncompensated resistance is required in the simulations to fit the data at all concentrations. The method takes advantage of the fact that the distortion due to solution IR drop will scale linearly with concentration (because the current is proportional to concentration), and thus only the correct value of R_u will allow a match between simulation and experiment at all concentrations. This method was one of those employed in the present work.

Electrochemical impedance spectroscopy¹³ applied to the supporting electrolyte and electrode of choice and with a dc potential in a presumed "double-layer region" allows estimation of the resistance from a Nyquist plot of the imaginary component of the impedance vs the real part. This method was also used.

Finally, it is possible to calculate the uncompensated resistance from the dimensions of the electrode, the position of the reference electrode, and the solution resistivity. For any geometry in which the spherical cap is not shielded by the holder, the resistance is

$$R_u = \frac{\rho r}{2\pi h} \left(\frac{1}{r} - \frac{1}{d} \right) \quad (1)$$

where ρ is the solution resistivity, d is the distance from the center of the drop to the tip of the reference electrode probe, and r and h are as defined in Figure 1.² (But see the correction in ref 14.) This geometry will be called an unshielded spherical cap. In order for eq 1 to be valid, the outer surface of the insulating holder must intersect the mercury drop normal to its surface as indicated by the dashed lines illustrating a tapered holder in Figure 1. (The holder in Figure 1C is actually a conically recessed holder.) With this geometry and a symmetrically disposed or very distant

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Table 1. Uncompensated Resistances (R_u) and Electrode Areas (A) from Analysis of Cyclic Voltammograms of 0.980 mM Ferrocene^a

scan rate /V s ⁻¹	large drop size		medium drop size		small drop size	
	R_u/Ω	$10^2 A/\text{cm}^2$	R_u/Ω	$10^2 A/\text{cm}^2$	R_u/Ω	$10^2 A/\text{cm}^2$
0.200	295 ^b	2.11	360 ^c	1.34	440 ^d	0.817
0.500		2.18		1.35		0.830
1.00		2.26		1.38		0.863
2.00		2.27		1.43		0.896
5.00		2.27		1.43		0.903
10.00		2.27		1.43		0.903
20.00		2.29		1.46		0.930
40.00		2.32		1.48		0.930

^a Working electrode: hanging mercury drop; 0.100 M Bu₄NPF₆ in acetonitrile at 25 °C. In the simulations, spherical geometry was used, and the diffusion coefficients of ferrocene and the ferrocenium ion were set at 2.5×10^{-5} and 1.72×10^{-5} cm²/s, respectively. The standard heterogeneous electron-transfer rate constant was set a 1 cm/s, which results in reversibly shaped voltammograms over the range of scan rates employed. ^b Total resistance giving the best fit at all scan rates. Resistance compensated by positive feedback = $R_{\text{comp}} = 150 \Omega$. Resistance included in simulation = $R_{\text{sim}} = 145 \Omega$. ^c $R_{\text{comp}} = 200 \Omega$, $R_{\text{sim}} = 160 \Omega$. ^d $R_{\text{comp}} = 270 \Omega$, $R_{\text{sim}} = 170 \Omega$.

counter electrode, the current lines near the working electrode will be virtually radial and eq 1 will accurately predict R_u . For eq 1 (and 3 to follow) the reference tip can be located anywhere in the accessible spherical surface at distance d from the center of the electrode.

With small mercury drop electrodes, d/r is usually very large so that eq 1 approaches

$$R_u = \rho/2\pi h \quad (2)$$

The more common structure for hanging mercury drop electrodes, indicated by the solid lines in Figure 1, features a holder whose lower surface is a plane that does not intersect the drop normal to its surface. This geometry will be called a shielded spherical cap. An approximate equation for the case of a complete sphere ($h = 2r$) was derived by Britz and Bauer¹⁵ and later corrected by Taylor and Barradas.¹⁶ This treatment was designed to predict the solution resistance with the dropping mercury electrode whose geometry, as noted above, is close to that of a complete sphere. Using the same methods employed earlier,^{15,16} we have obtained an expression for R_u for any shielded

spherical cap ($0 < h \leq 2r$). The result is

$$R_u = \frac{\rho}{2\pi(h-r)} \ln\left(\frac{dh}{r(h-r+d)}\right) \quad (3)$$

For a distant reference electrode, eq 3 becomes

$$R_u = \frac{\rho}{2\pi(h-r)} \ln\left(\frac{h}{r}\right) \quad (4)$$

Equations 3 and 4 pertain to the limit of the ratio of holder radius to drop radius approaching infinity. These equations are approximate because they do not account for the nonlinear current lines that exist in solution near the intersection of the holder with the mercury drop. A more exact treatment would require solving Laplace's equation for this geometry as was done for the circular disk embedded in an insulating plane ($R_u = \rho/4r_{\text{disk}}$ for a distant reference electrode).¹⁷ The greatest errors associated with eq 3 will be encountered for disklike spherical caps (small h/r as in Figure 1C), and its use for such electrodes is not recommended. For a hemisphere ($h/r = 1$) eq 3 reduces to eq 1.

We will also need to make use of the standard mensuration formulas for the area and volume of spherical caps:¹⁸

$$A = 2\pi rh \quad (5)$$

$$V = \frac{\pi h^2(3r-h)}{3} \quad (6)$$

Table 1 summarizes the analysis of cyclic voltammetric data for oxidation of 0.980 mM ferrocene in acetonitrile containing 0.100 M Bu₄NPF₆ at 298 K. The working electrodes were hanging mercury drops of three sizes as produced by a commercial electrode assembly (see Experimental Section). The voltammograms were recorded with partial positive-feedback compensation, and additional resistance was introduced into the simulations such that the calculations matched experiment at all scan rates. Spherical diffusion geometry was employed in the simulation, and the total area was computed from the spherical radius, which is an input parameter in the program. The diffusion coefficient of ferrocene appropriate to the present conditions was estimated from the literature to be 2.5×10^{-5} cm²/s.^{19–24} The diffusion coefficient of the ferrocenium ion was 1.72×10^{-5} cm²/s.²⁵ As expected, D_{Fc^+} has no effect on the peak currents and it affects the peak position only very weakly.

Examples of fits of simulation to experiment at one scan rate and two different concentrations are presented in Figure 2. Also shown are simulations without inclusion of the residual uncompensated resistance to illustrate the concentration-dependent distortion that occurs.

For the data at 0.98 mM, it was found that the same value of total uncompensated resistance provided adequate fits at all scan rates, the values being 295, 360, and 440 Ω for the large, medium, and small electrodes, respectively (Table 1). The electrode area that provided the best fit showed a significant trend with scan rate, smaller values being found for the smaller scan rates. This is believed to be due to shielding by the holder near the top of the drop. At small scan rates, the diffusion length is larger than the thickness of the ring of solution between the holder and the

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Table 2. Summary of Uncompensated Resistances and Electrode Areas from Various Concentrations of Ferrocene^a

data set ^b	concn/mM	large drop size		medium drop size		small drop size	
		R_u/Ω	$10^2 A/cm^2$	R_u/Ω	$10^2 A/cm^2$	R_u/Ω	$10^2 A/cm^2$
A	0.980	295	2.28 ± 0.02	360	1.44 ± 0.02	440	0.91 ± 0.02
	4.80	295	2.27 ± 0.01	360	1.42 ± 0.01	440	0.88 ± 0.01
B	1.00	300	2.30 ± 0.03	340	1.44 ± 0.02	430	0.90 ± 0.02
	2.02	300	2.35 ± 0.03	340	1.48 ± 0.02	430	0.92 ± 0.02

^a See footnote a of Table 1 for conditions. ^b Data sets obtained on different days. In set A, the resistance compensated by positive feedback, R_{comp} , was 150, 200, and 270 Ω for the large, medium, and small drops, respectively. For set B, R_{comp} was 150, 270, and 270 Ω for the large, medium, and small drops, respectively.

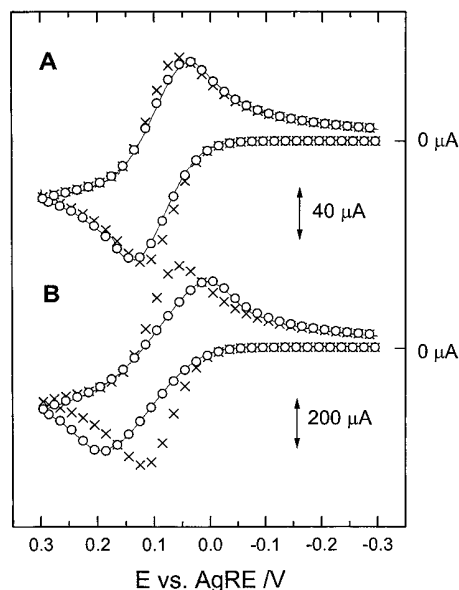


Figure 2. Cyclic voltammograms of 0.980 mM (A) and 4.80 mM (B) ferrocene obtained at the large hanging mercury drop electrode at 10 V/s in 0.100 M Bu₄NPF₆ in acetonitrile (full curves). 150 Ω was compensated electronically by positive feedback. Symbols: \times , simulations with no solution resistance included; \circ , simulations with 145 Ω of resistance included. Other simulation parameters: $k_s = 1.00$ cm/s, $\alpha = 0.50$, $E^\circ = +0.082$ V vs AgRE, $D_{Fc} = 2.5 \times 10^{-5}$ cm²/s, $D_{Fc^+} = 1.72 \times 10^{-5}$ cm²/s, $r = 0.0427$ cm (0.98 mM) and 0.0425 cm (4.80 mM). Simulations employed spherical geometry.

top of the drop, resulting in less current and thus an apparently smaller area from the analysis. For the remainder of the data, only averages of the results for 2–40 V/s will be reported.

In Table 2 these averages are reported for two sets of data, obtained on different days, each set including results for two different concentrations of ferrocene. For each set, it was found that the same R_u provided an adequate match between simulation and experiment at all scan rates at both concentrations. The agreement between the values of R_u obtained for the three electrode sizes on each of the 2 days was very good, the largest difference being 20 Ω . Differences in the evaluated areas from the two sets of data were scarcely larger than the measurement error attesting to the reproducibility of drop formation with the static mercury drop electrode. Taken together, these results indicate that the procedure provides reproducible values of R_u and electrode area. Next, these values will be compared with R_u and area obtained by other methods.

A traditional way of determining the drop area is to collect 30–50 drops and obtain the combined drop weight. Then, from

Table 3. Dimensions, Areas, Volumes, and Uncompensated Solution Resistances for Hanging Mercury Drop Electrodes^a

quantity	method	large drop size	medium drop size	small drop size
(1) r/cm	photographic	0.0426	0.0351	0.0288
(2) h/cm	photographic	0.0788	0.0639	0.0532
(3) $10^2 A/cm^2$	calc from eq 5	2.11	1.41	0.96
(4)	simulation	2.30	1.45	0.90
(4)	drop weight	2.24	1.43	0.86
(6) $10^4 V/cm^3$	calc from eq 6	3.19	1.77	0.98
(7)	drop weight	3.16	1.61	0.74
(8) R_u/Ω	calc from eq 2 ^b	220	271	326
(9)	calc from eq 4 ^b	295	361	436
(10)	simulation	298	350	435
(11)	impedance spectroscopy	265 ± 9	335 ± 14	384 ± 27

^a The radius was determined from measurement of the horizontal diameter from the photographs. The height, h , was measured from the base of the drop to the surface of the holder. A very slight asymmetry was detected, diameters measured at +45 and -45° being about 2% smaller than the horizontal diameter for the large drop. The drops were immersed in acetonitrile when photographed. ^b The resistance of the thread of mercury in the capillary bore is calculated to be about 5 Ω . This resistance is in series with the solution resistance and will be reflected in the experimentally determined R_s .

the density of mercury and the assumption that each drop is a perfect sphere, the area and volume can be calculated. When this approach was applied, the areas found were $2.24 (\pm 0.02) \times 10^{-2}$, $1.43 (\pm 0.02) \times 10^{-2}$, and $0.86 (\pm 0.03) \times 10^{-2}$ cm². These results are identical (within 5%) to the average values obtained by simulation (Table 2), a result that reflects the fact that the hanging mercury drops are close to complete spheres, $h \approx 2r$ (see below). The agreement also suggests that a proper choice of diffusion coefficient was made for simulation of the ferrocene voltammograms. For hanging mercury drop electrodes with sizes significantly smaller than complete spheres (Figure 1B), the drop-weight method will undoubtedly fail, based as it is on the assumption that the detached drops are complete spheres.

To test these indirect methods of obtaining electrode area and volume, photographs of the three electrodes were obtained with magnification and the dimensions were determined from enlargements. The results are given in Table 3, which also gives the area calculated by eq 5, the volume from eq 6, and R_u from eqs 2 (unshielded spherical segment) and 4 (shielded spherical segment) using the resistivity of 0.100 M Bu₄NPF₆ in acetonitrile at 298 K, 109 Ω cm.²⁶

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We have also determined R_u for the three sizes of hanging mercury drop electrodes by electrochemical impedance spectroscopy. The results are given in Table 3 along with those obtained by the other methods.

Concerning the area of the electrodes, it is clear from Table 3 that the values calculated from the drop dimensions agree fairly well with those obtained by simulation of the ferrocene voltammograms. The agreement between areas from the drop-weight method and simulation is even better, though this may result from a fortuitous cancellation of errors. We advocate the determination of electrode area by voltammetric measurements with a substance, like ferrocene, with a known diffusion coefficient. Of course, methods other than cyclic voltammetry can be employed, chronocoulometry being a popular alternative.

Simulation of the ferrocene voltammograms proved to be an effective and reproducible method of determining the uncompensated solution resistance. The values so obtained are in excellent agreement (<3%) with those calculated from eq 4 (shielded spherical segment) and the measured dimensions of the drop (Table 3). The inadequacy of the earlier equation for the unshielded spherical segment (eq 2) is apparent, the calculated R_u being 25% lower than measured (Table 3). The values of R_u obtained by impedance spectroscopy are significantly lower than those obtained by simulation of ferrocene voltammograms. We observed some frequency dependence of R_u evaluated in this way and have arbitrarily reported values obtained between 1 and 10 kHz. The method of determining R_u from simulations of the voltammograms (Figure 2) offers the advantage of making the determination under conditions that are nearly identical to those to be used in the contemplated voltammetric study of another system. Nevertheless, improved reproducibility of the method would be highly desirable. The present approximate $\pm 10 \Omega$ variability limits the accuracy of parameter evaluation.

The nature of an analysis of error depends on the experiment to be performed. For example, if the objective of the planned experiments is to determine the standard heterogeneous electron-transfer rate constant, k_s , by cyclic voltammetry, the data will comprise a series of cyclic voltammograms at various scan rates and concentrations. The analysis will involve simulation with inclusion of the residual uncompensated resistance and evaluation of k_s by finding the value that provides best agreement between simulation and experiment for all of the voltammograms. In essence, one is obtaining the value of k_s by examining the difference between anodic and cathodic peak potentials, ΔE_p , though in fact the entire current-potential curve is used.

Values of ΔE_p for various values of the kinetic parameter ψ are available²⁷ and were fit to a logarithmic function. In eq 7, D is

$$\psi = \frac{k_s}{\sqrt{\pi D F v / RT}} \quad (7)$$

the common diffusion coefficient of reactant and product, v is the scan rate, and a one-electron reaction is assumed. The result is given in eq 8, with ΔE_p expressed in millivolts. The derivative of

$$\ln \psi = -1.11 \ln(\Delta E_p - 59.2) + 3.55 \quad (8)$$

eq 8 was taken to determine the error in k_s , Δk_s , resulting from a given uncertainty in ΔE_p , $\Delta(\Delta E_p)$, which in turn arises from inaccurate knowledge of R_u . The result is

$$\frac{\Delta k_s}{k_s} = \frac{1.11 \Delta(\Delta E_p)}{59.2 - \Delta E_p} \quad (9)$$

How does error in the resistance, ΔR_u , affect the error in peak separation, $\Delta(\Delta E_p)$? The error in the position of the cathodic peak will be $I_{pc} \Delta R_u$ and that of the anodic peak $I_{pa} \Delta R_u$ where I_{pc} and I_{pa} are the cathodic and anodic peak currents, respectively. Assuming that the voltammogram is close to reversible as will be the case when the method is pushed to its limit for measuring large k_s and that a switching potential about 150 mV negative of the half-wave potential is used, $\Delta(\Delta E_p)$ will be given approximately by²⁸

$$\Delta(\Delta E_p) = (I_{pc} - I_{pa}) \Delta R_u = 730 F A D^{1/2} c^* (F v / RT)^{1/2} \Delta R_u \quad (10)$$

where c^* is the concentration of reactant. Substituting eq 10 into eq 9 gives

$$\frac{\Delta k_s}{k_s} = \frac{800 F A D^{1/2} c^* (F v / RT)^{1/2} \Delta R_u}{59.2 - \Delta E_p} \quad (11)$$

The term in the denominator on the right side of eq 11 may be regarded as the critical increase in peak separation needed to be certain that one is not at the reversible limit of 59.2 mV. In practice, a value like 10 mV ($\Delta E_p = 69.2$ mV) for this increase is reasonable. What value of k_s will correspond to ΔE_p of 69.2 mV at, e.g., 100 V/s? Inserting this value along with $D = 2.5 \times 10^{-5}$ cm²/s into eqs 7 and 8 gives $k_s = 1.5$ cm/s. What will be the error in k_s ? Inserting these same parameter values (along with $A = 0.021$ cm² (the large hanging mercury drop electrode) and $c^* = 1.00$ mM) into eq 11 with our estimate for ΔR_u of 10 Ω gives $\Delta k_s / k_s = 0.5$, a 50% error.

This result is consonant with the empirical observation that determination of k_s by cyclic voltammetry with mercury drop electrodes of ordinary size fails for k_s of the order of 1 cm/s when the uncertainty in R_u is probably a few ohms.²⁹ The form of eq 11 suggests some strategies for reducing the error in measurements of k_s . Reducing the electrode area or the concentration has the effect of decreasing the current and lowering the effect of the uncertainty in the resistance. Of course, the signal-to-noise ratio suffers if concentrations are too low, but lowering the area by using microelectrodes is a well-established approach for reducing the effects of solution resistance.

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