

Pseudopolarography at the Mercury Hemisphere Ultramicroelectrode: Theory and Experiment

Samuel P. Kounaves

Department of Chemistry, Tufts University, Medford, Massachusetts 02155

The theoretical expressions for pseudopolarography at a hemispherical mercury ultramicroelectrode are derived and compared with experimental data at varying deposition times and low and high electrolyte concentrations and with previous theory for other electrodes. It is shown that, even though several of the physical conditions are different, the behavior of both the pseudopolarographic half-wave potential and the limiting peak stripping current is similar to that for the HMDE. The fit between the theory and the experimental data was excellent. A correction term for the increase in the limiting current due to the deposition occurring at ultramicroelectrodes during a slow scan is described. The deviation of the limiting peak stripping current with increasing negative deposition potentials seen in this and previous works is discussed and attributed to adsorption of trace organics on the mercury electrode surface.

INTRODUCTION

Trace heavy metals play a central role in many biogeochemical processes. Their toxicity and bioavailability in aqueous systems has been shown to be directly related to the chemical forms in which they exist, i.e., their chemical speciation.¹ Especially promising in speciation studies has been an electrochemical technique referred to as pseudopolarography or stripping polarography.²⁻⁸ In its most basic form, a pseudopolarogram is a plot of the amount of a specific metal ion which has been reduced (deposited) into a mercury electrode as a function of the applied reduction potential (at constant deposition time). Even though any method that gives a response proportional to the total amount of metal deposited in the mercury (q_d) may be used to construct the pseudopolarogram, anodic stripping voltammetry (ASV)⁹ has been the method of choice since the initial description of the technique. The advantages of ASV derive from the fact that

the metal ions in solution are reduced and *preconcentrated* into the mercury before the anodic voltammetric scan is made. Depending on the total deposition time, the peak current for each metal being oxidized back into solution may be several orders of magnitude greater than if a direct cathodic voltammetric scan had been used. Because the resulting pseudopolarographic curve is analogous to that obtained in classical polarography, many of the same theoretical treatments and the large amount of experimental data already accumulated in the literature can be applied to its analysis. Pseudopolarography is one of the few techniques which allows for the direct study of metal ion complexation parameters such as metal coordination number, dissociation constants, kinetics, and redox potentials.

Since the concept of pseudopolarography was first introduced 25 years ago by Matson and Fitzgerald,² it has been developed both theoretically and experimentally³⁻⁸ not only for the hanging mercury drop (HMDE) but also for various mercury film electrodes (MFE). Because of the requirement for a supporting electrolyte, rigorous pseudopolarographic speciation studies using these "macro" electrodes have been limited to either natural waters requiring no added electrolyte (e.g., seawater) or well-defined synthetic or natural water solutions which include a minimum level of added electrolyte.

The advent of ultramicroelectrodes (UME) has made it easier to apply electrochemical techniques to a larger variety of neat natural water samples. Because of their size, typically less than 20 μm , UMEs possess several very desirable characteristics in terms of such properties as transport rates, capacitive charging, and reduction in iR drop.¹⁰ They are also well suited to speciation studies using pseudopolarography because of the reproducibility of mass transport at their surface, an essential property for any concentration technique such as ASV. A number of papers have appeared describing the use of mercury UMEs for ASV of trace metals.¹¹⁻¹⁴ Recently, Wang and Zadeii¹³ showed the advantage of the Hg UME for speciation studies in water samples of low ionic strength using pseudopolarography.

The use of pseudopolarography for speciation work requires a well-defined and "pure" mercury electrode. Mercury films formed on metals such as Pt or Au are really Hg-Pt or Hg-Au amalgam film electrodes. Mercury "films" formed on glassy carbon or carbon fibers are actually loosely-adhering "mercury-droplet films". Only two types of "pure" mercury electrodes are known; the classical hanging mercury drop electrode (HMDE), and the Hg film electrode (Ir-MFE)¹⁵ or

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(2) (a) Matson, W. R. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1968. (b) Fitzgerald, W. F. Ph.D. Thesis, Woods Hole Oceanographic Institute and Massachusetts Institute of Technology, Cambridge, MA, 1969.

(3) (a) Branica, M.; Novack, M.; Bubic, S. *Croat. Chem. Acta* 1977, 49, 539-547. (b) Bubic, S.; Branica, M. *Thalassia Jugosl.* 1973, 9, 47-53. (c) Sipos, L.; Valenta, P.; Nürnberg, H. W.; Branica, M. In *Lead in the Marine Environment*; Branica, M., Konrad, Z., Eds.; Pergamon Press: Oxford, U.K., 1980. (d) Nelson, A.; Mantoura, R. F. C. *J. Electroanal. Chem. Interfacial Electrochem.* 1984, 164, 253-266. (e) Branica, M.; Pizeta, I.; Maric, I. *J. Electroanal. Chem. Interfacial Electrochem.* 1986, 214, 95-102.

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the more recent *Ir-based Hg semisphere ultramicroelectrode* (Ir-HgUME).¹⁶ Of the two, the HMDE has been problematic in speciation studies because of the difficulties associated with accurately describing the convective geometry around the hanging mercury drop and in producing Hg drops of micron diameter. Only the Ir-based Hg UME provides a "pure" mercury substrate with well-defined diffusion geometry.¹⁶ In either case, pure mercury microelectrodes do not come in any other geometry except spherical or hemispherical,^{15,16} and thus our theoretical description is reasonably limited to this geometry.

The following work was undertaken to derive the theoretical pseudopolarographic response at a hemispherical Hg UME and to compare it with experimental data. One would not necessarily expect the response to be the same as that described for either the HMDE^{5,6} or MFE^{7,8} since there is no forced convection during deposition, no waiting period before the anodic scan is initiated, and under appropriate size and time domains, no concentration gradients within the mercury hemisphere.

The theoretical expressions for pseudopolarography at the mercury hemisphere UME are derived and compared with the experiment at several electrolyte concentrations and with previous theory for other electrodes.

THEORY

For this derivation we assume a metal ion species O that is reduced to R and is soluble in mercury. In contrast to the classical ASV experiment we assume that the solution is kept quiescent during the entire deposition step and that there is no waiting period before the anodic scan. We will also assume that the electrode is a mercury hemisphere of radius r such that $r \ll (D_0t)^{1/2}$, where D_0 is the diffusion coefficient and t is the characteristic time. For square wave anodic stripping voltammetry (SWASV), t_d is the characteristic time for the deposition step while $1/f$ is the characteristic time for the stripping step. In both cases, the value of the characteristic time may be selected so that the electrode behaves as an ultramicroelectrode.¹⁰ In addition, because $r \ll (D_0t)^{1/2}$, there are no concentration gradients established in the mercury hemisphere during the deposition step; instead, it slowly "fills up" at a rate which varies according to the ratio of the concentrations of O (C_O) and R (C_R) at the electrode surface.

It should be noted that during the rapid SWASV stripping step used in our experimental work below, steady-state diffusion is not achieved on the aqueous side nor is thin-film theory applicable on the mercury side. However, within one set of points collected at the same mercury electrode, the proportionality between peak stripping current, i_p , and q_d should remain constant.

The relationship between the applied deposition potential E_d and the SWASV peak stripping current i_p gives a sigmoidal curve similar to that in polarography because of the proportionality between i_p and the deposition charge q_d , which in turn is a function of the deposition potential E_d and deposition time t_d , in other words $i_p \propto q(E_d, t_d)$. The limiting value that i_p reaches on the pseudopolarographic plateau (i_{pL}) is analogous to that in polarography or steady-state voltammetry.

The general equation for the steady-state current i_{ss} at any time during the reduction of a metal ion at a hemispherical mercury ultramicroelectrode is given by

$$i_{ss} = nF2\pi r^2 k_0 \left[C_O \gamma_O \exp\left(-\alpha \frac{nF}{RT}(E - E^\circ) - C_R \gamma_R \exp\left((1 - \alpha) \frac{nF}{RT}(E - E^\circ)\right)\right) \right] \quad (1)$$

where γ_O and γ_R are the activity coefficients for O and R, respectively, α is the transfer coefficient ($0 < \alpha < 1$), k_0 is the charge-transfer rate constant, and all the other symbols have their usual meaning.¹⁷ To simplify the integration of this expression for obtaining the deposition charge q_d , we make appropriate substitutions for C_O and C_R .

The expression for C_O can be obtained from the solution of the equation for the concentration gradient at a hemispherical surface

$$i/nF2\pi r^2 = D_0[\partial C_O(r,t)/\partial r] \quad (2)$$

Under steady-state conditions the derivative of the concentration with respect to time is zero, allowing the right side of eq 2 to be approximated by the linear term $D_0[C_O^* - C_O]/\delta_{ss}$, where δ_{ss} is the steady-state diffusion layer thickness and C_O^* is the concentration of O in the bulk solution. Furthermore, we have that $\delta_{ss} = 2\pi r^2 nFD_0 C_O^*/i_L$, where for an UME $i_L = 2\pi r nFD_0 C_O^*$, thus for a hemispherical UME we get $\delta_{ss} = r$. This allows us to write for the concentration at the surface of the electrode

$$C_O = C_O^* - (i_{ss}/2\pi r nFD_0) \quad (3)$$

For a hemispherical UME with the condition that $r \ll (D_0t)^{1/2}$ the uniform concentration of R at any time t is given by

$$C_R = 3i_{ss}t/2\pi r^3 nF \quad (4)$$

Substituting eqs 3 and 4 in eq 1 and letting $\beta = 3D_0\gamma_R/r^2\gamma_O$ and $\theta = (E_d - E^\circ)nF/RT$ will then give i_{ss} as a function of time and deposition potential

$$i_{ss} = \frac{2\pi r nFD_0 C_O^*}{1 + \frac{3tD_0\gamma_R}{r^2\gamma_O} \exp(\theta) + \frac{D_0}{r\gamma_O k_0} \exp(\alpha\theta)} \quad (5)$$

To obtain the total deposition charge q accumulated in a hemispherical mercury UME for a deposition time of t_d at a potential E_d , under quiescent conditions, we integrate eq 5 from 0 to t_d to give

$$q = \frac{2\pi r nFC_O^* D_0}{\beta \exp(\theta)} \log \left[1 + \frac{\beta t_d \exp(\theta)}{1 + \frac{D_0}{r\gamma_O k_0} \exp(\alpha\theta)} \right] \quad (6)$$

This expression can be further simplified if we consider only reversible reactions with very fast kinetics. In that case k_0 becomes much larger than D_0 so that the right side of the denominator approaches zero and eq 6 further simplifies to

$$q = \frac{2\pi r nFC_O^* D_0}{\beta \exp(\theta)} \log [1 + \beta t_d \exp(\theta)] \quad (7)$$

Figure 1 shows the charge deposited in terms of the ratio q/q_L (where q_L is the charge accumulated over the same t_d but at a diffusion-limited potential) as a function of the deposition potential E_d (relative to the standard half-wave potential $E_{1/2}$) for various deposition times. The relationship of q/q_L with E_d mirrors the plot that would be obtained no matter what reliable technique is used to measure q . When $q/q_L = q_L/2$ the pseudopolarographic half-wave potential $E_{1/2}^*$ is obtained. Making this substitution in eq 7 and solving for

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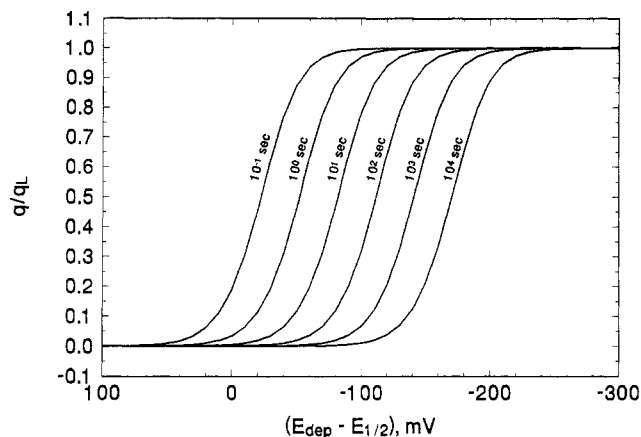


Figure 1. Theoretically calculated dependence of accumulated charge on deposition potential at various deposition times, for $r = 10^{-3}$ cm and $C_0 = 10^{-9}$ mol/cm³.

$E_{1/2*}$ give

$$E_{1/2*} = E^\circ + \frac{RT}{nF} \ln \left[\log (1 + \beta t_d \exp(\theta)) \right] + \frac{RT}{nF} \ln (\beta/2) + \frac{RT}{nF} \ln (t_d) \quad (8)$$

It can be shown that for any reasonable t_d the second term on the right side of eq 8 will be negligible in comparison with the other terms and that eliminating it will cause an error of only about 1% in the calculated value of $E_{1/2*}$. Omitting the term and substituting for β result in the simplified expression

$$E_{1/2*} = E^\circ + \frac{RT}{nF} \ln \left(\frac{3D_0\gamma_R}{2r^2\gamma_O} \right) + \frac{RT}{nF} \ln (t_d) \quad (9)$$

Even though the $E_{1/2*}$ response for the Hg UME was not necessarily expected to be the same as any of those derived previously for the HMDE,^{5,6} this approximate theoretical expression does indeed turn out to be the same except for r^2 in place of δr , a condition brought about by the relationship $\delta_{ss} = r$, which obtains at the hemispherical UME. As will be shown later though, the steady-state spherical diffusion can cause significant deviations in the experimentally acquired pseudopolarograms if certain factors are not taken into account.

EXPERIMENTAL SECTION

Reagents. All solutions were prepared from 99.999% Cd(NO₃)₂, HClO₄ (Aldrich, Milwaukee, WI), 99.9995% Hg₂(NO₃)₂, and KNO₃ (ALFA-Johnson Matthey, Ward Hill, MA) using 18-MΩ deionized water from a Barnstead Nanopure system (Barnstead Co., Newton, MA). The nitrogen gas used was ultra-high-purity grade (Northeast Airgas, Inc.) passed through an oxygen-adsorbing filter (OxiClear, VWR Scientific, Boston, MA).

Apparatus. Square wave anodic stripping voltammetry was performed using a EG&G PAR Model 273 potentiostat/galvanostat (EG&G PAR, Princeton, NJ) interfaced to an IBM PS/2-30286 computer with custom data acquisition and control software. All electrochemical measurements were made using a three-electrode system consisting of a saturated calomel electrode (SCE) as reference with a KNO₃ bridge adjusted to the ionic strength of the sample electrolyte, a platinum wire as counter electrode, and a hemispherical mercury ultramicroelectrode with a radius of 10 μm prepared on an iridium disk substrate fabricated as previously described.¹⁶ The iridium disk was successively polished using a high-speed rotating wheel with 600- and 1200-grit silicon carbide (CARBIMET, Buehler Ltd., Lake Bluff, IL) and 1.0-, 0.3-, and 0.05-μm alumina (MICROPOLISH, Buehler Ltd.) and then electrochemically characterized to assure a defect-free glass/iridium seal.

The mercury hemisphere was formed by coulometric deposition at -0.3 V vs SCE in a solution containing 8 mM Hg(II) and 0.1

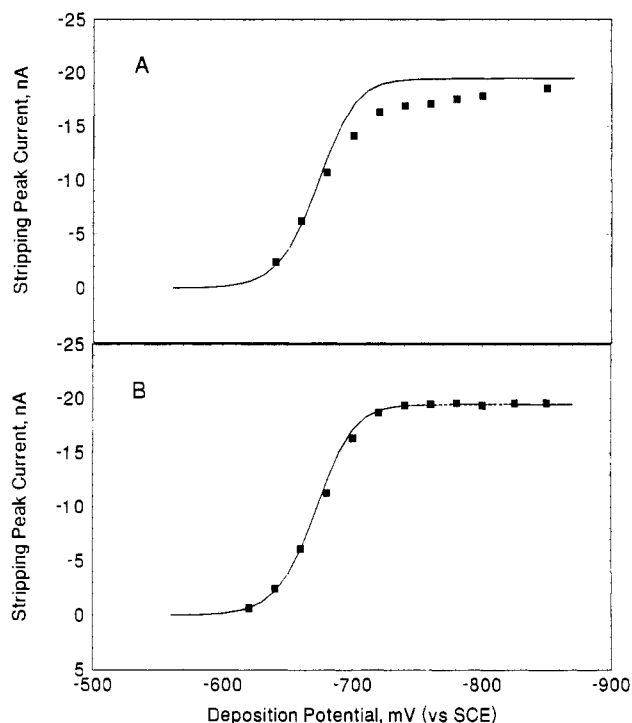


Figure 2. Experimental (■) pseudopolarograms for cadmium in 1.0 M KNO₃, $r = 10^{-3}$ cm, $t_d = 10$ s, with (A) and without (B) organic contamination, and the theoretical curves (—) for the same conditions plotted as a function of q/q_L normalized to t_d .

M HClO₄. The geometry of the deposited mercury was carefully controlled both by measuring the deposition charge and by microscopic observation. After deposition of the mercury hemisphere, the electrode was removed from the mercury solution, rinsed carefully with deionized water, and then transferred to the sample cell. Unless otherwise noted, a deposited Hg hemisphere was used only for one set of pseudopolarographic points, even though use of the same Hg surface for several runs over an entire day did not appear to negatively affect the pseudopolarographic curves.

Procedure. The solutions studied were at pH 5.4 and were unbuffered, consisting of 5×10^{-7} M or 1×10^{-6} M Cd(II) with KNO₃ as electrolyte at concentrations varying from 10^{-4} to 1.0 M. Several experiments were also run in 0.01 M HClO₄, but no observable differences were noted in the stripping polarograms. To avoid systematic errors, the deposition potentials comprising the individual pseudopolarograms were randomly chosen. Samples were purged with nitrogen gas for 20 min at the start of each experiment and thereafter kept under a nitrogen gas blanket.

Because of the unique characteristics of UMEs associated with high mass-transport rates and the steady-state diffusional flux, the sample solutions were kept quiescent during the preconcentration step and there was no equilibration period before the anodic scan was started. Unless otherwise indicated, all stripping measurements were carried out with square wave ASV with a SW amplitude of 40 mV, a SW step height of 5 mV, and a SW frequency of 150 Hz (effective scan rate of 750 mV/s). Pseudopolarograms were constructed with and without background current subtraction, but in all cases, no effect on the slope of the pseudopolarogram was evident.

RESULTS AND DISCUSSION

Variation of $E_{1/2*}$ with Deposition Time. For all electrolyte concentrations studied, the pseudopolarograms obtained were sigmoidal in shape. Typical results are shown in Figure 2 for 10^{-6} M Cd(II) in 1.0 M KNO₃ and a deposition time of 10 s. For these, and all other curves constructed, a plot of E_d vs $(i_{pL} - i_p)/i_p$ gave a slope of about 30 mV and allowed for a relatively accurate determination of $E_{1/2*}$. The theoretical curve (solid line) was calculated using eq 7, normalized both in terms of q/q_L and to fit the experimental

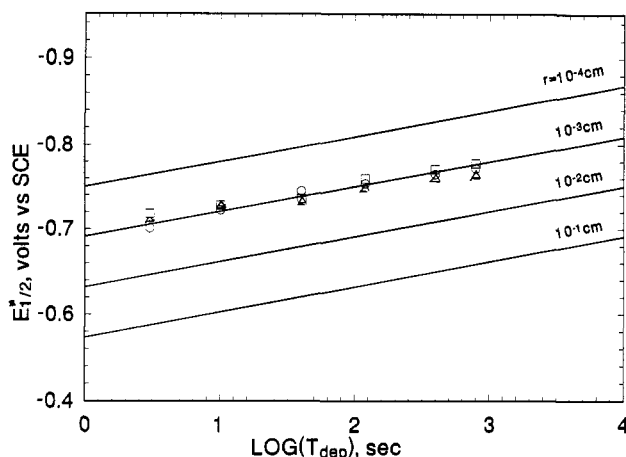


Figure 3. Experimental $E_{1/2}^*$ values, for cadmium in 1.0 M (\square), 10^{-2} M (\circ), and 10^{-4} M (Δ) KNO_3 , obtained for each t_d , plotted as a function of the log of the deposition time. The theoretical values (—) were calculated using eq 9 for electrodes with the indicated radii.

data, and is valid for an electrode with $r = 10^{-3}$ cm and $t_d = 10$ s. The fit in terms of $E_{1/2}^*$ was excellent for cases where i_{pL} was flat (Figure 2B) and also for the cases where we assumed that the slope of i_{pL} approaches the theoretical value (Figure 2A). The reasons for this will be discussed in more detail below. Similar pseudopolarograms were obtained for deposition times, t_d , of 3, 40, 120, 400, and 800 s.

Figure 3 shows the experimental $E_{1/2}^*$ values (\square , \circ , Δ) obtained for each t_d plotted as a function of the log of the deposition time. The solid lines are the theoretical values calculated using eq 9 for electrodes with radii of 10^{-4} , 10^{-3} , 10^{-2} , and 10^{-1} cm. The fit between theory and the experimental data is very good over the entire range of deposition times and electrolyte concentrations studied.

Variation of i_{pL} with E_d . From the theoretical work presented here and those previously reported,⁵⁻⁸ $\Delta i_{pL}/\Delta E_d$ is predicted to attain a constant plateau once the diffusion-limited region is reached, i.e. $\Delta i_{pL}/\Delta E_d = 0$. The only analogous situation in which the limiting current does not exhibit a flat plateau is that for classical polarography where the limiting current i_L increases due to the larger contribution of the charging or residual current at more negative potentials. This effect though, is not operative in pseudopolarography since there is no continuous change of the potential involved. Each point is in effect a coulometric experiment at a specific potential, and the measured ASV response is for a specific metal ion.

The determination of whether the positive slope of $\Delta i_{pL}/\Delta E_d$ is exceeding or approaching the "true" value of i_{pL} is itself not a trivial matter. In some cases i_{pL} appears to eventually reach a plateau but in many others no such leveling occurs even when the potential is taken to the point where H_2 formation begins. To make such a determination one must be able to predict the SWASV peak current. There is at present no theoretical treatment for the response of SWASV at a semispherical mercury ultramicroelectrode. If the theory for SWASV at a mercury film electrode¹⁸ is used to estimate the experimental values of i_{pL} , we would need to know the value for the total charge deposited. There is no way to accurately obtain this value so as to use it with confidence in the theoretical equations to calculate the peak height. In addition, there has been no equivalency formally shown between SWASV at mercury film electrodes and mercury hemisphere ultramicroelectrodes.

Table I. Characteristics Reported in the Literature and from This Work for the Pseudopolarographic Diffusion-Limited Current Plateau i_{pL} with Various Experimental Parameters

| electrode ^a | tech- nique ^b | metal | electrolyte | $\Delta i_{pL}/\Delta E_d$ | ref |
|------------------------|-----------------------------|-------|---|----------------------------|-----------|
| HMDE | LS | Cu | seawater | + | 2b |
| HMDE | LS | Cd | 0.7 M NaClO_4 | + | 3b |
| HMDE | LS | Cd | 0.7 M NaCl | 0 | 3b |
| MFE | LS | Pb | 0.6 M NaClO_4 , HCO_3^- | + | 3c |
| HMDE | DP | Cu | est water, pH 3 | + | 3d |
| HMDE | DP | Cu | est water, pH 3, UV ^c ed | 0 | 3d |
| HMDE | DP | Cd | 0.7 M NaCl | + | 3e |
| TMGE | LS | Tl | seawater, EDTA | + | 4 |
| HMDE | LS | Cd | 1.0 M KCl | 0 | 5a |
| HMDE | LS | Cd | 0.1 M KNO_3 , en | 0 | 5b |
| HMDE | LS | Cu | seawater, pH 3 | 0 | 5c |
| MFE | SC | Pb | geother water, Cl | + | 7 |
| RDE | LS | Pb | 0.7 M NaCl | + | 8 |
| RDE | DP | Pb | 0.1 M Na/HAc | + | 13 |
| MCCF | DP | Pb | 0.1 M Na/HAc | + | 13 |
| MCCF | DP | Pb | 0.01 M Na/HAc | + | 13 |
| MCCF | DP | Pb | 0.1 M Na/HAc | + | 13 |
| MCCF | LS | Pb | 0.1 M Na/HAc | 0 | 13 |
| HgUME | SW | Cd | 1.0 M, KNO_3^c | + | this work |
| HgUME | SW | Cd | 0.0001 M KNO_3^c | + | this work |
| HgUME | SW | Cd | 1.0 M KNO_3 | 0 | this work |
| HgUME | SW | Cd | 0.0001 M KNO_3 | 0 | this work |

^a HMDE: hanging mercury drop electrode. TMGE: tubular mercury graphite electrode. MFE: mercury film electrode (stationary disk). RDE: rotating disk electrode (mercury film). MCCF: mercury-coated carbon fiber UME. HgUME: Ir-based mercury hemisphere UME. ^b LS: linear scan ASV. DP: differential pulse ASV. SW: square wave ASV. SC: linear staircase ASV. ^c Assumed to be contaminated with organic material.

To determine whether the increasing slope of i_{pL} with E_d is exceeding or approaching the theoretical value, we relied on a statistical/error analysis for the theoretical curves and experimental data. When a relatively accurate prediction for the value of $E_{1/2}^*$ was assumed and a fit to the lower values of i_{pL} was allowed, the values of $E_{1/2}^*$ for all of the experiments always showed a determinate error of 8–14 mV. On the other hand, for a fit to the higher values of i_{pL} we had an indeterminate error of ± 2 –4 mV. Thus, this technique, at least, indicates that the slope of i_{pL} vs E_d is approaching the theoretically predicted value.

In the initial phase of this research, all of the pseudopolarograms obtained had a positive slope of $\Delta i_{pL}/\Delta E_d$ (Figure 2A), contrary to the theoretical predictions. Several months into the research work, through an accidental discovery, we were able to obtain pseudopolarograms showing a constant slope of $\Delta i_{pL}/\Delta E_d = 0$ (Figure 2B). As will be discussed in more detail below, this fortuitous occurrence has led to a possible explanation for the deviation of i_{pL} .

Previous Studies Showing $\Delta i_{pL}/\Delta E_d > 0$. Several previous investigators have taken note of the deviation of i_{pL} with increasing negative deposition potentials, but differing mechanisms have been proposed for its cause. Seitz et al.⁴ (see Table I for conditions) attributed the slow rise to the deterioration of the mercury surface by accumulation of foreign metals, indicating a significant overpotential for deposition. This appears a reasonable explanation, especially since the sample was seawater and the high level of Cl and other organic materials could cause such problems. Similar results have also been obtained in several other studies using seawater samples.^{2b,5b} The apparent increase of i_{pL} in this type of situation is most likely due to a delayed attainment of the proper i_{pL} due to the deteriorated or covered surface of the mercury, thus requiring a higher overpotential for an equivalent deposition. In these cases, the behavior of i_{pL}

(18) Kounaves, S. P.; O'Dea, J. J.; Chandrasekhar, P.; Osteryoung, J. *Anal. Chem.* 1987, 59, 386–389.

appears to be substantially corrected by simply renewing the mercury electrode surface or eliminating the adsorbent.^{4,5a} This same procedure, however, did not affect our initial experiments reported here nor apparently has it in many previous studies using only simple electrolyte solutions.^{3c,5a,5b,8}

In the work by Huizenga and Kester³ the effect was proposed to be due to the *loss of an intermediate species in the reduction step of Pb(II) to Pb(0)*. This explanation does not appear to be supported by other studies which have also used Pb(II), or other M(II) → M(I) systems, and have not encountered the same phenomena.^{3b,5a,5b,13}

Finally, Wang and Zadeii¹³ attributed the continued rise of i_{pL} in their work to the *significant plating of the metal that occurs during the scanning period as a result of the unique diffusional flux at UMEs*. This explanation is valid for the UME case or any system in which significant deposition can occur during a relatively slow anodic scan. However, this contribution to the rise of i_{pL} is not operative in this or other research using fast scan rates or in previous studies which used large size electrodes and long deposition times. This effect can also be easily overcome either by using a fast scan rate or by returning to the same initial potential before each scan is started.

Possible Mechanisms for $\Delta i_{pL}/\Delta E_d > 0$. The immediate question that arises from the behavior of i_{pL} is whether it is a direct result of the deposition step or an artifact of the stripping technique used to measure q_d or C_R (i.e., DP, LSV, SWASV). From Table I, the behavior of i_{pL} would appear not to be directly correlated to either the electrodes, electrolytes, or techniques used. There is no basis for suspecting that the measuring technique itself is the cause of the deviation, and with lack of any data to the contrary, we can assume that the ASV will generally give a signal proportional to either q_d or C_R . Previous unpublished work by this author has shown that medium exchange during the ASV step, even though sometimes affecting the size and shape of the ASV peak, has no effect on the slope of the pseudopolarographic wave plateau. Except for the effect of scan rate on i_{pL} when UMEs are used (a separate issue which will be addressed below), it appears that the positive slope of $\Delta i_{pL}/\Delta E_d$ is most likely due to processes occurring *during* the deposition step. One can then reasonably assume that i_{pL} deviates from theory because the deposition current i_d is either suppressed or enhanced by some effect that is a function of the deposition potential.

The simplest mechanism to postulate is one in which i_{pL} increases because of some *physical* process which promotes an increased deposition current i_d . For all previous studies using the HMDE, MFE, or RDE, some form of stirring is used during the deposition step. For the stripping step, the stirring is stopped, and after a 15–30-s rest period the scan is started. It has been assumed that, even though very small, some convection or vibration will cause some deposition during the scan. However, if this were true, short deposition times would produce larger deviations since the scan period would comprise a larger portion of the deposition period. This is contrary to what has been shown to occur in this or previous studies.⁸

Adsorption on the Mercury Surface. Of the several mechanisms which could explain the behavior of i_{pL} ,^{4,8,13} the results of this study support the case that the positive slope is due to organic adsorption on, and/or deterioration by, the mercury electrode surface. The event leading to this conclusion was the sudden change in our pseudopolarographic data as a result of simply changing the cartridges of our deionized (DI) water supply unit. Even though the conductivity of the water was an acceptable 18.2 M Ω , another research group using the same water for HPLC studies found our DI

water to be contaminated by several unknown trace organic compounds. After further investigation, the problem was found to be that the PVC plumbing from the building DI unit feeding our local DI unit contained a noticeable amount of algae growth. The organics thus produced had overloaded the ability of our local unit to effectively remove them. By replacing the cartridges, which were only two months old and still acceptable by conductivity standards, the pseudopolarograms run with the new DI water showed a flat i_{pL} plateau (Figure 2b). Monitoring and maintaining the organic contaminants to the lowest possible levels have since allowed the generation of pseudopolarograms conforming to theory. These results are a vivid reminder of what effects even trace organic adsorbents can have on the reduction kinetics at the mercury surface.

In addition to the above, the assumption that the positive slope of $\Delta i_{pL}/\Delta E_d$ is caused by organic adsorption is indirectly supported by many of the results already in the literature. For example, in experiments where the mercury surface was exposed to the analyte solution for extended periods of time (usually > 400 s),^{4,5a} $\Delta i_{pL}/\Delta E_d$ became very positive and eventually the entire curve was distorted. In both cases, changing the mercury film⁴ or drop^{5a} significantly restored $\Delta i_{pL}/\Delta E_d$ closer to zero. In the work by Nelson and Mantoura,^{3d} UV irradiation was used to destroy organics in the sample solution, after which, the pseudopolarograms obtained show a marked decrease of $\Delta i_{pL}/\Delta E_d$.

Adsorption Effects on the Rate of Reduction. The behavior observed in this and previous studies is most likely a direct result of a decrease in the charge-transfer rate (and corresponding rate constant k_0) due to the adsorption of a monolayer electroinactive organic film on the mercury surface. This organic layer can influence k_0 by modifying the potential gradient in the double layer. The effect on the overall shape of the pseudopolarogram will also depend on the diffusion constant of the adsorbent, its rate of adsorption on the mercury, and its electrical charge. In almost all cases the effect of adsorbed organics is to decrease or totally inhibit the reduction of metal ions at the mercury surface. The effect of these conditions on classical polarography has been well established.^{19,20,21} For example, the addition of 6×10^{-5} M tetrabutylammonium sulfate (TBAS) to a 3×10^{-3} M Cd²⁺ solution, and its subsequent adsorption on the mercury electrode surface, will decrease the polarographic wave of Cd²⁺ by about 60%.¹⁹ This occurs even though Cd²⁺ has a very large k_0 in the absence of TBAS. At lower concentrations, the adsorption of TBAS manifests itself by a positive slope of the polarographic plateau, analogous to those seen in pseudopolarography. At partial surface coverages i_d is decreased overall but as the potential becomes more negative the existence of the substantial overvoltage causes an increase of i_d . We believe that this is the same mechanism that is operative in pseudopolarography and is responsible for the increase of i_{pL} with E_d .

Correction of i_{pL} for UMEs. When UMEs are used for pseudopolarography, the effect of the increased mass transport rate due to steady-state spherical diffusion is clearly evident when the anodic scan is started from the deposition potential, especially when low scan rates are used.¹³ This effect can be easily corrected for by adding an additional term to i_d in eqs 6 and 7 to take into account the extra deposition occurring during the scan. In this case the true

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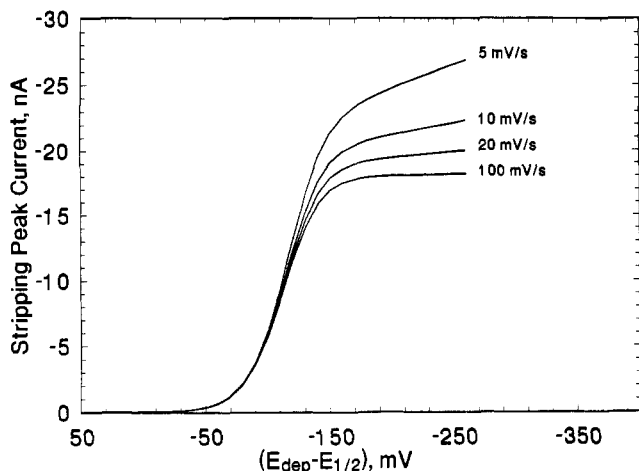


Figure 4. Theoretical pseudopolarographic curves for an UME with different scan rates using the corrected deposition time t_d as indicated in eq 10 for $r = 10^{-3}$ cm and $t_d = 10$ s.

deposition time t_{td} is given by

$$t_{td} = t_d + \frac{(E_d - E_{1/2})}{\nu} \quad (10)$$

where ν is the effective scan rate in volts per second.

Figure 4 shows the theoretical pseudopolarographic curves for an UME with conditions as those used for the experimental work described here. As can be seen, the increase of i_{pL} only becomes noticeable for scan rates of less than about 100 mV/s. Using this correction to account for the deviation of the experimental data shown in Figure 2 would imply a scan rate of about 20 mV/s. The actual effective scan rate for the SWASV used in this work was 750 mV/s (150 Hz). Even though all of our pseudopolarograms were constructed with SWASV data taken at scan rates of 750 mV/s, all showed about the same increase of i_{pL} . Thus, in our experimental data the increase of i_{pL} is clearly not due to any such scan rate effect. A clear example of this type of process can be seen in the work of Wang and Zadeii.¹³

CONCLUSIONS

The equations for pseudopolarography at a mercury hemisphere ultramicroelectrode have been derived and compared with the experiment. We have shown that, even though several of the physical conditions are different, the behavior of $E_{1/2}^*$ and i_{pL} for a Hg UME is similar to that for the HMDE, differing only by the substitution of r for δ in the denominator of the second term in eq 9. The fit between theory and experimental data was found to be excellent.

Even though we plan to carry out further and more rigorous studies of the nontheoretical behavior of the pseudopolarographic wave plateau, the results described here along with the available literature data convince us that this phenomenon arises from the adsorption of a partial monolayer film on the mercury surface. This film is most often probably composed of trace organics but may also include inorganic substances which can react with the mercury (such as chloride). Trace organics are ubiquitous and difficult to remove. Even when the utmost care is taken to ensure their exclusion, enough may remain in the various reagents/solutions to present a problem for experiments requiring long deposition times. Even with such problems still remaining to be more fully understood and solved, the use of pseudopolarography with the iridium-based mercury ultramicroelectrode promises to provide both the rigorous theoretical basis and experimentally reproducible values of i_{pL} and $E_{1/2}^*$ needed for speciation studies.

ACKNOWLEDGMENT

This work was supported in part by Grants from the U.S. Environmental Protection Agency through the Northeast Hazardous Substance Research Center and the Tufts Center for Environmental Management. The information contained in this document does not necessarily reflect the views of the agency or the centers, and no official endorsement should be inferred. I also wish to thank the reviewers of this paper for their helpful comments and Mr. Wen Deng for his assistance with the laboratory work.

RECEIVED for review February 3, 1992. Accepted September 28, 1992.