

CCA-1229

YU ISSN 0011-1643

UDC 541.135

Original Scientific Paper

Application of ASV for Trace Metal Speciation II. Digital Simulation of Neopolarogram Using Hanging-mercury-drop Electrode

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Received February 4, 1980

A program for the digital simulation of neopolarography is described and the results of neopolarograms using hanging mercury drop electrodes are discussed.

INTRODUCTION

The physico-chemical forms in which a certain metal ion occurs in the aquatic system significantly influence its biogeochemical pathways and cycles. Therefore, it is of utmost importance to determine the possible ionic states of metal ions at the concentration actually present in natural waters. The distributions of ionic and complex species are usually theoretically calculated on the basis of the stability constants of the respective trace metal complexes and the concentrations of metals and ligands present in the natural water. An experimental verification of these models has not been possible so far, owing to the very low concentrations at which trace metals occur in nature. Under such circumstances, none of the classical experimental methods for the investigation of complex-constants can not be used because of their low sensitivity. In the first paper of this series¹, the principle of a new, modified anodic stripping voltammetry method for the determination of the ionic form of trace metal ions as reported. By this method, such concentrations limits can be avoided. The method consists of successive ASV cycles at various deposition potentials. By plotting peak current vs. deposition potential, a d.c. polarogram can be reconstructed because the anodic peak current is proportional to the amount of amalgam deposited. Instead of direct current points, an integral of the deposition current over the time of accumulation points is obtained. The curve achieved in such a way, usually called a neopolarogram¹², will reflect both the thermodynamic and kinetic properties of the depolarizer, as well as the geometric and hydrodynamic characteristics of the electrode and the cell. This method has been developed from the anodic stripping voltammetry praxis relating to the investigation of the dependence of stripping current maxima on the deposition potential. The latter has been used for the detection of the optimum deposition potential range^{2,3}. It has been noticed that the altitude⁴ and the position⁵ of the neopolarogram strongly depend on the concentrations of ligands added to the solution. In

the case of a reversible, labile complex formation in the solution, the neopolarogram is shifted to a more negative potential in the same way as the classical d. c. polarogram⁶. Based on this fact, a new ASV method for the detection of the complex-formation constants at a very low concentration of a central metal atom was developed^{1,6-9}. The first theories of totally irreversible neopolarograms were given by Zaharov¹⁰ and Stromberg and Baleckaja¹¹. Zirino and Kounaves¹² have developed an approximate theory of reversible neopolarograms using a hanging mercury drop electrode. An expression for the half-wave potential of the neopolarogram, which is in a simple way related to the d. c. polarogram half-wave potential, has been postulated. Turner and Whitfield¹³ have extended this theory to the case of the parallel existence of several complex ionic forms of some trace metal ions in multi-ligand systems. They have checked their theory by measuring the electrochemical availability of lead at trace levels in the seawater. Shuman and Cromer¹⁴ have developed a new, more rigorous theory of neopolarograms with hanging mercury drop electrode for reversible and nonreversible charge transfers. By ignoring the spherical diffusion in and toward the electrode the authors have made their theory more applicable to a plane thick mercury film electrodes than to a HMDE.

The great advantages that this new ASV method offers can be utilized only if its sensitivity will be extended. The aim of this series of papers is to elaborate properties of the neopolarograms obtained using different types of electrode (HMDE, a rotating disk electrode covered with a thin mercury film and a stationary glassy carbon disk electrode connected to a vibrating stirrer¹⁵). By the combination of appropriate electrochemical technique (d. c., a. c., lin. scan) and type of electrode, the optimum conditions for trace metal characterization even at very low concentrations of metal ion and different complex constants values and the complexation rates can be find out. To compare the data obtained by the experiments with lead, mathematical and digital simulation models of neopolarograms were developed.

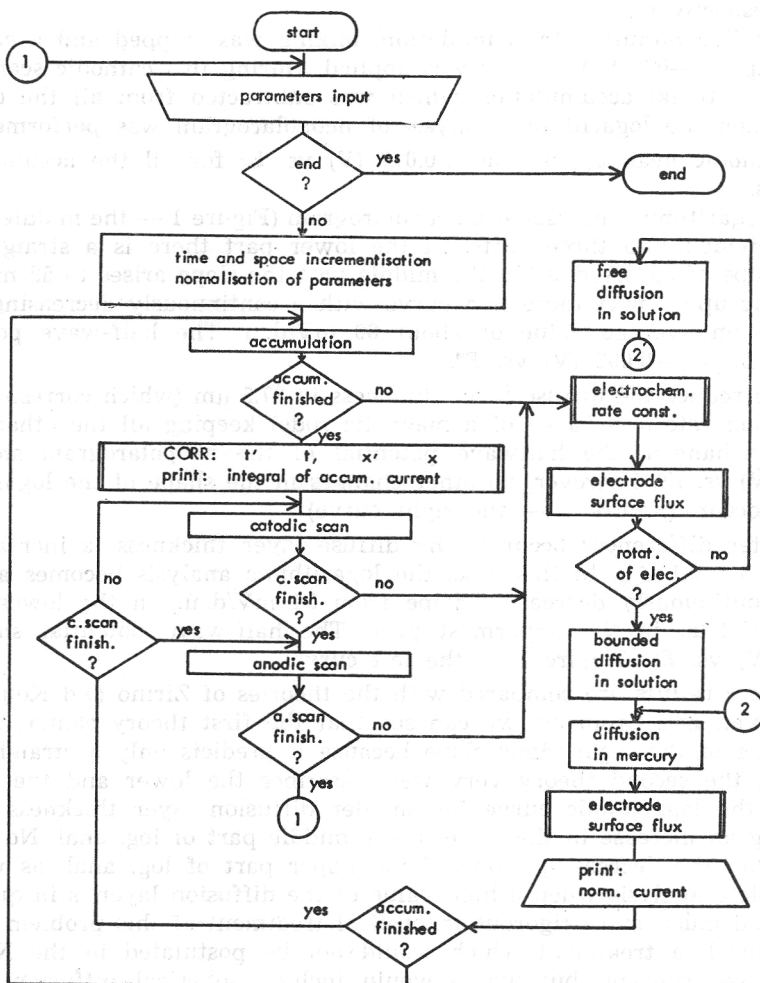
In this communication some results relating to the digital simulation of reversible neopolarograms using hanging mercury drop electrode are presented.

DIGITAL SIMULATION PROGRAM

The program was in accordance with the method of S. W. Feldberg¹⁶ and based on the program developed by I. Ružić¹⁷. The electroactive surface of drop was used supposing a totally ideal sphere. Mixing of the solution was simulated by a finite number of space increments through which diffusion layer could grow. The diffusion layer thickness was supposed constant and the experimental rotation speed of magnetic rod was not taken into account. The solution was mixed only during the accumulation of metal ions into mercury in the form of amalgam. During the cathodic jump to -0.300 (V) vs. E^0 following every accumulation and during the anodic stripping scan, there was no mixing. No rest period before the anodic scan was introduced. The rate of cathodic jump was identical to the anodic scan rate. During the simulation of accumulation, we used a time increment of a hundred time greater ($\Delta t' = 100 \Delta t$) and a space increment of ten times greater ($\Delta x' = 10 \Delta x$) than during the simulation of the cathodic jump and the anodic stripping process. That is why a subroutine CORR was introduced to change the program constants $\Delta t'$ to Δt and $\Delta x'$ to Δx , to correct all the variables which were normalized by the ratio $\Delta t/\Delta x$ (k_s , δ , r , Φ etc.) and to redefine the concentrations of the depolarizer and amalgam in new space increments. The precision of the program was controlled by the results of Nicholson and Shain¹⁸ for the given sphericity. Both the anodic and cathodic currents were normalized by the relation $\Phi = i/(nFAc_{ox}^*$

$D_{ox}^{1/2} (F \Delta E / RT \Delta t)^{1/2}$. The program was written on a FORTRAN and run on a UNIVAC 1110 (Sperry rand) computer. The logarithmic analyses of polarograms were calculated on a PDP-11 DIGITAL computer. The flow chart of the program is presented in Table I. The main component of the program is the time-potential loop which can be divided into accumulation part which is the potential constant and a potential scan part with a linearly changed potential. At the end of the first part, the subroutine CORR is called to redefine the program constants. The loop consists of routines for the simulation of diffusion in a mercury drop and in the solution. The subroutine CORR changed the bounded diffusion in the solution (which corresponded to mixed solution) to the free diffusion in the solution which corresponded to nonagitated solution during the potential scan. The subroutines for calculating the electrochemical rate constants and electrode surface flux were called for every new time-increment. During one 20 minutes run, the currents for two ASV cycles could be simulated.

TABLE I



RESULTS AND DISCUSSION

The basic simulated neopolarogram had the following electrochemical experimental and program constants: the standard constant of the electrochemical reaction rate was $k_s = 40 \text{ cm s}^{-1}$, the coefficient of transition was $\alpha = 0.5$, the number of electrons transferred was $n = 1$, both diffusion coefficients were $D_{\text{ox}} = D_{\text{R}} = 4 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, the temperature of the solution was $T = 298 \text{ K}$, the viscosity of the solution was $0.01 \text{ cm}^2 \text{ s}^{-1}$, the surface of the mercury drop was $A = 0.025 \text{ cm}^2$, the rate of the voltage scan was $\text{RTVS} = 0.1 \text{ Vs}^{-1}$, the time of accumulation was $T = 300 \text{ s}$, the diffusion layer thickness was $\delta = 59 \text{ }\mu\text{m}$ which corresponds, over Levich's equation, to the magnetic rod rotation rate of $\omega = 4 \text{ s}^{-1}$, the potential increment was $\Delta E = 0.00002 \text{ V}$, the normalized diffusion coefficients were $DD = D_{\text{ox}} \cdot \Delta t / \Delta x^2 = 0.3$, the time increment was $\Delta t = 2 \cdot 10^{-4} \text{ s}$ during the voltammetric scan and $\Delta t' = 2 \cdot 10^{-2} \text{ s}$ during the period of accumulation, the space increments were $\Delta x = 0.5 \text{ }\mu\text{m}$ and $\Delta x' = 5 \text{ }\mu\text{m}$ for voltammetric scan and the accumulation period, respectively.

After five minutes of accumulation, mixing was stopped and a cathodic scan of up to $-0.300 \text{ (V) vs. } E^0$ was applied. During this cathodic scan there was an additional accumulation which was subtracted from all the current values when the logarithmic analysis of neopolarogram was performed.

An anodic peak appears at $+0.027 \text{ (V) vs. } E^0$ for all the accumulation potentials.

The logarithmic analysis of a neopolarogram (Figure 1 — the middle curve) can be divided into three parts. In the lower part there is a straight line with a slope of 59 mV/d. u. , in the middle part the slope arises to 52 mV/d. u. and in the upper part there is a curve with a continuously decreasing slope and with an average value of about 66 mV/d. u. The half-wave potential value is $E_{1/2} = -0.092 \text{ (V) vs. } E^0$.

If we reduce the diffuse layer thickness to $37.5 \text{ }\mu\text{m}$ (which corresponds to the rotation rate $\omega = 10 \text{ s}^{-1}$ of a magnetic rode) keeping all the other parameters unchanged, the halfwave potential of the neopolarogram shifts to $-0.099 \text{ (V) vs. } E^0$. However, no other changes in the shape of the logarithmic analysis occur. (Figure 1 — the right curve)

Greater differences occur if the diffuse layer thickness is increased to $357 \text{ }\mu\text{m}$ ($\omega = 0.1 \text{ s}^{-1}$). In this case, the logarithmic analysis becomes a curve with a continuously decreasing slope from 54 mV/d. u. , in the lowest part, to 58 mV/d. u. , in the uppermost part. The half-wave potential shifts to $-0.052 \text{ (V) vs. } E^0$. (Figure 1 — the left curve)

If these results are compared with the theories of Zirino and Kounaves¹² and Shuman and Cromer¹⁴, we can see that the first theory cannot explain the change of the logarithmic slope because it predicts only a straight line. However, the second theory very well describes the lower and the middle parts of the logarithmic curve for smaller diffusion layer thickness values predicting an increase in the slope in the middle part of log. anal. No theory can explain the decreasing slope of the upper part of log. anal. as well as the complete analysis when a high value of the diffusion layer is in question. A new and much more rigorous theoretical treatment of this problem should be developed, a treatment which would not be postulated in the Nernst's diffuse layer concept, but which would include spherical diffusion of the

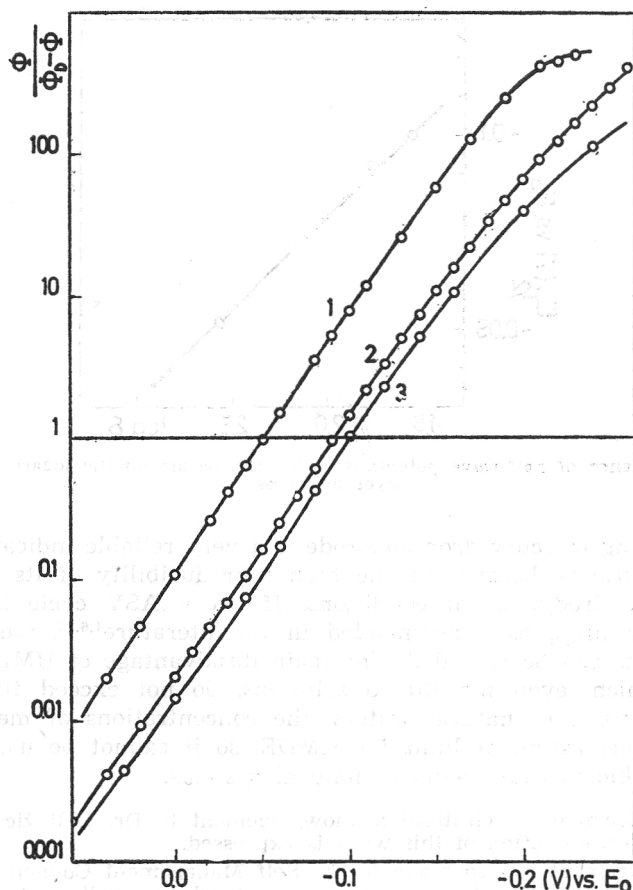


Figure 1. Logarithmic analyses of simulated neopolarograms at different values for the following diffusion layer thicknesses:

- 1) $\delta = 375 \mu\text{m}$, $E_{1/2} = -0.052 \text{ (V) vs. } E^0$
- 2) $\delta = 59 \mu\text{m}$, $E_{1/2} = -0.092 \text{ (V) vs. } E^0$
- 3) $\delta = 37.5 \mu\text{m}$, $E_{1/2} = -0.099 \text{ (V) vs. } E^0$

amalgam through the mercury drop electrode and the convective mass transport through the solution.

Figure 2. show the linear dependence of the half-wave potential of the neopolarogram on the logarithm of the diffuse layer thickness, which is in an agreement with both theories.

Digital simulation can give us many answers about the properties of neopolarograms. We can follow these change properties with the change of electrochemical, hydrodynamical or experimental parameters and establish empirical interdependences which may be used for comparison with theoretical predictions. These interdependences are specially important for the processes for which no theories exist. They are always easier to obtain by digital simulation than by the experiments, if only we know the nature of the mechanism.

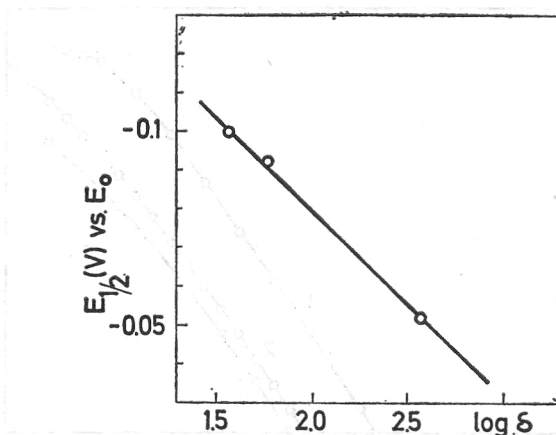


Figure 2. Dependence of half-wave potentials of neopolarogram on the logarithm of diffusion layer thickness.

The hanging mercury drop electrode is a very reliable indicator electrode for neopolarography because of the high reproducibility of its electroactive surface and hydrodynamical conditions. If every ASV cycle is performed from the new drop, as recommended in the literature^{1,6,14}, well developed neopolarograms can be recorded. The main disadvantage of HMDE is its low sensitivity which, even for stirred solutions, do not exceed 10^{-7} mol dm⁻³ of the depolarizer. In natural waters, the concentrations of metal ions are below this concentration of limit for HMDE, so it cannot be used for direct neopolarographic measurements in natural systems.

Acknowledgement. — Grateful acknowledgement to Dr. I. Ružić for generous help during the preparation of this work is expressed.

Acknowledgement is also made to the Self Management Council for Scientific Research of S. R. Croatia for support of this work, as well as to the National Bureau of Standards, Washington, D. C., U.S.A., for support of this work under Grant NBS/IG/-191/JF.

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SAŽETAK

Digitalna simulacija neopolarograma na visećoj živinoj kapi

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Opisan je program za digitalnu simulaciju neopolarograma na visećoj živinoj kapi. Prodiskutirani su rezultati za jednoelektronski neopolarogram.

CENTAR ZA ISTRAŽIVANJE MORA
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Prispjelo 4. veljače 1980.