Electrochemical Kinetic Measurements and Metal Speciation with the Vibrating Dropping Mercury Electrode

Milivoj Lovrić, Tomislav Magjer, and Marko Branica

Center for Marine Research Zagreb, »Ruđer Bošković« Institute,
POB 1016, Zagreb, 41001, Croatia, Yugoslavia

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The vibrating dropping mercury electrode (VDME) is app-
lied to the characterization of ionic species and to electroanaly-
tical measurements of metal ion concentrations in water sam-
ples strongly polluted with different kinds of surface active
substances (SAS). The $Cd^{2+}/CdNTA^-$ system in citrate buffer
solution at pH = 6 was chosen as a model for the effect of a
preceeding homogeneous chemical reaction on the reversible
charge transfer of »free« metal ions. The influence of Triton-
-X-100 on the Cd^{2+} polarographic wave is a good example of
nonionic SAS interference with metal ion charge transfer. The
possibilities of the VDME for electrochemical measurements of
methylene-blue and iatrorubine in NaCl and KNO_3 supporting
electrolytes are discussed. The VDME with its short drop life
time of up to 200 drops/s is more convenient and reliable than
other kinds of electrodes for kinetic measurements and for the
analysis of samples which are highly polluted by organics.

INTRODUCTION

Modern electrochemical research greatly promotes environmental wa-
ter chemistry. By its direct application to water samples, electrochemistry,
as a non-destructive method, provides much useful data on the speciation
of microconstituents in the natural aquatic system. The investigation of
the relationship between different ionic species as constituents of the non-
living environment and living beings in natural waters is also possible.
The bio-availability, geochemical reactivities and transport properties of
trace metals in natural waters are determined mainly by the distribution
of the chemical species and the kinetics of their redistribution after an
interaction with life and/or physical reactants. Characterization of metal
associations with various organic ligands in nature is a very active area
of research.[1] The role of metal-ligand association kinetics and the inter-
facial phenomena between solid-liquid phases are especially important.
This is particularly important in broadening our knowledge of basic bio-
-geo-chemical transport processes and in predicting the anthropogenic
influence on them.

The determination of stability constants of complexes of certain metal ions with different ionic species present in natural waters is still at the center of interest of many environmental electrochemists. Calculation of the distribution of sea-water microconstituents in the form of various complex species at the naturally-occuring concentration level depends on knowledge of stability-constants of the interactions between all the micro- and the macro-constituents of a sea. Many very ambitious and sophisticated computer programs for ionic-species-distribution-determination failed to give the expected results because some of the constants were not known. It is interesting to note that the stability-constant can be measured at a much higher concentration level than the naturally--occuring one.

Two kinds of complexes of an electroactive metal ion can be succesfully measured by polarographic methods: very unstable complexes which dissociate completly during the measurement time and very stable complexes which do not dissociate at all during the measurement time. The stability constants of the first kind of complexes can be estimated from the shift in half-wave potential of the polarographic wave of the central metal-ion with variation in ligand concentration. The stability constants of complexes of the second kind can be estimated from the ratio of the polarographic waves corresponding to the reduction of the »free« metal ion and the metal-complex species. Between these two limiting cases there is a large number of complexes which are moderately stable. Since they dissociate to a certain extent during the measurement time, the heights of the polarographic waves corresponding to the »free« metal ion and its complex species do not reflect the real distribution in the bulk of the solution.

The stability of a given complex is only a relative quality depending on the measurement time. Shortening the measurement time can make the complex virtually stable and, vice versa, extension will make the complex virtually unstable. As a result the various polarographic methods can sometimes also be applied for stability measurements of a certain number of moderately stable complex species. In many cases neither classical nor pulse polarography can be successful in determining the stability constant of certain complex species because of the kinetic contribution to the current which could be suppressed only by employing the streaming mercury electrode.[2]

The results of electroanalytical experiments in natural waters can be significantly biased by the adsorption of non-electroactive substances (of natural origin or pollutants) which may block the charge transfer process. At low SAS concentrations, the adsorption can decrease the reversibility of the electrochemical reaction. Disappearance of the polarographic wave could even happen at very high SAS concentrations.[3] These effects cannot be avoided by decreasing the duration of the excitation signal, but only by a very short contact between the electrode surface and the solution, which can be achieved by decreasing the drop life time.

Recently, a new device for a short drop-life time electrode (up to 200 drops per second), the so-called vibrating dropping mercury electrode (VDME), has been described.[4]

The aim of the present work is to describe the potentialities of the VDME in determining the ionic species distribution. Experimental studies on the Cd(II)-NTA system have been undertaken to show the advantages of this new device in lowering the kinetic current in order to achieve more accurate measurements of the bulk concentration of the »free« cadmium ions (Cd^{2+}) only. The Cd-NTA system was chosen because it has been well described by many authors.[5] The mean values of the stability constant[5,6,7] (between $\log K_{CdNTA} = 9.03$ and $\log K_{CdNTA} = 10.70$) depend on the nature of the supporting electrolyte. The dissociation rate constant was determined[5,8] as $k_d = (3.0 \times c_{H^+} + 1.6)$ s^{-1}.

Experiments with the VDME under conditions where the electrochemical reaction of certain metal ions is inhibited by SAS will be also presented.

EXPERIMENTAL

All d.c. and pulse polarographic measurements were performed with a PAR 174 polarograph. A mechanical drop trigger was used in the work with DME. The vibrating mercury electrode has been described previously.[4]

All measurements were performed using the three electrode system: a saturated NaCl calomel reference electrode, and a platinum wire as auxiliary electrode.

Solutions were prepared from »analytical grade« chemicals and doubly distilled water. A stock solution of the disodium salt of H_3NTA was prepared from H_3NTA by adding an appropriate amount of NaOH and it was kept in a plastic bottle. The cadmium stock solution was prepared from $CdCl_2 \times H_2O$ and tetra distilled water. Methylene-blue and Triton-X-100 ($C_8H_{17}(C_6H_4)(OCH_2)_{9-10}OH$, »Rohm and Haas«, Milano) were dissolved in tetra distilled water one day prior the experiment. The iatrorubine chloride ($C_{19}H_{17}NO_4Cl$) was synthesized at the Faculty of Pharmacy and Biochemistry, University of Zagreb, by the Feist method.[9]

All experiments were performed at 20°C. The total concentration of electroactive species was $2 \cdot 10^{-4}$ (mol/dm^3) for Cd^{2+} and iatrorubine and $1 \cdot 10^{-3}$ (mol/dm^3) for methylene blue. The supporting electrolyte was 0.1 (mol/dm^3) citrate buffer which also provided the desired pH in the solution.

RESULTS AND DISCUSSION

Measurements of Cd^{2+} in 0.1 (mol/dm^3) $NaClO_4$ show that the VDME behaves in a similar way as the DME and that the linear relationship between the current density and the square root of the drop life-time is obeyed up to 150 drops per second (Figure 1). The straight line in Figure 1. emanates from the origin, similar to the requirement of the Ilkovič equation. Although there is evidence of a linear i_d vs. $m^{2/3} t^{1/6}$ relationship for rapidly dropping electrodes operating at one mercury column height,[14,15] this relationship does not have to satisfy the Ilkovič equation.[13] Since the mercury flow rate depends on dropping rates if short controlled drop times are provided by mechanical means,[13,14] and since under these conditions, the mechanical drop knocker causes frequent movements of the capillary tip, so that the development of each drop in a quiet solution can not be assumed explicitly, the factor of proportionality between i_d and $m^{2/3} t^{1/6}$ may differ from that defined by the Ilkovič equation. So, there is not enough evidence to prove that VDME rigorously obeys the
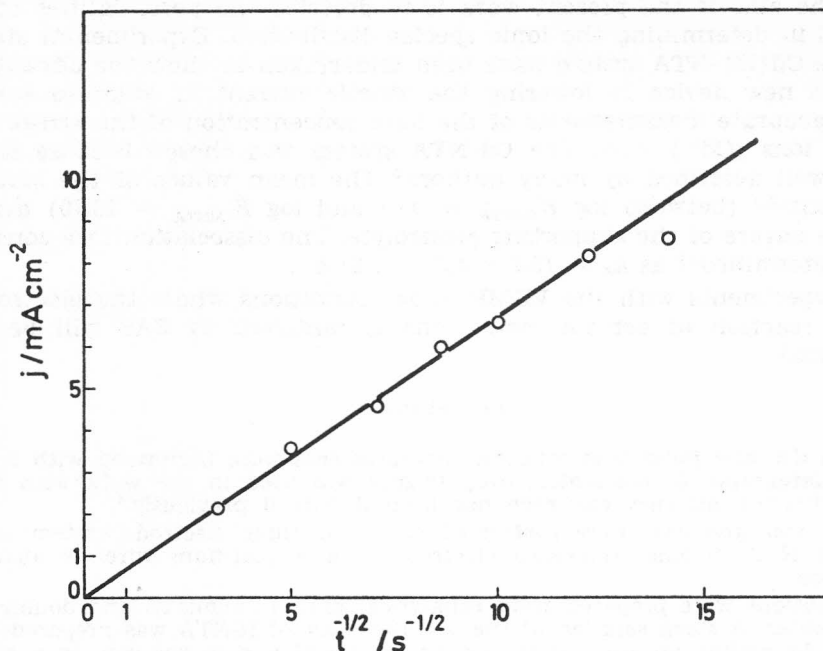
Figure 1. Dependence of the limiting current density of Cd^{2+} on the dropping rate at VDME. $[Cd^{2+}]=2\times10^{-4}$ (mol/dm^3), $\mu=0.1$ (mol/dm^3), pH=2, perchlorate supporting electrolyte

Ilkovič equation, but we must point out that the results from Figure 1. were not obtained at a single mercury column height. For proper VDME functioning, the height of the mercury reservoir has to be changed according to the drop life-time and the average mercury flow rate varies from measurement to measurement. The capillary parameters are presented in Table I. Note that the mercury flow rate is inversly proportional to the drop life-time. Thus the area of drop surface at the end of its life-time does not depend on the dropping rate. Oscillographic measurements of the reproducibility of drop sizes and dropping rates, described in a previous paper,[4] and presently submitted evidence of a regular dependence of limiting current on the mercury flow rate and measurement time confirm that VDME works with a series of small, discrete drops and not with a vibrating stream.

The addition of Na_2HNTA to the solution of cadmium causes the expected decrease of the »free« Cd^{2+} wave and the appearance of a se-

TABLE I

Capillary Parameters

drop life time/(s)	0.1	0.01	0.005
reservoir height/(cm)	10.	75.	120.
mercury flow rate/(mg/s)	0.48	4.1	7.6

cond wave at —0.880 (V) vs. CSE. This wave can be attributed to the direct reduction of the CdNTA⁻ species.[5]

Comparison of diffusion currents of the »free« Cd^{2+} and CdNTA⁻ waves gives a ratio of the diffusion coefficients $D_{CdNTA}/D_{Cd} = 0.5$, which is in good agreement with the literature.[5]

Figure 2. shows the polarographic results for the »titration« of Cd^{2+} with Na_2HNTA in 0.1 (mol/dm³) citrate buffer, pH = 6. The diffusion currents of »free« Cd^{2+} and CdNTA⁻ waves, normalised by their maximal values, are plotted against the total concentration of Na_2HNTA added. The experiments were performed in two ways: with a dropping mercury electrode (drop life time $t = 4$s) using d.c. (curves 1 and 1') and pulse (curves 3 and 3') excitation techniques, and with the vibrating dropping mercury electrode using d.c. technique at dropping rates of 10 drops/s (curves 2 and 2') and 100 drops/s (curves 4 and 4'). Curves A and B represent the theoretically calculated equilibrium concentration of Cd^{2+} and CdNTA⁻ if no citrate ions are present for a stability constant of a CdNTA⁻ complex of 2×10^{10} (dm³/mol). These curves serve as a reference for the estimation of the probable influence of citric anions on ionic distribution of cadmium complex species.
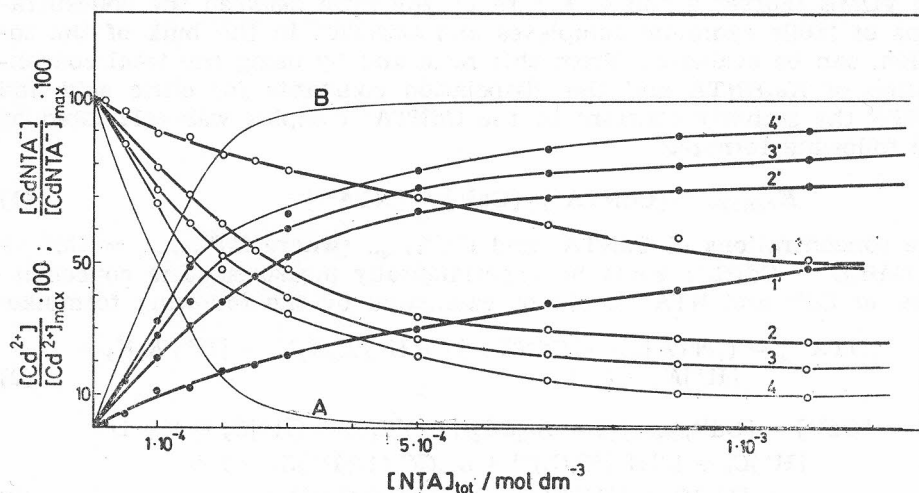

Figure 2. Ionic species distribution measurements in the Cd/CdNTA system: Cd^{2+} (1—4) and CdNTA⁻ (1'—4'). Theoretical distribution, if no citrate ions are present: Cd^{2+} (A) and CdNTA⁻ (B). Techniques: d.c. pol., $t=4$ s (1 and 1'); pulse pol., $t=57$ ms (3 and 3'); VDME $t=0.1$ s (2 and 2') and $t=0.01$ s (4 and 4'). [Cd^{2+}]=2×10^{-4} (mol/dm³), pH=6, 0.1 (mol/dm³) citrate buffer, 20 °C

The amplitude of the kinetically controlled Cd^{2+} wave depends on the measurement time. The results obtained with the VDME are comparable with results of pulse polarography at DME with a pulse duration time of 57 ms. If the drop life time of VDME is only 10 ms (for 100 drops/s), the kinetic contribution to the limiting current of the Cd^{2+} wave is almost two times smaller than the one obtained by pulse polaro-

graphy (curves 4 and 3, Figure 2.). On the contrary, if the drop life time on the VDME is 100 ms (or 10 drops/s), the result shows a larger kinetic contribution than for pulse polarography (curves 2 and 3, Figure 2).

The difference between curves A and 4 in Figure 2 can be attributed to the complexation of Cd^{2+} with citrate anions. According to the reported stability constants of CdH_2L and $CdHL^-$ (where H_4L is the symbol for citric acid) and the dissociation constants for citric acid,[7] cadmium ions are practically completely complexed by citrate ions at pH = 6 in the absence of Na_2HNTA. At pH = 6 the $CdHL^-$ complex is the predominant one. After addition of Na_2HNTA, redistribution between the various cadmium complex species occurs, but due to the higher concentration of citrate anions ($C_{H_4L} = 0.06$ mol/dm³), a certain number of cadmium-citrate complexes coexists with the $CdNTA^-$ complex species. In a 1 molar $NaClO_4$ solution, with a total citrate concentration of up to 0.03 mol/dm³, only one reversible d.c. polarographic wave has been obtained. The small current decrease, never exceeding 10%, can be attributed to the diffusion coefficient change, since the same results were obtained with normal DME and VDME with 100 drops per second. This is in good agreement with the literature.[10] It can be concluded that dissociation of the cadmium--citrate complex species is too fast to be detected even by the VDME.

From the diffusion currents of the polarographic waves, measured by the VDME (curves 4 and 4′, Figure 2), the ratio between the concentrations of labile cadmium complexes and $CdNTA^-$, in the bulk of the solution, can be evaluated. From this ratio and by using the total concentration of Na_2HNTA and the dissociation constants for citric acid and H_3NTA the stability constant of the $CdNTA^-$ complex was calculated by the following formula:

$$K_{CdNTA^-} = [CdNTA^-] \cdot [Cd^{2+}]^{-1} \cdot [NTA^{3-}]^{-1} \tag{1}$$

The concentrations of $CdNTA^-$ and $Cd^{2+}_{,,free,,}$ (where $Cd^{2+}_{,,free,,} = Cd^{2+} + CdH_2L + CdHL^-$) could be experimentally measured. The concentrations of Cd^{2+} and NTA^{3-} could be calculated by the following formulae:

$$[NTA^{3-}] = ([NTA]_{tot} - [CdNTA^-]) ([H^+]^3K_1K_2K_3 + [H^+]^2K_2K_3 + [H^+]K_3 + 1)^{-1} \tag{2}$$

$$[Cd^{2+}] = [Cd^{2+}_{,,free,,}]\{1 + L_{tot}CC_2([H^+]^2C_3C_4 + [H^+]C_3 + 1 + 1/[H^+]C_2 + 1/[H^+]^2C_1C_2)^{-1} + L_{tot}CC_1(1/[H^+]C_1 + 1 + [H^+]C_2 + [H^+]^2C_2C_3 + [H^+]^3C_2C_3C_4)^{-1}\}^{-1} \tag{3}$$

where:

$C_1 = [HL^{3-}][H^+]^{-1}[L^{4-}]^{-1};$ $C_2 = [H_2L^{2-}][H^+]^{-1}[HL^{3-}]^{-1};$
$C_3 = [H_3L^-][H^+]^{-1}[H_2L^{2-}]^{-1};$ $C_4 = [H_4L] [H^+]^{-1}[H_3L]^{-1};$
$CC_1 = [CdHL^-][Cd^{2+}]^{-1}[HL^{3-}]^{-1};$ $CC_2 = [CdH_2L][Cd^{2+}]^{-1}[H_2L^{2-}]^{-1};$
$K_3 = [HNTA^{2-}][H^+]^{-1}[NTA^{3-}]^{-1};$ $K_2 = [H_2NTA^-][H^+][HNTA^{2-}];$
$K_1 = [H_3NTA][H^+]^{-1}[H_2NTA^-]$

L_{tot} and NTA_{tot} are total concentrations of citrate anions and NTA, respectively, added to the solution. The constants $C_1, C_2, C_3, C_4, CC_1, CC_2, K_3, K_2$ and K_1, needed for calcutation of K_{CdNTA^-} were found in the literature.[7]

For pH = 6, the evaluated result:

$$K_{CdNTA} = (2.1 \pm 0.1) \times 10^{10} \quad (dm^3/mol)$$

(4)

is in agreement with the literature.[5,6,7]

The reported value of the K_{CdNTA} constant (eq.4) is a mean value of five particular results obtained from the experimental values for [CdNTA$^-$] and [Cd^{2+},,free,,] corresponding to NTA$_{tot}$ values ranging from $3 \cdot 10^{-4}$ to $1.1 \cdot 10^{-3}$ (mol/dm^3) (see Figure 2). It is worth noting that the K_{CdNTA} constant value reported in this work belongs to the group of highest values reported for the CdNTA$^-$ stability constant.[7] The values compiled from the literature[7] cover a very wide range between $1 \cdot 10^8$ and $1 \cdot 10^{10}$ (dm/mol). It is known that the determination of the stability constant depends on succesful elimination of the kinetic contribution and on proper estimation of the influence of rival ligands present in the solution. An understimated value of the stability constant appears as a consequence of failure in this procedure. The high value for the stabilitiy constant of CdNTA$^-$, reported in this paper, could be a proof that our measurements and calculations were correct. The theoretical fitting of our results for the »free-cadmium« distribution, if the value for K_{CdNTA} from eq.(4) is used, resembles curve 4 on Figure 2.

The VDME electrode can be described as a d.c. polarographic electrode with pulse characteristics. Its main feature is a very short measurement time which can be easily modified. Obviously, the problem of the low ratio between the faradaic and the charging currents, which is the main disadvantage of d.c. polarographic technique, appears at a VDME in pronounced form. This problem could be solved if the VDME-vibrator could be synchronised with the recording instrument. Improvement of the VDME device in this direction is in progress. The synchronisation could enable us to use the pulse and the differential pulse polarographic modes and to improve the sensitivity.

The VDME works in such a way that renewal of the electrode surface is very fast and contact between the electrode and the solution is very short. As the influence of the surface active substances (SAS) depends mainly on the age of the electrode, the VDME appears to be superior to all other polarographic techniques including pulse polarography. One of the most commonly used model substances for the investigation of the SAS effect on electrochemical reactions is Triton-X-100. Its activity on the suppression of the differential pulse peak current of Cd^{2+} is well documented.[3] Depending on the measuring time and the convection regime in the solution, T-X-100 may act as a powerful suppressor at a concentration of between 1.0 mg/l (HMDE in stirred solution with an accumulation time of 60 s) and 40 mg/l (DME, $t = 2$ s). As previously described,[4] the VDME is extraordinarily resistant to the influence of SAS. The effect of T-X-100 on the Cd^{2+} reduction wave at the VDME, shown in Figure 3, confirms this behaviour. The amount of T-X-100 required for the suppression of the Cd^{2+} reduction current at the VDME with $t = 1/100$ s (Figure 4., curve 3) is more than one order of magnitude higher (700 mg/1) than for the suppression of the DME current with $t = 2$ s. Normally, if the frequency is smaller (VDME, $t = 0.1$ s, curve 2,

Figure 3.) the required amount of T-X-100 for suppression is smaller (100 mg/1), but still higher than what occurs in nature. This property of the VDME is understandable if one bears in mind that the amount of material adsorbed on the surface of the electrode is, in principle, diffusion controlled and thus time dependent. In measurements carried out
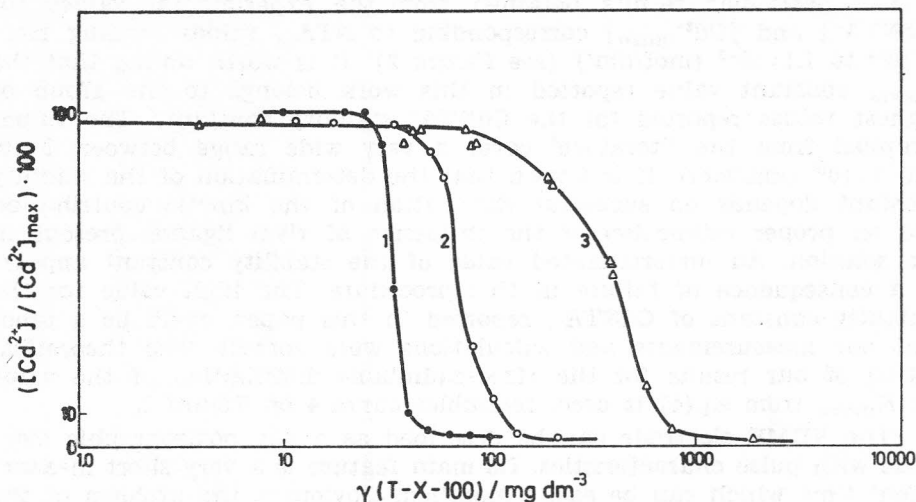

Figure 3. Dependence of the polarographic-wave-plateau current (VDME) and the differential pulse peak current[3] of Cd^{2+} on the T-X-100 concentration. VDME: $t = 0.1$ s (2) and $t = 0.01$ s (3); DME:[3] $t = 2$ s (1). $[Cd^{2+}] = 5 \times 10^{-4}$ (mol/dm³), 0.1 (mol/dm³) NaCl, pH = 6, 20 °C (Curve 1 reproduced by the courtesy of the authors)

in the presence of SAS, the VDME is not only comparable to pulse polarography on DME, but superior to this technique because in the latter case adsorption does not depend only on the potential excitation duration, but on the whole drop-life time. Only if a suitable waiting potential exists such that adsorption is forbidden, is pulse polarography able to rival with VDME. However, most types of SAS adsorb in such a broad potential range that the waiting potential could hardly be chosen outside this range.

Two other illustrations of VDME characteristics are shown in Figures 4. and 5. Data on the measurements of high concentrations of methylene-blue in KNO_3 are shown in Figure 4. While d.c. and pulse polarography are influenced by different kinds of rearrangements of the methylene-blue adsorbed on the electrode surface,[12] measurements with the VDME yield an unaffected wave even at 1×10^{-3} (mol/dm³) methylene-blue. The VDME cannot avoid adsorption, but with $t = 10$ ms the coverage of the electrode surface is smaller than unity, and the main distortion of the faradaic process is avoided. The undistorted wave reflects only a simple redox process and colud serve as a reference for distinguishing between redox and surface effects.
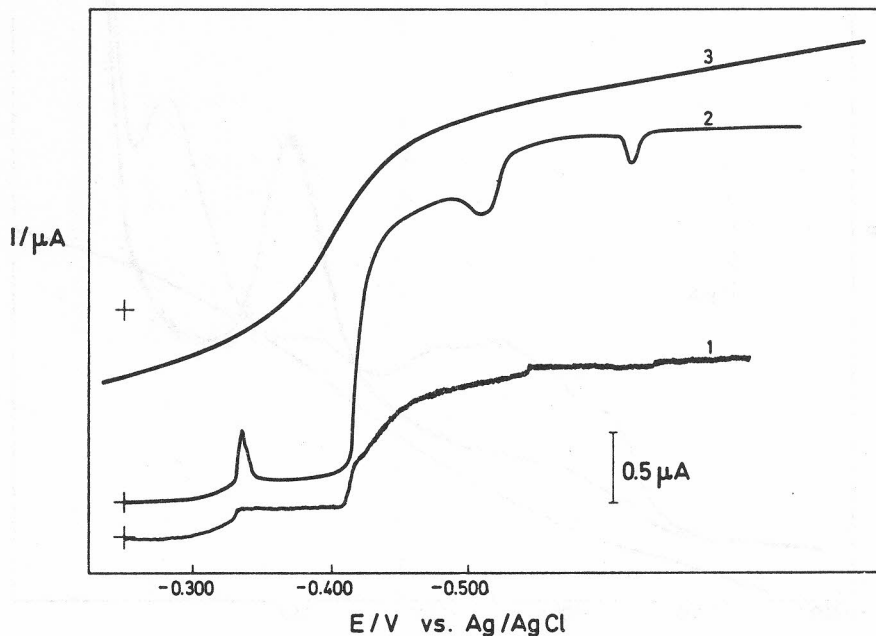
Figure 4. The d.c. (1), pulse (2), and VDME (3) polarography of methylene-blue. [MB]=1×10^{-3} (mol/dm³), 0.1 (mol/dm³) KNO₃, 20 °C, pH=8. DME: t=0.5 s (1, 2); VDME: t=0.01 s (3). Crosses denote points of zero current

The last example (Figure 5.) illustrates the behaviour of iatrorubine in the NaCl electrolyte at pH=8 for the three different methods. Iatrorubine is an alkaloid of the berberinic group[9] known to have one faradaic reduction wave and a strong, pH dependent catalytic hydrogen wave. In the d.c. and pulse polarography on DME, the influence of adsorption (the prewave in d.c. and the composeit maximum on the pulse polarogram) is conspicuous. Besides, the catalytic wave of hydrogen develops a very high maximum whose origin is still under study. The VDME polarogram indicates total suppression of the hydrogen maximum, as well as of the first reduction prewave. This is another example showing that the VDME suppresses the adsorption effects very effectively even if the surface active substances are electroactive themselves.

In conclusion it can be said that besides the already destribed characteristics,[4] the VDME affords significant possibilities if applied to ionic species characterization and stability-constant measurements. Its high insensitivity to SAS is an extraordinary property, displayed by no other electrode. The use of the VDME is simple and reliable. The measurement time (which corresponds to the pulse duration time in pulse polarography) can be easily controlled by changing the drop frequency. The development of polarography can be achieved either by introduction of new excitation signals or by improvement of the electrodes used. The VDME
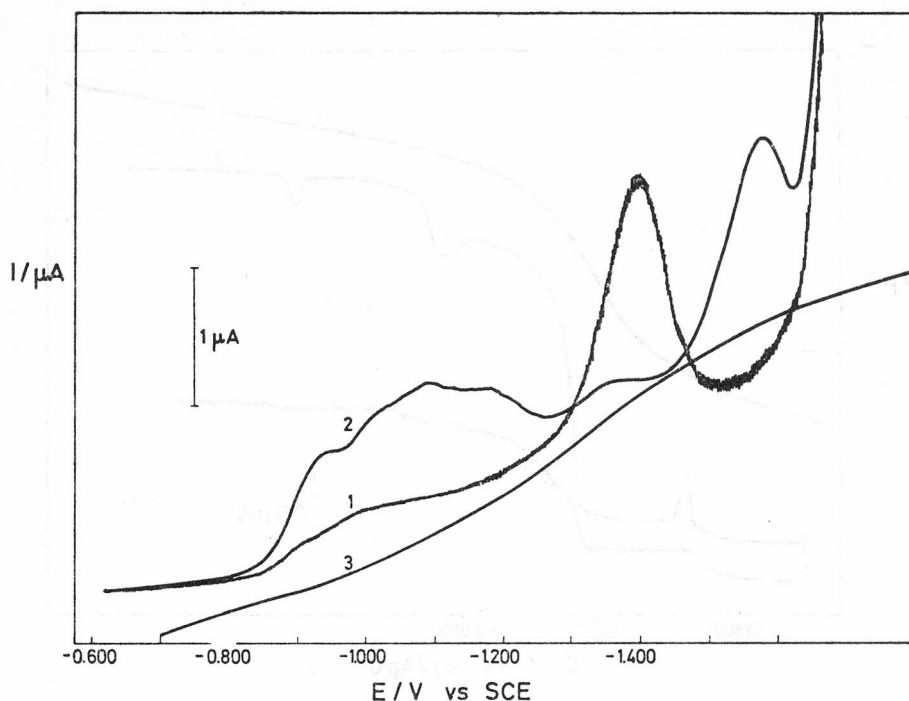
Figure 5. The d.c. (1), pulse (2) and VDME (3) polarography of iatrorubine. DME: $t=0.5$ s (1, 2); VDME: $t=0.01$ s (3). [Iatrorubine] $=2\times10^{-4}$ (mol/dm³), pH $=8.0$, 20 °C, $\mu=0.5$ (mol/dm³)

device could represent a significant step forward when coupled with the most sophisticated currently known polarographic techniques.

REFERENCES

1. Proceedings of the Sixth International Symposium *The Chemistry of Mediterranean, Thalassia Jugosl.* **16** (1980) 95—434.
2. J. Koryta and I. Kössler, *Collect. Czech. Chem. Commun.* **15** (1950) 241.
3. Z. Kozarac, S. Nikolić, I. Ružić, and B. Ćosović, *J. Electroanal. Chem.* **137** (1982) 279.
4. T. Magjer, M. Lovrić, and M. Branica, *Croat Chem. Acta* **53** (1980) 101.
5. B. Raspor and M. Branica, *J. Electroanal. Chem.* **59** (1975) 99.
6. C.V.D.' Alkaine and J. Koryta, *Collect. Czech. Chem. Commun.* **34** (1969) 2138.
7. L.G. Sillen and A.E. Martell, *Stability Constants of Metal-Ion Complexes* Chem. Soc. London, 1964.
8. J. Koryta, *Collect. Czech. Chem. Commun.* **24** (1959) 3057.

9. Š. Komorsky-Lovrić and Z. Gašparec, *Croat. Chem. Acta 54* (1981) 97.

10. L. Meites, *J. Amer. Chem. Soc.* **73** (1951) 3727.

11. J. Čižek, J. Koryta, and J. Koutecky, *Collect. Czech. Chem. Commun.* **24** (1959) 663.

12. V. Svetličić, J. Tomaić, V. Žutić, and J. Chevalet: *J. Electroanal. Chem.* **146** (1983) 71.

13. D. R. Canterford: *J. electroanal. Chem.* **77** (1977) 113; **97** (1979) 113.

14. A. M. Bond and R. J. O'Halloran: *J. Electroanal. Chem.* **97** (1979) 107; **68** (1976) 257.

15. A. M. Bond and R. J. O'Halloran: *J. Phys. Chem.* **77** (1973) 915.

SAŽETAK

Elektroanalitička primjenjivost živine elektrode koja vibrira

M. Lovrić, T. Magjer i M. Branica

Prikazana je primjenjivost živine elektrode koja vibrira na određivanje konstanti stabilnosti kompleksa metalnih iona i na mjerenje koncentracija metalnih iona u uzorcima voda koje su jako zagađene površinsko aktivnim tvarima (PAT). Kao model za prirodni sistem kod kojeg dolazi do utjecaja homogene kemijske reakcije koja prethodi elektrokemijskom procesu (npr. disocijacija kompleksa) na polarografsku redukciju »slobodnog« metalnog iona, izabran je sistem Cd²⁺/CdNTA⁻ u citratnom puferu (pH = 6). Opisan je utjecaj Tritona-X-100 na polarografski val Cd²⁺ kao primjer utjecaja neionskih PAT na elektrodne procese metalnih iona. Diskutira se primjenjivost živine elektrode koja vibrira na elektrokemijska mjerenja metilenskog plavog i jatrorubina jer su ove supstance površinski i elektro-aktivne. Život jedne kapi kod živine elektrode koja vibrira traje samo 5—10 (ms) pa je zbog toga ova elektroda pogodnija i pouzdanija od drugih za mjerenje elektrokemijske kinetike i za analizu uzoraka veoma zagađenih organskim tvarima.