

## STUDY OF LABILE COMPLEXES BY DIFFERENTIAL PULSE POLAROGRAPHY

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### ABSTRACT

Criteria for the determination of the peak potential  $E_p^r$  of reversible and same cases of quasireversible electrode reactions in the differential pulse polarography are proposed. On the base of the  $E_p^r$  values found De Ford and Hume's, as well as Leden's functions are recommended to be used for the determination of stability constants of complexes. The procedure proposed was tested by studying the labile systems: Cu(II) – glycine and Bi(III) – fluoride. The first is reversibly reduced and the second – quasireversibly. It was found that  $\lg \beta_{CuA} = 7.8$ ,  $\lg \beta_{CuA_2} = 14.9$  ( $I = 0.1$ );  $\lg \beta_{BiF} = 4.6$  and  $\lg \beta_{BiF_2} = 9.3$  ( $I = 0.1$ ). A satisfactory good coincidence between the results obtained by the procedure proposed and the literature data is observed.

*Keywords:* differential pulse polarography, determination of stability constants.

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### INTRODUCTION

Classic polarography is used to study labile complexes [1-3]. To determine the composition and stability of the complexes the equation of De Ford and Hume [3], describing the shift of the potential  $E_{1/2}^r$  of the reversible polarographic wave from the ligand concentration  $C_L$ , is applied. When the reduction of the metal ion is reversible,  $E_{1/2}^r$  is determined very precisely from all data of the polarographic curve. In the cases of quasireversible reduction,  $E_{1/2}^r$  is determined from the data at the foot of the curve, where the reduction is reversible [3]. The experimental values of  $E_{1/2}^r$  and  $C_L$ , are very often treated by the Leden's method [2], instead of that of De Ford and Hume, and then more precise results are obtained.

To observe a shift of  $E_{1/2}^r$  of the polarographic curve, the ligand excess has to be at least 10-100 times more than the metal ion concentration, that in classical

polarography is about  $10^{-4}$  mol l<sup>-1</sup>. On the other hand the ligand concentration can not be more than 0.1 or 1 mol l<sup>-1</sup>, because of the limited solubility of the ligand or change of the pH value and the ionic strength of the solution. This ligand concentration range limits the capabilities of the classical polarography to study complexes with low stability as well as to study a stepwise complexation. The cases indicated are more frequently available in the practice.

It is well known [4] that the peak potential,  $E_p$ , in the differential pulse polarography (d.p.p.) corresponds to  $E_{1/2}$  of the wave in the classic polarography. When the d.p.p. reduction of metal ion is reversible then

$$E_p^r = E_{1/2}^r - \frac{\Delta E}{2}$$

( $\Delta E$  is the amplitude of the pulse potential) and labile complexes could be studied by De Ford and Hume's

function and Leden's method without any complications. The functions could be applied to quasireversible d.p.p. reduction also, if  $E_p^r$  is known. The main problem that has to be solved is to identify the reversibility and quasireversibility of the reactions, as well as to determine  $E_p^r$  in the cases of quasireversible reduction of metal ions.

This study is aimed at identifying reversible and quasireversible d. p. p. peaks and confirming the application of the methods for study of labile complexes in the classical polarography to d.p.p. data, obtained by reversible and in some cases of quasireversible reduction of metal ions.

### THEORY

In classical polarography the wave shape depends on the reversibility of the electrochemical reaction. When the reduction is totally reversible or irreversible the polarographic wave is symmetrical against the middle point. An asymmetry is observed if the reduction is quasireversible. At the foot of the quasireversible wave the reduction is reversible and the curve is steeper than at the end where the irreversibility is the most strongly expressed [3]. A similar behaviour of the curves is observed in normal pulse polarography. The peak in the d. p. polarography is the first derivative of the curves in the normal pulse polarography and it is symmetrical only in the cases of reversible or irreversible reduction. When the reduction is fully reversible, the d.p.p. peak is tight and its  $W_{1/2}$ -value (the width of the peak at 1/2 of its height) depends on the number  $z$  of the electrons transferred in the reaction as well as on the amplitude  $\Delta E$  of the potential applied. The theoretical value of  $W_{1/2}$  at given  $\Delta E$  and  $z$ -values is read out from a plot [4]. At quasireversible reduction the left half (a tighter half) of the asymmetric peak could be due to fully reversible reduction. This assumption is true if the width of the tighter half of the peak at 1/2 of its height is equal to 1/2 of the theoretical  $W_{1/2}$ -value for reversible electrode reactions.

The above features of d.p.p. peaks can be utilized as criteria in distinguishing reversible from quasireversible peaks. When the experimental data about  $W_{1/2}$  of a symmetrical peak or about the width of the tighter half of an asymmetrical peak satisfy the

theoretical values, read out from the plot [4], the potential  $E_p$  could be accepted as  $E_p^r$  and De Ford and Hume's (eq. 1), as well as Leden's functions  $F_i$  (eq. 2) could be applied:

$$-\Delta E_p = -(E_p^c - E_p^s) = \frac{RT}{zF} \ln \sum_{j=0}^n \beta_j' C_L^j \quad (1)$$

$$F_0 = \exp \frac{zF}{RT} \Delta E_p = \sum_{j=0}^n \beta_j' C_L^j \quad (2)$$

$$F_1 = \frac{F_0 - 1}{C_L} = \beta_1' + \sum_2^n \beta_j' C_L^{j-1}$$

...

$$F_n = \frac{F_{n-1} - \beta_{n-1}'}{C_L} = \beta_n'$$

where  $E_p^c$  and  $E_p^s$  are peak potential of complex (c) and simple (s) metal ions, respectively;  $C_L$  is the total ligand concentration;  $\beta_j'$  is the formal stability constant of  $ML_j$  complex.

To verify the criteria proposed, the systems Cu(II) - glycine and Bi(III) - fluoride ions are chosen because of the copper(II) reversible reduction at dropping mercury electrode in different electrolytes, while the reduction of Bi(III) in the most cases is quasireversible [3]. At pH lower than 9 copper(II) is bound with glycine (HA) in four complexes: CuHA, CuA, CuA<sub>2</sub> and CuA<sub>3</sub>. The logarithmic values of the constants at ionic strength of 1 mol l<sup>-1</sup> are:

$$\lg \beta_{CuA} = 8.39, \lg \beta_{CuHA} = 10.62, \lg \beta_{CuA_2} = 15.32$$

and

$$\lg \beta_{CuA_3} = 16.96 \quad [5].$$

Inspection on the  $\lg \beta$  values shows that at pH range from 6 to 8 and a ligand concentration lower than 0.1 mol l<sup>-1</sup> the complexes CuA and CuA<sub>2</sub> predominate in the solution only. According to other references the values of the constants of CuA and CuA<sub>2</sub> complexes at an ionic strength of 0.1 mol l<sup>-1</sup> are:

$$\lg \beta_{\text{CuA}} = 8.1$$

and

$$\lg \beta_{\text{CuA}_2} = 15.1 \quad [6]$$

and that of the constant of the CuA complex is  $\lg \beta = 8.18$  [7].

The literature data for the complexes of Bi(III) - F<sup>-</sup> system are scarce. The formation of the complexes BiF and BiF<sub>2</sub> is only reported. The logarithmic values of their stability constants at ionic strength, I = 2 are respectively 4.7 and 8.3 [8].

## EXPERIMENTAL

### Apparatus and solutions

The voltamperometric analyses were carried out with the 646 VA Processor and the 647 VA Stand from Metrohm (Switzerland). A static mercury drop as working electrode, Ag/AgCl reference electrode and a carbon auxiliary electrode were used.

The potentiometric measurements were performed with pH-meter (Jenway, England) using a glass pH electrode.

The stock solutions of Cu(II) (0.015 mol l<sup>-1</sup>) and Bi(III) (0.05 mol l<sup>-1</sup>) were prepared by dissolution of Cu(NO<sub>3</sub>)<sub>2</sub> in water and Bi(NO<sub>3</sub>)<sub>3</sub> in 2 mol l<sup>-1</sup> HNO<sub>3</sub>.

The stock water solutions of glycine (1 mol l<sup>-1</sup>) and fluoride ions (0.1 mol l<sup>-1</sup>) were prepared from gly-

cine (p.a.) and NaF (p.a.). Working solutions of Cu(II), Bi(III) and the ligands with the concentrations given below were used for the determinations. A phosphate buffer (0.05 mol l<sup>-1</sup>; pH 7.0 ± 0.1) and a mixture of 0.01 M HNO<sub>3</sub> + 0.1 M KNO<sub>3</sub> were used as supporting electrolytes for Cu(II) and Bi(III), respectively.

### Procedure

#### Cooper (II) - glycine

10 ml of phosphate buffer and 10 µl of copper working solution were introduced in the electrochemical cell. Oxygen was removed by bubbling of pure nitrogen through the solution for 10 minutes. The cathodic peak of Cu(II) was registered by d.p.p. at an amplitude of 50 mV and a scan rate of the potential - 10 mV s<sup>-1</sup> (U. Step=6 mV, T. Step=0.6 s). The current and potential of the peak were measured. Volumes from 2 µl to 100 µl of the glycine working solution were successfully introduced in the cell. After each glycine volume added the solution was purged with nitrogen for 5 minutes. The analytical signal was registered and the peak potential and the current were measured.

#### Bi(III) - fluoride ions

10 ml of mixture HNO<sub>3</sub> + KNO<sub>3</sub> and 20 µl of bismuth working solution (5.10<sup>-3</sup> mol l<sup>-1</sup>) were introduced in the cell and the procedure, described for Cu(II) - glycine determinations was followed, fluoride ions being added (from 5 µl to 200 µl) instead of glycine.

Table 1. Results from the regression analysis of the F<sub>0</sub> - function:  $F_0 = 1 + \beta_1' C_L + \beta_2' C_L^2$ .

Studied system	Total concentration of HA/F <sup>-</sup> mol l <sup>-1</sup>	Number of experiments	Correlation coefficient	Regression equation
Cu(II)-HA	1.10 <sup>-4</sup> ÷ 1.10 <sup>-3</sup>	9	0.995	$F_0 = 1.1 + 1.8 \cdot 10^3 C_{\text{HA}} + 7.0 \cdot 10^6 C_{\text{HA}}^2$
	2.10 <sup>-3</sup> ÷ 1.10 <sup>-2</sup>	10	0.986	$F_0 = 83 - 1.1 \cdot 10^5 C_{\text{HA}} + 3.9 \cdot 10^7 C_{\text{HA}}^2$
Bi(III)- F <sup>-</sup>	1.10 <sup>-5</sup> ÷ 7.10 <sup>-5</sup>	7	0.993	$F_0 = 1.1 + 2.6 \cdot 10^3 C_{\text{F}^-} + 1.0 \cdot 10^7 C_{\text{F}^-}^2$

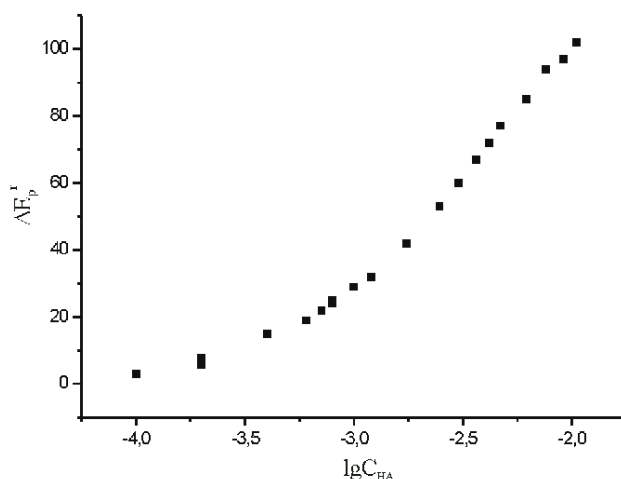


Fig. 1. Semilogarithmic function  $\Delta E_p^r = f(\lg C_{HA})$  of the system Cu(II)-glycine.

## RESULTS AND DISCUSSION

### Cu(II) - glycine

The experiments are carried out at 20°C in a phosphate buffer (pH 7.0±0.1) and an ionic strength  $I = 0.1$ . The copper concentration in the cell was  $4.10 \cdot 10^{-6}$  mol l<sup>-1</sup> and the glycine concentration was varied from  $2.10^{-4}$  to  $1.10^{-2}$  mol l<sup>-1</sup>. The upper limit of the glycine concentration was restricted by the appearance of not-well shaped copper peak.

In all glycine concentrations studied a single cathodic copper peak is observed. Its symmetrical form, the half-width  $W_{1/2}$  and the current  $i_p$  in the absence of ligand, do not change when ligand is added to the solution. The potential  $E_p$  is changed, only. The glycine concentration shifts  $E_p$  of the single copper peak to more negative potentials and the system Cu(II) - glycine is classified by us as fully labile on the d.p. polarographic time scale [9].

The experimental value of  $W_{1/2}$  of the copper peak is very close to the theoretical one, that at  $z=2$  and  $\Delta E=50$  mV is 60 mV [4]. Hence, the reduction of Cu(II) is reversible. The lability of the chemical reactions and the reversibility of the electrode reaction give us the reason to apply the equations of De Ford and Hume, as well as these of Leden to calculate formation constants. The semilogarithmic function of  $\Delta E_p^r$  from  $\lg C_{HA}$  is given in Fig. 1. Approximately two linear sections are observed, that indicates the formation of at least two

complexes. The two linear sections were investigated individually by Leden's functions and the results of the regression analysis are presented in Table 1. Reliable results for the formation constant of the CuA complex are obtained in the lower concentration range of the ligand, where the complex CuA predominated. By the same reason, the constant of CuA<sub>2</sub> complex is calculated from the  $F_0$  function, applied at the higher ligand concentrations. The same results for  $\beta'_1$  and  $\beta'_2$  were obtained by the regression analysis of the  $F_1$ -function:

$$F_1 = \beta'_1 + \beta'_2 C_{HA}$$

The ligand A (A is anion of glycine) and copper (II) ions participate in side reactions with the ions of the solution. A is a weak base and it is protonated ( $pK_1 = 9.8$  and  $pK_2 = 12.4$  [6]), the copper(II) ions form a complex with  $HPO_4^{2-}$  ions ( $\lg \beta_1 = 3.2$  [8]), and the value of the total constant  $\beta_j$  ( $j = 1; 2$ ) is calculated by the equation:

$$\lg \beta_j = \lg \beta'_j + \lg \alpha_{Cu(HPO_4)} + j \lg \alpha_{A(H)}$$

where  $\alpha$  denote the side reaction coefficient:

$$\alpha_{L(H)} = 1 + 10^{9.8} \bar{C}_{H^+} + 10^{12.4} (\bar{C}_{H^+})^2$$

and

$$\alpha_{Cu(HPO_4)} = 1 + 10^{3.2} C_{HPO_4^{2-}}$$

Table 2. The values of  $\alpha$ -coefficients calculated and stability constants found at  $I = 0.1$ .

Complex	$\alpha$ -coefficients calculated			Formation constants		Literature data	
	$\lg \alpha_{A(H)}$	$\lg \alpha_{F(H)}$	$\lg \alpha_{M(HPO_4)}$	Formal $\lg \beta'_j$	Total $\lg \beta_j$	Total $\lg \beta_j$	$I$ $\text{mol l}^{-1}$
CuA	2.8	-	1.7	3.3	$7.8 \pm 0.3$	8.10	0.1
CuA <sub>2</sub>	2.8	-	1.7	7.6	$14.9 \pm 0.2$	15.1	0.1
BiF	-	1.15	-	3.4	$4.6 \pm 0.2$	4.7	2
BiF <sub>2</sub>	-	1.15	-	7.0	$9.3 \pm 0.2$	8.3	2

The values of  $\alpha$  - coefficients calculated and  $\beta_j$  - values, determined by us, as well as the literature data about  $\beta_j$  are given in Table 2. A good coincidence is observed between the results obtained and literature data.

#### ***Bi(III)-fluoride ions***

The investigations were carried out in a solution of  $0.1 \text{ mol l}^{-1} \text{ KNO}_3$ ,  $0.01 \text{ mol l}^{-1} \text{ HNO}_3$ ,  $1.25 \cdot 10^{-5} \text{ mol l}^{-1} \text{ Bi(III)}$  and from  $5.10^{-4}$  to  $1.10^{-3} \text{ mol l}^{-1} \text{ KF}$  concentration. At concentration of KF higher than  $1.10^{-3} \text{ mol l}^{-1}$ , the shape of the bismuth peak is destroyed and the pH of the solution increased as the weak acid HF is formed. The temperature ( $20 \pm 1^\circ\text{C}$ ) and the ionic strength ( $I = 0.1$ ) were kept constant during the experiments. In the presents and in the absence of the fluoride ions the shape of the bismuth peak and the peak current values were the same. A shift of the peak potential in a negative direction with an increase of the ligand concentration was observed. Hence the rate of the chemical reactions between Bi(III) and  $F^-$  is much higher than the rate of the electrode reaction and the system is fully labile.

The bismuth(III) peak in the presence of fluoride ions is an asymmetrical one, that indicates a quasireversible reduction of the Bi(III). The width of the left half of the peak at  $1/2$  of its height is about 25 mV. This value is  $1/2$  of the theoretical value of  $W_{1/2}$  at  $z=3$  and  $\Delta E = 50 \text{ mV}$  [4], and it could be accepted that by the increasing part of the peak, from the beginning up to potential  $E_p$  the reduction is reversible and  $E_p = E_p^r$ .

Owing to the lability of the Bi(III) system and the acceptance that  $E_p = E_p^r$ , the Leden's functions for a

reversible reduction were applied. The results of the regression analysis of  $F_0$  - function are given in Table 1. The regression equation proves the presence of two complexes BiF and BiF<sub>2</sub>, whose logarithmic values of the formal stability constants are 3.4 and 7.0, respectively. The calculated values of the total  $\beta$  constants using the  $\alpha$  - coefficient of the side protonation reactions of the fluoride ions ( $pK_{HF} = 3.17$ ), are given in Table 2. The difference observed between our results and the literature data could be explained by the different ionic strength at which experiments were performed.

#### **CONCLUSIONS**

The results obtained prove that the criteria proposed could be used to determine  $E_p^r$  of reversible and quasireversible electrode reactions in the differential pulse polarography. At quasireversible electrode reaction the reversibility should be valid up to a potential equal to  $E_p$ . From the  $E_p^r$  - values found the formation constants of the complexes could be calculated applying De Ford and Hume's, as well as Leden's functions.

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