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Article

Electroreduction of Bi(III) Ions in the Aspect of Expanding the "Cap – Pair" Effect

Agnieszka Nosal – Wiercińska [1,*] and Sławomira Skrzypek [2]

[1] Department of Analytical Chemistry, Institute of Chemical Sciences, Faculty of Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland
[2] Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, University of Lodz, Tamka 12, 91-403 Lodz, Poland
* Correspondence: anosal@poczta.umcs.lublin.pl; Tel.: +48 81 5375627

Abstract: The paper discusses the electroreduction of Bi(III) ions in the aspect of expanding the "cap – pair" effect. The "cap – pair" rule is associated with the acceleration of the electrode's processes by organic substances. The interpretation of the "cap – pair" effect mechanism was expanded to include the effect of supporting electrolyte concentration on the acceleration process and the type of electrochemical active as well as used protonated organic substances. It has also been shown that the phenomena occurring at the electrode/solution interface can influence a change in the dynamics of the electrode's process according to the "cap – pair" rule.

Keywords: "cap – pair" effect; electrochemistry; electroreduction of Bi(III); active complexes; catalytic activity

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1. Introduction

Research into electrode processes taking place in aqueous solutions is one of the basic topics of modern electrochemistry due to its practical aspect. The most common examples are the use of lead batteries in cars, lithium-ion batteries in cell phones, control and prevention of corrosion, which is decisive for the life and reliability of many devices or sensors used in monitoring environmental pollution. Besides these examples, there are many other areas of human activity using from electrochemical engineering applications, such as bioelectronics, electrochemical waste disposal or electrochemical synthesis of oxidants. The use of electrochemical methods is also observed in diagnostics and medical therapy, e.g. when determining and searching for new drugs or biomaterials.

The commonly used electrochemical techniques have many advantages, among which we can distinguish: relatively low cost of equipment, ease of miniaturisation and automation, high sensitivity, precision, accuracy, and simplicity of measurement.

It should be noted that in the extensive spectrum of analytical techniques, few methods satisfy all these criteria. Electrochemical measurement techniques such as square Wave Voltamperometry (SWV), Pulse Differential Voltamperometry (DPV), Square Wave Stripping Voltamperometry (SWAdSV) or Cyclic Voltamperometry (CV) are commonly used to determine depolarisers and biologically active compounds as well as to study electrode mechanisms [1-5]. At present, one of the fastest developing techniques is electrochemical impedance spectroscopy (EIS), which allows for determining the mechanisms of processes taking place at the electrode/solution interface or to investigate the applicability of new electrode materials [6].

A very important stage of electrochemical research is the choice of a suitable working electrode. Carbon electrodes are commonly used, the most popular are glass carbon electrodes (GCE) [7, 8], carbon paste electrode (CPE) [9], boron-doped diamond electrode (BDDE) [10] or carbon printed electrodes (SPE) [11, 12]. These are solid electrodes, which due to processes taking place on their surface, both during their preparation and use and a lack of reproducibility of the surface during mechanical cleaning are, however, characterised by worse reproducibility than mercury electrodes,

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with a constant change of parameters (range of useful potentials, residual current) and low stability. As a result, their practical application in determining electrode mechanisms is very limited.

Mercury as an electrode material, despite its defects, also has several important advantages [13-15], such as:

- neutrality to most electrolytes,
- high hydrogen overvoltage,
- ease of amalgam formation with most metals,
- exceptional smoothness and good surface definition.

At present, the electrode with the highest coefficient of repeatability, precision and surface reproducibility is the electrode with controlled growth of the surface of the drops (Controlled Growth Mercury Drop Electrode - CGMDE), developed by Kowalski [16] and introduced into ongoing production by companies such as Bioanalytical Systems (BAS), USA; Methrom, Poland or MTM-ANKO Kraków, Poland.

Gaining knowledge into the influence that organic substances have on the rate of electrode reactions is of great analytical importance as well as in developing technological and pharmacological characteristics. Organic substances may inhibit, accelerate, or not affect the electrode's process.

The conditions under which an organic substance acts as a catalyst were formalised in 1978 by the Sykut team defining them as a "*cap-pair*" rule [17]. It follows that the non-active electrochemical organic substance molecule must contain sulphur or nitrogen atoms with free electron pairs that are able to form coordination bonds with the depolariser ions, while the depolariser redox potential must be within the labile equilibrium for adsorption of the organic substance with the working electrode surface. The mechanism for the catalytic effect of metal cations electroreduction under "*cap-pair*" conditions, includes both chemical reactions and heterogeneous processes of charge transfer between the electro-active particle of the complex and the depolarised working electrode. The formation of electroactive complexes with depolarisers is possible both in the adsorption layer for zinc(II) ions [18-20], cadmium [21] indu(III) [22, 23] and bismuth(III) [24-29], and outside the layer for europium(III) ions [30]. The goal of this current paper was to collect and summarise studies on the kinetics and mechanism of action for selected organic substances on the electroreduction of Bi(III) ions in chlorate(VII) solutions in terms of expanding the interpretation of the "*cap-pair*" effect mechanism.

It was pointed out:

- effect of changes of water activity and used active (cysteine (CE) and cystine (CY)) and non-active (methionine (MT)) electrochemically accelerating organic substances on the mechanism and kinetics of Bi(III) ion electroreduction,
- influence of protonation changes of selected amino acids (homocysteine (HCE), homocystine (HCY) and ethionine (ET)) on the mechanism and kinetics of Bi(III) ion electroreduction,
- the effect of the mixed adsorption layers forming (6 – mercaptopurine (6MT) – surfactant, 6-thioguanine (6TG) – surfactant and azathioprine (AZA) – surfactant) on the mechanism and kinetics of Bi(III) ion electroreduction.

The practical aspect of these studies is related to the possibility of directing and indicating new ways of determining depolarisers as well as substances that may cause a disturbance of homeostasis in a living organism. This can help determine the complex mechanism of action for certain drugs in the body to help monitor a patient's health.

2. Results and Discussion

2.1. Kinetics and mechanism of Bi(III) ion electroreduction process in the presence of selected amino acids in chlorate(VII) solutions with different water activity.

The influence of both water activity and selected amino acids on the kinetics and mechanism of the Bi(III) ion electroreduction process in 1 mol·dm^{-3} – 8 mol·dm^{-3} chlorates(VII) was demonstrated.

The presence of methionine [31], cysteine [32] or cystine [32, 33] in the supporting electrolyte solution causes both an increase of the slope of the polarographic wave and the SWV current of the Bi(III) ion electroreduction peaks, which indicates an increase in the reversibility of the Bi(III) ion electroreduction process [19]. Such observations also result from the course of CV voltammetric curves. Small changes in the distance between the anodic and cathodic peak potentials $\Delta E_{(a-c)}$ along with a change in the polarisation rate indicated that the process of the electroreduction of Bi(III) ions in 1 mol·dm^{-3} - 8 mol·dm^{-3} chlorate(VII) in the presence of the amino acids under study is controlled by the kinetics of the reaction preceding the transition of electrons [19]. The acceleration of electrode processes only by organic substances that have free electron pairs of sulphur or nitrogen atoms, suggests the formation of complexes under specific conditions that exist on the electrode's surface. The obtained results indicate that in the case of methionine a Bi-methionine complex is formed on the electrode's surface. In the case of cysteine and cystine, respectively, mercury cysteine thiolates (I) and (II) [34, 35], which can form an active complex from Bi(III), are adsorbed for mercury. Therefore, cysteine and cystine are a bridge in the formation of these complexes. It has been found that Bi(III) reacts with mercury (II) cysteine thiolate $Hg(SR)_2$ [31]. The real rate constants k_f (taking into account the influence of the double layer) of the Bi(III) ion electroreduction as a function of the electrode's potential determined from impedance measurements [31] indicated that also in the presence of substances catalysing the Bi(III) ion, the electroreduction process is carried out in stages. In addition, the effect of catalysts on the transition of the first electron is usually much more significant than on the transition of the other electrons. This is evidence that Bi(III) ion complexes with the accelerating substance are formed already before the first electron passes, which is the slowest stage and determines the speed of the whole process. The nature of changes $\ln k_f = f(E)$ [31] in chlorate(VII) solutions in the presence of all studied amino acids show the differences in the mechanism of electroreduction process in solutions with high water activity compared to solutions with low water activity. The determined standard rates constants k_s [31-33] indicated that the catalytic action of amino acids increases in the cystine < methionine < cysteine series - for chlorates(VII) with high water activity. For higher chlorates(VII) concentrations (from 5 mol·dm^{-3} to 8 mol·dm^{-3}), a comparable effect of amino acids on the Bi(III) ion electroreduction rate is observed (Figure 1).

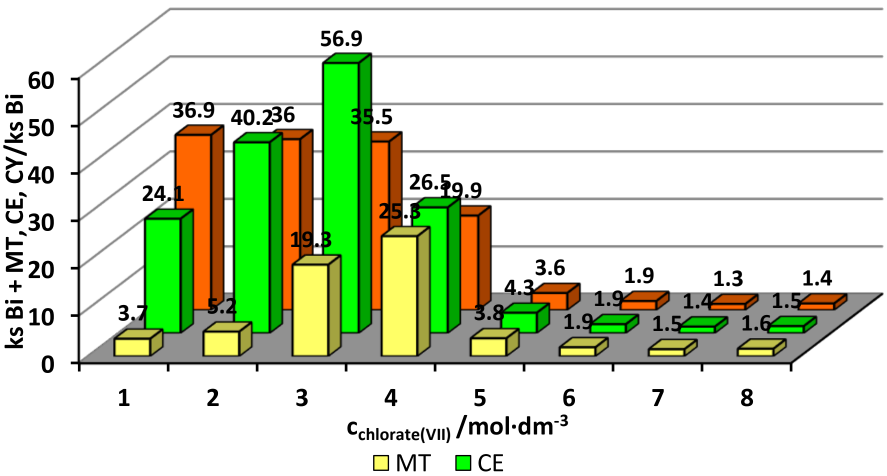

Figure 1. The catalytic activity defined by the k_s Bi+amino acids/ k_s Bi for 1 - 8 mol·dm^{-3} chlorates(VII).

2.2. Effects of protonation of some amino acids on the kinetics and mechanism of Bi(III) ions electroreduction.

Significant differences in the kinetics and mechanism of the Bi(III) ion electroreduction process were observed due to the change of $HClO_4$:$NaClO_4$ ratio in 2 mol·dm^{-3} - 6 mol·dm^{-3} chlorate(VII) solutions [36] and the presence of homocysteine, homocystine or ethionine [29, 37, 38].

The increase in SWV peak current of the Bi(III) ion electroreduction along with a simultaneous decrease in the peak width at half of its height, indicates an increase in the reversibility of the Bi(III) ion electroreduction process in the presence of the studied amino acids [29, 37, 38]. The magnitude of

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this effect depends on the concentration of amino acids and changes in the ratio of $HClO_4$ and $NaClO_4$ in solutions of chlorates(VII) with different water activity [29, 37, 38].

Confirmation of such changes in the reversibility of the electrode's process is a clear reduction in the distance between the anode and cathode peaks taken from the cyclic voltammetry curves.

The investigations indicated a multistage character of the electrode's process also in the presence of HCE, HCY and ET, control of the rate of Bi(III) ion electroreduction process by a chemical reaction [19]. It was indicated that active complexes are formed on the electrode's surface, which mediates electron transfer. It should also be noted that due to the mentioned electrochemical reactivity of both homocysteine and homocystine, which react with mercury in the same way as cysteine and cystine [39], we can discuss Bi - $Hg2(SR)_2$ or Bi - $Hg(SR)_2$ complexes. According to the literature reports [31], Bi(III) reacts with mercury cysteine thiolate - $Hg(SR)_2$. This form of anodic mercury oxidation in the presence of homocysteine or homocystine is adsorbed in the range of Bi(III) reduction potentials (~ 0 mV) and is loosely bonded to the electrode's surface [34, 35]. However, in the case of polarographically non-active ethionine, complexes of type Bi - ethionine are formed on the electrode's surface [39, 40].

The real rate constants k_f of the Bi(III) ion electroreduction as a function of the electrode potential that was determined from the impedance measurements [31] indicate differences in the mechanism of the electroreduction process in solutions differing in the degree of amino acid protonation. The correlation of kinetic parameters shows that both the water activity and the presence of amino acids to a different degree of protonated amino acids affect the rate of electroreduction of Bi(III) ions. The k_s values indicate that the catalytic action of amino acids increases in the ET< HCY < HCE series for chlorates(VII) with a high-water activity of 2 mol·dm^{-3}. For 4 and 6 mol·dm^{-3} chlorates(VII), a comparable effect of the amino acids studied on the rate of the Bi(III) ion electroreduction is observed, especially for HCE and HCY. However, the catalytic action of ethionine is slightly higher compared to cysteine and cystine derivatives [38, 40] (Figure. 2 a, b, c). As the quantity of $NaClO_4$ in the base electrolyte solution increases, the amino acid catalytic activity increases. On the other hand, an increase in the quantity of $HClO_4$ in chlorate(VII) solutions causes much smaller changes in the kinetics of the Bi(III) ion electroreduction process in the presence of homocysteine, homocystine and ethionine. The highest catalytic activity was observed in 2 mol·dm^{-3} chlorates(VII) for the highest quantity of sodium salt of chloric acid(VII) (2C solution) [41].

a

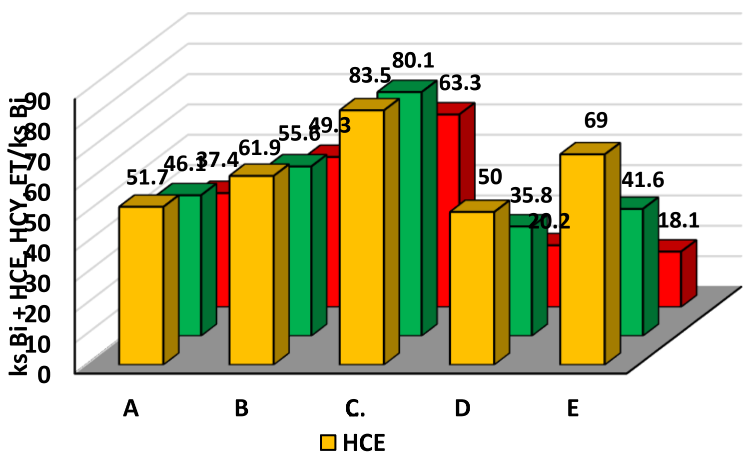

Figure 2. a. The catalytic activity defined by the k_s Bi+amino acids/ k_s Bi for 2 mol·dm^{-3} chlorate(VII).

b

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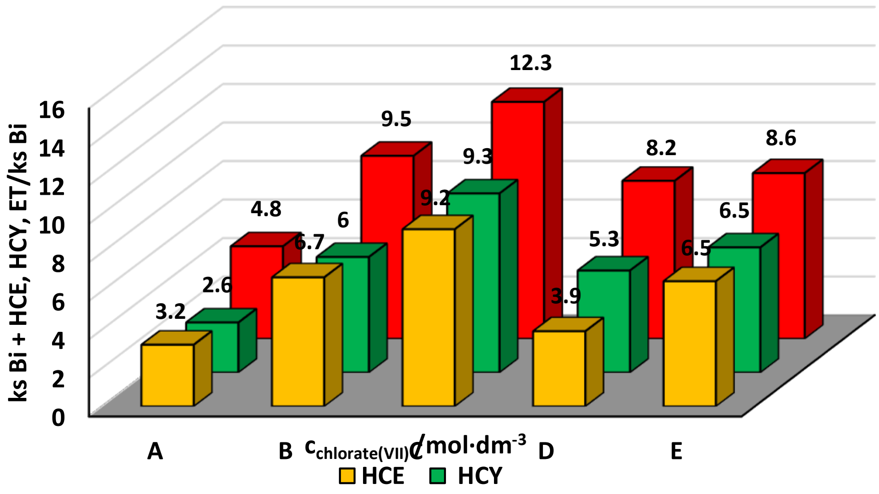

Figure 2. b. The catalytic activity defined by the k_s Bi+amino acids/ k_s Bi for 4 mol·dm^{-3} chlorate(VII).

c

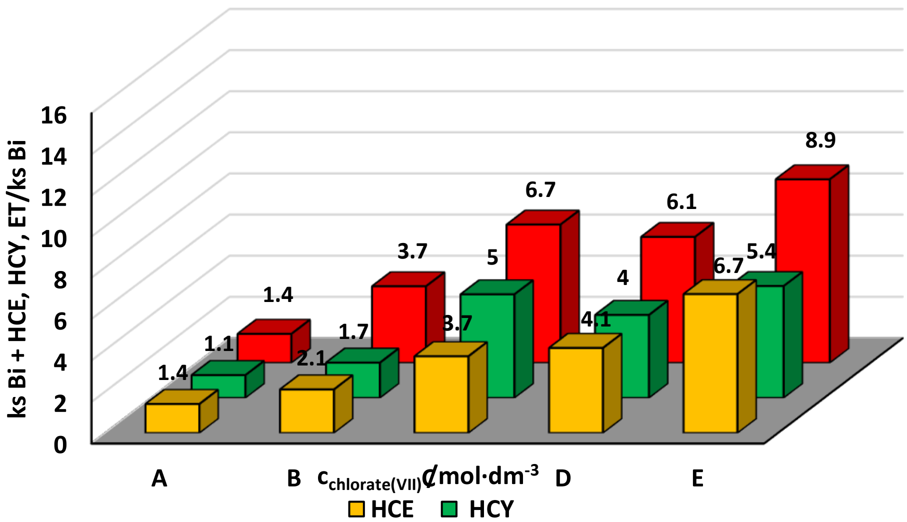

Figure 2. c. The catalytic activity defined by the k_s Bi+amino acids/ k_s Bi for 6 mol·dm^{-3} chlorate(VII).

2.3. Influence of mixed thiopurine derivatives-nonionic surfactant adsorption layers on kinetics and mechanism of Bi(III) ion electroreduction.

The introduction of thiopurine derivatives (6-mercaptopurine, 6-thioguanine, azathioprine) to solutions of Bi(III) ions in 2 mol·dm^{-3} chlorates(VII) indicates an increase in the reversibility of Bi(III) electroreduction [31] (an increase in the SWV peak current for Bi(III) ion electroreduction as well as a simultaneous reduction in the width of SWV peaks at half their height [42-44]). The effect of the studied surfactants (Tween 80 and Triton X – 100) on the figure of the SWV peaks Bi(III) ions electroreduction in 2 mol·dm^{-3} chlorates(VII) at a constant concentration of accelerating substance (1·10^{-3} mol·dm^{-3} 6TG, 6MP, AZA) depends on a change in the electrode process reversibility towards inhibition [42-44].

Similar changes of the reversibility of Bi(III) electroreduction due to the presence of thiopurine derivatives or surfactants are indicated by the CV voltammograms. The values ΔE_{a-c} decrease compared to those obtained for the basic electrolyte (1·10^{-3} mol·dm^{-3} Bi(III) in 2 mol·dm^{-3} chlorates(VII)). So, the electrode process becomes faster. This is particularly noticeable with 6TG and

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6MP. The addition of surfactants to such a system affects $\Delta E_{a\text{-}c}$ increase. There is a change in the dynamics of the catalytic action of thiopurine derivatives [42-44].

The study pointed to the control of the multistage Bi(III) ion electroreduction process by the reaction of formation of active complexes Bi – thiopurine on the electrode's surface, certainly localised inside the adsorption layer which mediate in the transfer of electrons [19, 31]. The adsorption of 6TG, 6MP, AZA [45-48] should be mentioned, which will not limit the electrode's surface but will favourably shift the balance of these complexes.

However, changes in the mechanism of the Bi(III) ion electroreduction process in the presence of a mixture of thiopurine derivatives and surfactants in the base electrolyte solution were associated with the blocking of the electrode's surface by surfactants, which pushes the previously formed active complexes of Bi - thiopurine from the adsorption layer. The main role of Bi - thiopurine complexes has been indicated [42-44].

The kinetic parameter k_s determined by using of electrochemical techniques indicating the catalytic effect of thiopurine derivatives and changes in its magnitude in connection with the presence of 6TG – TritonX-100 and 6TG – Tween 80, 6MP – TritonX-100 and 6MP – Tween 80 or AZA – TritonX-100 and AZA – Tween 80 mixtures (Figures 3a, b) [42-44].

a

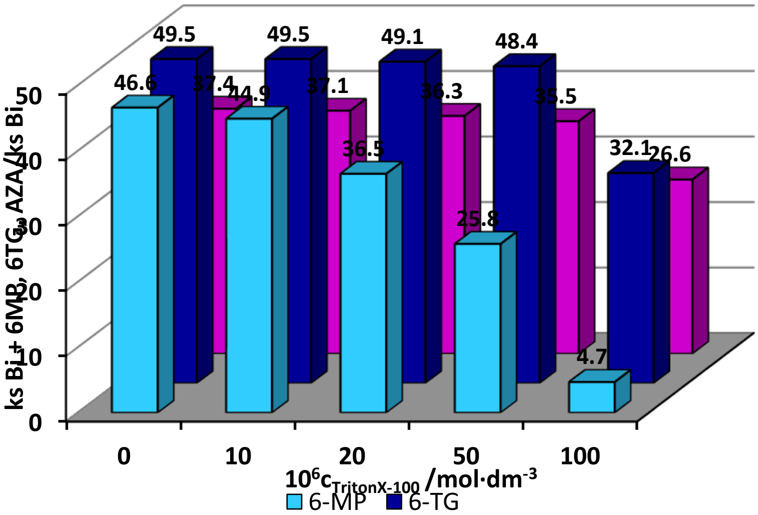

Figure 3. a. The catalytic activity defined by the k_s Bi+thiopurines/ k_s Bi for 2 mol·dm^{-3} chlorates(VII) and chosen of Triton X-100 concentrations.

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b

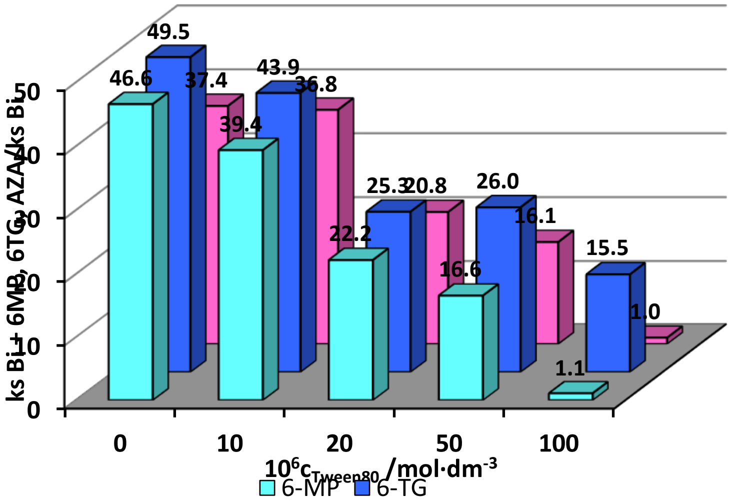

Figure 3. b. The catalytic activity defined by the k_s Bi+thiopurines/ k_s Bi for 2 mol·dm^{-3} chlorates(VII) and chosen of Tween 80 concentrations.

2.4. The electrode's mechanism.

The above considerations and literature data [19] suggest the following mechanism of the catalytic action of organic substances on the Bi(III) ion electroreduction in a solution with non-complexing properties, including transition stages:

- partial dehydration of Bi(III) ions and the formation of the active complex (I)

$$Bi(H_2O)_9^{3+} + x(\text{substance catalyzing})_{ads}$$

$$\rightarrow Bi(H_2O)_{(9-a)}^{3+}(\text{substance catalyzing})_x + aH_2O$$

- first electron transfer

$$Bi(H_2O)_{(9-a)}^{3+}(\text{substance catalyzing})_x + \bar{e} \rightarrow Bi(H_2O)_{(9-a)}^{2+}(\text{substance catalyzing})_x$$

- further dehydration and the formation of the active complex (II)

$$Bi(H_2O)_{(9-a)}^{2+}(\text{substance catalyzing})_x \pm y(\text{substance catalyzing})_{ads}$$

$$\rightarrow Bi(H_2O)_{(9-a-b)}^{2+}(\text{substance catalyzing})_{x \pm y} + bH_2O$$

- second electron transfer

$$Bi(H_2O)_{(9-a-b)}^{2+}(\text{substance catalyzing})_{x \pm y} + \bar{e}$$

$$\rightarrow Bi(H_2O)_{(9-a-b)}^{+}(\text{substance catalyzing})_{x \pm y}$$

- dehydration of Bi(III) ions and the formation of the active complex (III)

$$Bi(H_2O)_{(9-a-b-c)}^{+}(\text{substance catalyzing})_{x \pm y} \pm z(\text{substance catalyzing})_{ads}$$

$$\rightarrow Bi^{+}(\text{substance catalyzing})_{x \pm y \pm z} + (9-a-b-c)H_2O$$

- third electron transfer and amalgam formation

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$$Bi^{+}(\text{substance catalyzing})_{x\,\pm\,y\pm z}\ \bar{e}$$
$$\rightarrow\ Bi(Hg)\ +\ (x \pm y \pm z)(\text{substance catalyzing })_{ads}$$

where, active complex: Bi – substance catalysing or $Hg(SR)_2$ and a + b + c = 9 and a > b > c.

3. Material and Methods

3.1. Chemicals

All reagents: $NaClO_4$, $HClO_4$, $Bi(NO_3)_3{\cdot}5H_2O$, amino acids such as: methionine, cysteine, cystine, ethionine, homocysteine, homocystine and thiopurine derivatives such as: 6-mercaptopurine, 6-thioguanine, azathioprine and Triton X-100 and Tween 80 (Fluka) were of analytical grade. The water applied to prepare all solutions was purified in the Millipore system.

The supporting electrolytes x $mol{\cdot}dm^{-3}$ $NaClO_4$ + 1 $mol{\cdot}dm^{-3}$ $HClO_4$ (where $0 \le x \le 7$) or the 2, 4 and 6 $mol{\cdot}dm^{-3}$ chlorate(VII) solutions of $HClO_4$:$NaClO_4$ concentration ratios: (1:1) solution A, (1:4) solution B, (1:9) solution C, (4:1) solution D, (9:1) solution E were examined [36]. A solution of $1{\cdot}10^{-3}$ $mol{\cdot}dm^{-3}$ Bi(III) in the chlorates(VII) was the supporting electrolyte.

3.2. Apparatus

The electrochemical measurements were performed with an Autolab Fra 2/ GPES (Version 4.9) frequency response analyser (Eco Chemie, Utrecht, Netherlands). A three-electrode system consisting of Ag/AgCl/3M KCl electrode as a reference and a platinum wire as an auxiliary electrode, dropping or hanging mercury– electrode with a controlled increase rate and a constant drop surface (0.014740 cm^2), as a working electrode (MTM Poland) was used.

The all electrochemical measurements were made in thermostated cells at 298K.

Research on the mechanism of the electrode process was associated with a need to determine the kinetic parameters that were presented in paper [26].

4. Conclusions

In conclusion, the interpretation of the "*cap-pair*" effect mechanism was extended with increased detail by the influence of the supporting electrolyte concentration on the acceleration process and the type of electrochemical active organic substances used. It was also pointed out that the dynamics of the catalytic process of the substance's action on the electrode process has changed while respecting the assumptions of the "*cap-pair*" rule.

The rate of multistage Bi(III) ion electroreduction process in chlorates(VII) with different water activity is influenced by both the presence of catalysts and their protonisation.

Systematic studies on the kinetics and electrode mechanisms have clearly indicated a multistage process and the main role of active complexes (Bi - accelerating substance (electrochemical non-active or electrochemical active), mediating in the electron transition, localised in the adsorption layer. It has been shown that the first chemical stage of formation of unstable complexes is the most important and determines the kinetics of the overall Bi(III) ion electroreduction process. Then there is a partial loss of the hydration envelope by the Bi(III) ions, which change their electrostatic potential by locating near OHP. The adsorption of the catalytic substance on the electrode does not limit its surface but additionally activates it by positively shifting the Bi(III) ion complexing equilibrium (confirmation of the important role of adsorption in the cap-pair effect mechanism). The varied structure and properties of active complexes probably determine the different catalytic activity. It should also be noted that active complexes dominate in creating the adsorption equilibrium despite a change in the dynamics of the catalytic action of the substance on the electrode's process caused by blockage of the electrode's surface by physically absorbed surfactants. Therefore, the assumptions of the "cap - pair" rule are respected.

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All authors have read and agreed to the published version of the manuscript.

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