e-ISSN: 2687-6698 **Research Article**

Turkish Journal of Analytical Chemistry
TurkJAC
www.turkjac.org
2019

Application of a cyclic renewable silver amalgam liquid film electrode (R-AgLAFE) to study the electroreduction processes of Bi(III) ions in the presence of cysteine

Agnieszka Nosal-Wiercińska[1]*, Marlena Martyna[1], Małgorzata Wiśniewska[2], Selehattin Yilmaz[3], Nuray Denizhan[3]

[1] Maria Curie-Sklodowska University, Faculty of Chemistry, Institute of Chemical Sciences, Department of Analytical Chemistry, 20-031 Lublin, Poland
[2] Maria Curie-Sklodowska University, Faculty of Chemistry, Institute of Chemical Sciences, Department of Radiochemistry and Environmental Chemistry, 20-031, Lublin, Poland
[3] Çanakkale Onsekiz Mart University, Faculty of Sciences and Arts, Department of Chemistry, 17020, Çanakkale, Türkiye

Abstract

The cyclically refreshable liquid silver amalgam film silver-based electrode (R-AgLAFE) to study electrode processes under the "cap-pair" conditions were used. The effects of cysteine on the kinetics and the mechanism of Bi(III) electroreduction in chlorates(VII) have been studied. The methodology of the study is based on electrochemical methods: DC polarography, square wave voltammetric (SWV), and cyclic voltammetric (CV). The magnitude of the catalytic effect is related to the formation of the Bi(III)-Hg(SR)$_2$ active complexes mediating electron transfer equilibrium. This reaction controls the total rate of the process.

Keywords: Cysteine, R-AgLAFE electrode, "cap-pair" conditions, voltammetry, catalytic effect

1. Introduction

Determination of the active substance content is a routine activity in the process of pharmaceutical preparation production. Due to various structures and properties, a proper analytical method should be chosen for each analyzed substance [1]. The most commonly used analytical techniques include UV-VIS spectrophotometry, liquid chromatography, gas chromatography, mass spectrometry, and electrochemical methods. Voltammetry is an example of an electrochemical method that, in addition to chromatography, is becoming increasingly common due to its very large sensitivity at the level of pM, selectivity, or the possibility of conducting speciation analysis in real samples without their pre-treatment [2].

The fundamental factors that determine the suitability of the applied voltammetric method are the electrode and the supporting electrolyte. Supporting electrolytes can be acidic, neutral, or are many a times subsidized with organic substances which can act as catalysts or inhibitors of the electrode processes. The "cap-pair" rule [3] determines the conditions that indicate the catalytic activity of a substance [4–10] developed and used for electrode processes. It has been well known that a major role in accelerating the process is played by the ability of the organic substance to form complexes with the depolarizer and to locate the depolarizer reduction potential in the area of labile adsorption equilibrium of the organic substance.

The present study is based on the innovative electrode with the cyclic renewable liquid silver amalgam film (R-AgLAFE). It combines the advantages of a commercial mercury electrode allowing for equally accurate determination of analytical parameters and offering a significant reduction in the toxic mercury needed to produce an amalgam film and the generated waste [11,12].

The studies presented in this paper using an R-AgLAFE electrode address the effect of cysteine on the

Citation: A. Nosal-Wiercińska, M. Martyna, M. Wiśniewska, S. Yilmaz, N. Denizhan, Application of a cyclic renewable silver amalgam liquid film electrode (R-AgLAFE) to study the electroreduction processes of Bi(III) ions in the presence of cysteine, Turk J Anal Chem, 4(1), 2022, 1–5.
https://doi.org/10.51435/turkjac.1069294

***Author of correspondence:** agnieszka.nosal-wiercinska@mail.umcs.pl
Tel: +48 81 537 56 27
Fax +48 81 537 57 16

Received: February 07, 2022
Accepted: May 06, 2022

Bi(III) ions electroreduction process in the context of the "cap-pair" rule effect. Cysteine ((2R)-2-amino-3-mercaptopropionic acid) is an endogenous amino acid in the human body that is synthesized through two metabolic pathways. Nevertheless, it is often supplemented in the form of a drug, especially for its protective use [13,14]. The presence of a thiol group indicates that it is also involved in many reactions in the body, for example in the biosynthesis of fatty acids, many esters, and amino acids as well as in some metabolic processes [15]. Despite this, cysteine in the cells is found at very low levels [6] which is a defensive mechanism against its toxicity manifesting itself particularly dangerously against the central nervous system (CSN) [16,17]. The maintenance of physiologically low concentrations of cysteine in the cells is regulated by its incorporation into proteins and peptides, as well as by the aerobic and anaerobic metabolism. According to the literature data, it exhibits the ability to bind some metal cations in a composite unity [18,19], hence there is a need to study its action mechanism in the presence of metal ions. The essence of the bioanalytical research point of view is related to the possibilities of developing targeted drug therapies.

2. Experimental

2.1. Reagents and solutions

The following reagents were used to prepare the solutions: $NaClO_4$ (Sigma-Aldrich) (purity: 98%), $HClO_4$ (Sigma-Aldrich) (purity: 99.999%; density: 1.664 g/mL at 298 K) cysteine (Sigma-Aldrich) (purity: 96%) as well as redistilled water. 1 mol/dm^3 chlorate(VII) solution was applied as a supporting electrolyte. The choice was made by the poor complex-making properties of ClO_4^- ions, their susceptibility to water structure destruction, and the fact that they adsorb only to a small extent on the mercury surface [12].

The solutions of 1 mol/dm^3 chlorate(VII) were subsidized with the Bi(III) ions (at a concentration of 1×10^{-3} mol/dm^3. The measurements were performed with the cysteine concentration between 1×10^{-5} and 1×10^{-3} mol/dm^3. Only freshly prepared solutions of cysteine were used. The solutions were deaerated using the purge of nitrogen for cushioning. This gas was passed over the solution during the measurements. The measurements were commonly made at a temperature of 298 ± 0.1 K.

2.2. Apparatus

The experiments were performed in a thermostated vessel at 298 K using an electrochemical analyzer Autolab/GPES (version 4.9) (Eco Chemie, Ultrecht Holland) and a programmable tripod mtmanko M165D (mtmanko, Cracow, Poland).

The device is programmed for: pulse time which is 90 ms, an interval between the measurements of 800 ms, and 3 immersions of the electrode in the film of liquid silver amalgam. A three-electrode measuring cell was placed inside the tripod and the arrangement of the electrodes was as follows:

- an innovative electrode made of a cyclic renewable liquid silver amalgam film (R-AgLAFE) with an area of (0.1725 cm^2) as the working electrode,
- a silver/silver chloride electrode (Ag/AgCl) in 3 mol/dm^3 KCl as a reference electrode,
- a platinum wire as an auxiliary electrode.

The applied innovative electrode of the cyclic renewable liquid silver amalgam film R-AgLAFE [20] is characterized by: cyclic repeatability and reproducibility of the surface, excellent homogeneity of the film, and stability of the applied film thickness. This makes it an excellent alternative to the mercury drop electrode as it guarantees similar quality and performance parameters as those of HMDE. Moreover, it provides the opportunity to study electrode processes under the "cap-pair" conditions [12].

The applied electrochemical techniques that are: direct current (DC) voltammetry, cyclic voltammetry (CV), and square wave voltammetry (SWV) were used to determine the kinetic parameters of the (E_f^0), cathodic transition coefficient (α) standard rate constants (k_s) of the depolariser electroreduction and diffusion coefficient (D_{ox}) [20] of the process of Bi(III) ions electroreduction as well as in the presence of cysteine. In the voltammetric or polarographic measurements the optimal experimental operating conditions were as follows: the scan rate 5–1000 mV s^{-1} for the cyclic voltammetry (CV) and step potential 2 mV, pulse amplitude 20 mV, frequency 120 Hz for the square wave voltammetry (SWV). No fewer than three scans were performed for each measurement. The range of the potentials tested was constantly changed to study the variety of processes that can occur.

3. Results and discussion

The addition of cysteine (CE) to the basic electrolyte solution caused an increase in the current value of the SWV peaks while decreasing their width at the mid-height (Fig. 1). It was observed that the SWV curves, especially at smaller CE concentrations, were slightly distorted. This could be related to the changes in the adsorption layer of the R-AgLAFE electrode.

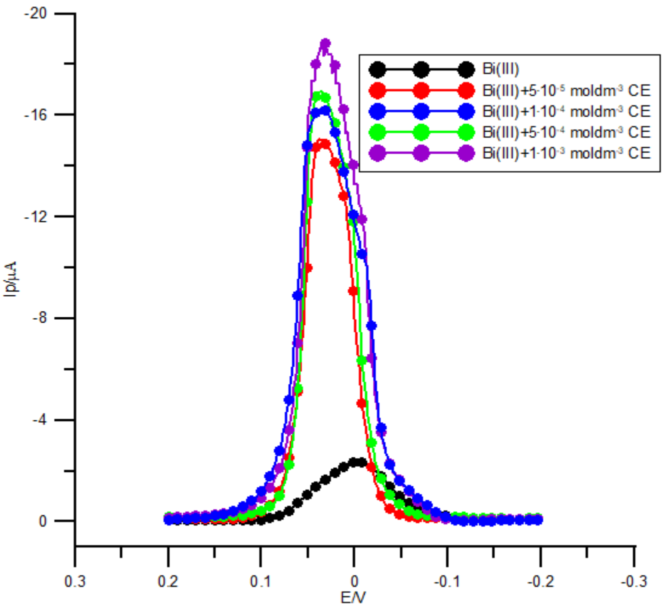

Figure 1. SWV peaks of the Bi(III) ions electroreduction in 1 mol/dm³ chlorate(VII) with the increasing cysteine concentration included in the legend

It seems that the mechanism proposed by Stankovich and Bard [21], Heyrovsky and co-workers [22,23] as well as Nosal-Wiercińska [23] explains the cysteine-mercury interactions in the most effective way. The reaction of cysteine with the mercury ions is the basis of its electrolytic activity on the mercury electrodes. The reaction involves the electrooxidation of mercury in two separate steps, to cysteine mercurous thiolate $Hg_2(SR)_2$ and cysteine mercuric thiolate $Hg(SR)_2$, respectively, which are both strongly adsorbed on the electrode surface [23]. Similar behavior of a compound that contains a thiol group in its structure (–SH), on the mercury and R-AgLAFE electrodes was presented in the paper [12].

Fig. 2 shows the cyclic voltammetry curves of Bi(III) ions electroreduction in the presence of cysteine. With the addition and increase of cysteine concentration in the chlorate(VII) solution, a decrease in the potential difference between the anodic and cathodic ΔE peaks is observed which indicates an increase in the reversibility of the Bi(III) ions electroreduction process. However, no significant changes in ΔE were observed with the change of the electrode polarization rate (Table 1) as well as with the increase of CE concentration.

Table 1. Changes in *ΔE* for the Bi(III) ions electroreduction process and in the presence cysteine in 1 mol/dm³ chlorate(VII) at the polarization rate *v*

$10^3 c_{Bi(III)} + 10^4 c_{CE}$ /mol dm^3	ΔE/ V							
	v/m Vs^{-1}							
	5	10	20	50	100	200	500	1000
0	0.0980	0.0970	0.1001	0.1020	0.1101	0.1262	0.1482	0.1712
0.5	0.0358	0.0370	0.0374	0.0393	0.0396	0.0458	0.0604	0.0674
1.0	0.0323	0.0334	0.0340	0.0351	0.0368	0.0436	0.0596	0.0643
5.0	0.0318	0.0324	0.0329	0.0337	0.0351	0.0429	0.0578	0.0627
10.0	0.0311	0.0319	0.0326	0.0333	0.0349	0.0413	0.0521	0.0601

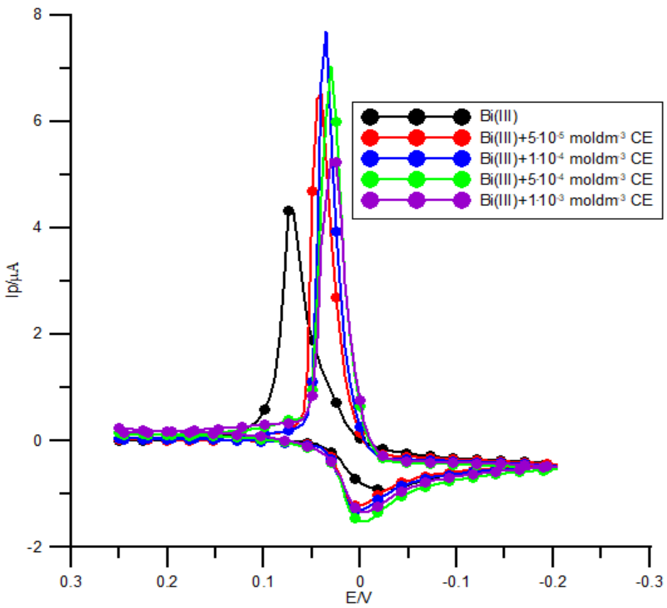

Figure 2. CV curves of the Bi(III) ions electroreduction in 1 mol/dm³ chlorate(VII) with the increasing cysteine concentration shown in the legend

This confirms the changes occurring in the adsorption layer on the R-AgLAFE electrode and what is more, it indicates a chemical reaction which will be the stage controlling the rate of Bi(III) ions electroreduction process. According to the assumptions of the "cap-pair" rule and the literature data [1,23–24], it will probably be the reaction of active complexes formation on the surface of the electrode which can mediate the electron transfer [23]. On the other hand, cysteine will be a bridge in the formation of these complexes.

A lack of change in the value of formal potential E_f^0 with the increasing cysteine concentration in the chlorate(VII) solutions (Table 2) confirms that the mentioned complexes do not form in the basic electrolyte solution [25].

The literature data [24,26–27] indicate a reaction of Bi(III) with mercury cysteine thiolate(II) $Hg(SR)_2$. This is the form of anodic oxidation of mercury in the presence of cysteine that adsorbs in the reduction potential range Bi(III) (~0 V) and is bound lability to the electrode surface [24]. It is supposed that, similarly to the mercury electrode used earlier, the active Bi(III)-$Hg(SR)_2$ complexes are obviously located inside the adsorption layer (Fig. 3).

Table 2. Values of formal potentials E_f^0 of 1 × 10⁻³ mol/dm³ Bi(III) ions electroreduction in 1 mol/dm³ chlorate(VII) and in the presence of cysteine

$10^3 c_{Bi(III)} + 10^4 c_{CE}$ /mol dm^3	E_f^0/ V
0	0.810
0.5	0.950
1.0	0.950
5.0	0.940
10.0	0.930

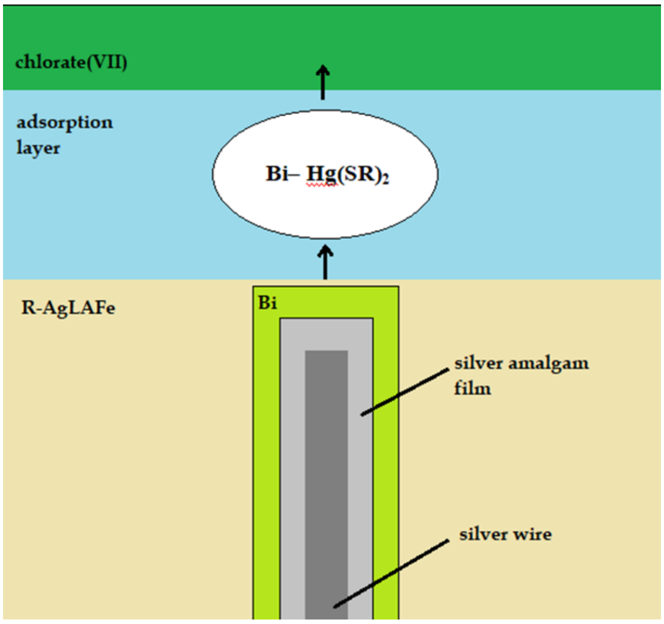

Figure 3. The reaction path obtained for the Bi(III) ions electroreduction in the presence of cysteine.

Based on the parameters of the cyclic voltammetry CV curves, the values of the transfer coefficients *α* and the standard rate constants k_s of the Bi(III) ions electroreduction and in the presence of cysteine (Table 3) were determined.

Table 3. Values of cathodic transition coefficients *α* and standard rate constants k_s of 1 × 10^{-3} mol/dm^3 Bi(III) electroreduction in 1 mol/dm^3 chlorate(VII) and in the presence of cysteine.

$10^3 c_{Bi(III)} + 10^4 c_{CE}$ / $mol\ dm^3$	α	$10^4 k_s$/ cm s^{-1}
0.00	0.25	0.360
0.50	0.53	5.370
1.00	0.57	8.110
5.00	0.59	10.05
10.0	0.61	12.78

The increase in the values of the transition coefficients *α* after the addition of cysteine into the basic electrolyte solution indicates an increase in the reversibility of the Bi(III) ions electroreduction process [25]. This also translates into an increase in the standard rate constants, confirming the catalytic action of the amino acid [25]. An increase in the concentration of cysteine in chlorate(VII) results in further increases in the mentioned kinetic parameters (Table 3).

4. Conclusions

The studies using an innovative electrode of cyclically renewable liquid silver amalgam film R-AgLAFE pointed out the catalytic effect of cysteine on the multistep electroreduction process of Bi(III) ions according to the "cap-pair" rule. The magnitude of the catalytic effect is related to the formation of active complexes mediating electron transfer equilibrium. The complex formation on the electrode surface is due to the adsorption of $Hg(SR)_2$, which increases the activity of the electrode without limiting its surface area. The composition of these complexes varies, which can be inferred from Marcus' theory [25], predicting the change of complexes in the ionic layer after the partial charge loss.

The "cap-pair" studies on the R-AgLAFE electrode proved to be valid and provide satisfactory results.

References

[1] C.N. Nunes, L.E. Pauluk, M.L. Felsner, V. Egéa dos Anjos, S.P. Quináia, Rapid screening method for detecting ethinyl estradiol in natural water employing voltammetry, J Anal Methods Chem, 2016, 3217080.

[2] M.D. Fayer, Dynamics of water interacting with interfaces, molecules and ions, Accounts Chem Res, 45, 2012, 45, 3–14.

[3] K. Sykut, G. Dalmata, B. Nowicka, J. Saba, Acceleration of electrode processes by organic compounds- "cap-pair" effect, J Electroanal Chem Interf Electrochem, 90, 1978, 299–302.

[4] D. Dalmata, Kinetics and mechanism of Zn(II) ions electroreduction catalyzed by organic compounds, Electroanal, 17, 2005, 789–793.

[5] P.A. Ajibade, F.P. Andrew, N.L. Botha, N. Solomane, Synthesis, crystal structures and anticancer studies of morpholinyldithiocarbamato Cu(II) and Zn(II) complexes, Molecules, 25, 2020, 3584.

[6] E.V. Vinogradova, X. Zhang, D. Remillard, D.C. Lazar, R.M. Suciu, Y. Wang, G. Bianco, Y. Yamashita, V.M. Crowley, M.A. Schafroth, M. Yokoyama, D.B. Konrad, K.M. Lum, G.M. Simon, E.K. Kemper, M.R. Lazear, S. Yin, M.M. Blewett, M.M. Dix, N. Nguyen, M.N. Shokhirev, E.N. Chin, L.L. Lairson, B. Melillo, S.L. Schreiber, S. Forli, J.R. Teijaro, B.F. Cravatt, An activity-guided map of electrophile-cysteine interactions in primary human T cells, Cell, 182, 2020, 1009–1026.

[7] A. Nosal-Wiercińska, Catalytic activity of thiourea and its selected derivatives on electroreduction of In(III) in chlorates(VII), Cent Eur J Chem., 8, 2010, 1–11.

[8] A. Nosal-Wiercińska, Intermolecular interactions in systems containing Bi(III)-ClO_4-H_2O-selected amino acids in the aspect of catalysis of Bi(III) electroreduction, Electroanal, 26, 2014, 1013–1023.

[9] S. Komorsky-Lovriˇc, M. Lovriˇc, M. Branica, Effect of ionic strength on Bi(III) reduction from perchlorate medium, J Electrochem Soc, 140, 1993, 1850–1853.

[10] O. Ikeda, K. Watanabe, Y. Taniguchi, H. Tamura, Adsorption effect of highly polarizable organic compounds on electrode kinetics, Bull Chem Soc Jpn, 57, 1984, 3363–3367.

[11] A. Nosal-Wiercińska, M. Martyna, V. Mirčeski, S. Skrzypek, Electroreduction of Bi(III) ions at a cyclically renewable liquid silver amalgam film electrode in the presence of methionine, Molecules, 26, 2021, 3972.

[12] A. Nosal-Wiercińska, M. Martyna, M. Grochowski, B. Baś, First electrochemical studies on "CAP-PAIR" effect for Bi(III) ion electroreduction in the presence of 2-thiocytosine on novel cyclically renewable liquid silver amalgam film electrode (R-AgLAFE), J Electrochem Soc, 168, 2021, 066504.

[13] A.J.L. Cooper, Biochemistry of sulfur containing aminoacids, Annu Rev Biochem, 52, 1983, 187–222.

[14] R. Hell, Molecular physiology of plant sulphur metabolizm, Planta, 202, 1997, 138–148.

[15] K. Saito, Regulation of sulfate transport and synthesis of sulfur-containing amino-acid, Curr Opin Plant Biol, 3, 2000, 188–195.

[16] M. Puka-Sundvall, P. Eriksson, M. Nilsson, M. Saudberg, A. Lehmann, Neurotoxicity of cysteine: interaction with gluta mate, Brain Res, 705, 1995, 65–70.

[17] R. Janaky, V. Varga, A. Hermann, P. Saransari, S. S. Oja, Mechanism of L-cysteine neurotoxicity, Neurochem Res, 25, 2000, 1397–1405.

[18] J.W. Olney, C. Zorumski, M.T. Price, J. Labruyere, L-cysteine. a bicarbonate-sensitive endogenous excitotoxin, Science, 248, 1990, 596–599.

[19] L. Zhu, L. Xu, B. Huang, N. Jia, L. Tan, S. Yao, Simultaneous determination of Cd(II) and Pb(II) using square wave anodic stripping voltammetry at a gold nanoparticle-graphene-cysteine composite modified bismuth film electrode, Electrochim Acta, 115, 2014, 471–477.

[20] A. Nosal-Wiercińska, The kinetics and mechanism of the electroreduction of Bi(III) ions from chlorates(VII) with varied water activity, Electrochim Acta, 55, 2010, 5917–5921.

[21] M. Stankovich, A. J. Bard, The electrochemistry of proteins and related substances I. Cystine and cysteine at mercury electrode, J Electroanal Chem, 75, 1977, 487–505.

[22] M. Heyrovský, P. Mader, V. Veselá, and M. Fedurco, The reactions of cystine at mercury electrodes, J Electroanal Chem, 369, 1994, 53–70.

[23] M. Heyrovský, P. Mader, S. Vavřička, V. Veselá, M. Fedurco, The anodic reactions at mercury electrodes due to cysteine, J Electroanal Chem, 430, 1997, 103–117.

[24] A. Nosal-Wiercińska, The catalytic activity of cysteine and cystine on the electroreduction of Bi(III) ions, J Electroanal Chem, 662, 2011, 298–305.

[25] H. Sumi, R.A. Marcus, Dynamical effects in electron transfer reactions, J Chem Phys, 84, 1986, 4894–4914.

[26] A. Nosal-Wiercińska, The influence of water activity on double layer parameters on the interface mercury/chlorates(VII) in the presence of cysteine, Croat Chem Acta, 86, 2013, 159–164.

[27] A. Nosal-Wiercińska, The role of active complexes in the multistep process of Bi(III) ion electroreduction in chlorate(VII) solutions with varied water activity in the presence of cystine, Electrochim Acta, 93, 2013, 397–403.