Application of the R-AgLAFE electrode for the Bi(III) electroreduction in the presence of 2-thiocytosine from chlorates(VII) with varied water activity

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Introduction

The electroreduction mechanism of depolarisers in the presence of organic substances is complicated, as it combines both electron-transfer and chemical steps [5,6], in which the substrate or intermediary compound loses part of its solvation envelope, resulting in the formation on the electrode surface of complexes involved in electron transfer [1-6]. An electrode with a cyclic renewable film of liquid silver amalgam R-AgLAFe [7], was used in work related to the study of electrode mechanisms in terms of the "cap - pair" effect. The mentioned electrode belongs to a new generation of voltammetric sensors. Its main advantages are the significant reduction of mercury consumption for the production of amalgam film and the generation of toxic waste. These functional advantages determined that R-AgLAFE was used to study the kinetics and mechanism of electroreduction of Bi(III) ions in the presence of 2-thiocytosine (TC) under conditions of varying water activity.

Methods

The investigations were carried out using an electrochemical analyser Autolab/GpES (version 4.9) made by Eco Chemie in a three-electrode system, in which the working electrode was an automated electrode with a cyclic renewable silver amalgam film R-AgLAFE (Fig.1). The chlorosilver electrode was the comparison electrode while the platinum spiral, the counter-electrode.The surface of the R-AgLAFE electrode (Fig.2) was visualised using a Nikon Eclipse MA200 optical microscope with the objective "Nikon Lu Plan Fluor 10x/0.30A" with the polarisation filter "MA2-PA" switched on. The illustration (Fig. 2) clearly shows that the liquid supersaturated (1 wt.%) silver amalgam forms a thin film on the surface of the silver substrate (wire) without destroying its texture [7]. Visible small discontinuities of the film, caused by its low mechanical strength, could appear during preparation of the electrode for imaging, while their influence on the course and repeatability of recorded voltammetry was not observed. The role of depolariser was played by Bi(III) ions ($1 \cdot 10^{-3}$ mol·dm^{-3} Bi(III)) while the basic electrolyte consisted of chlorate(VII) solutions in the concentration range from 1 mol·dm^{-3} to 8 mol·dm^{-3}. As a catalyst for the analysed process of electroreduction of Bi(III) ions, 2-thiocytosine was used at a concentration of $1 \cdot 10^{-3}$ mol·dm^{-3}.
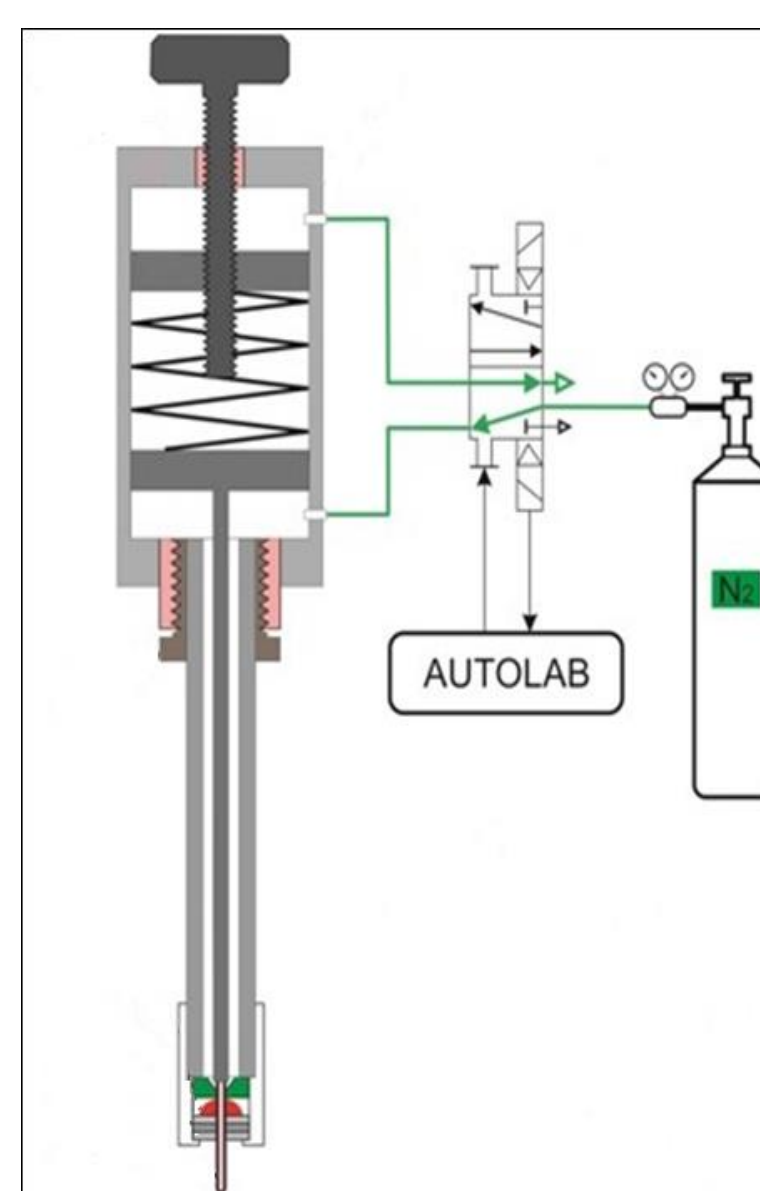

Fig.1. Vertical axial section of the R-AgLAFE electrode including power and control components [7].
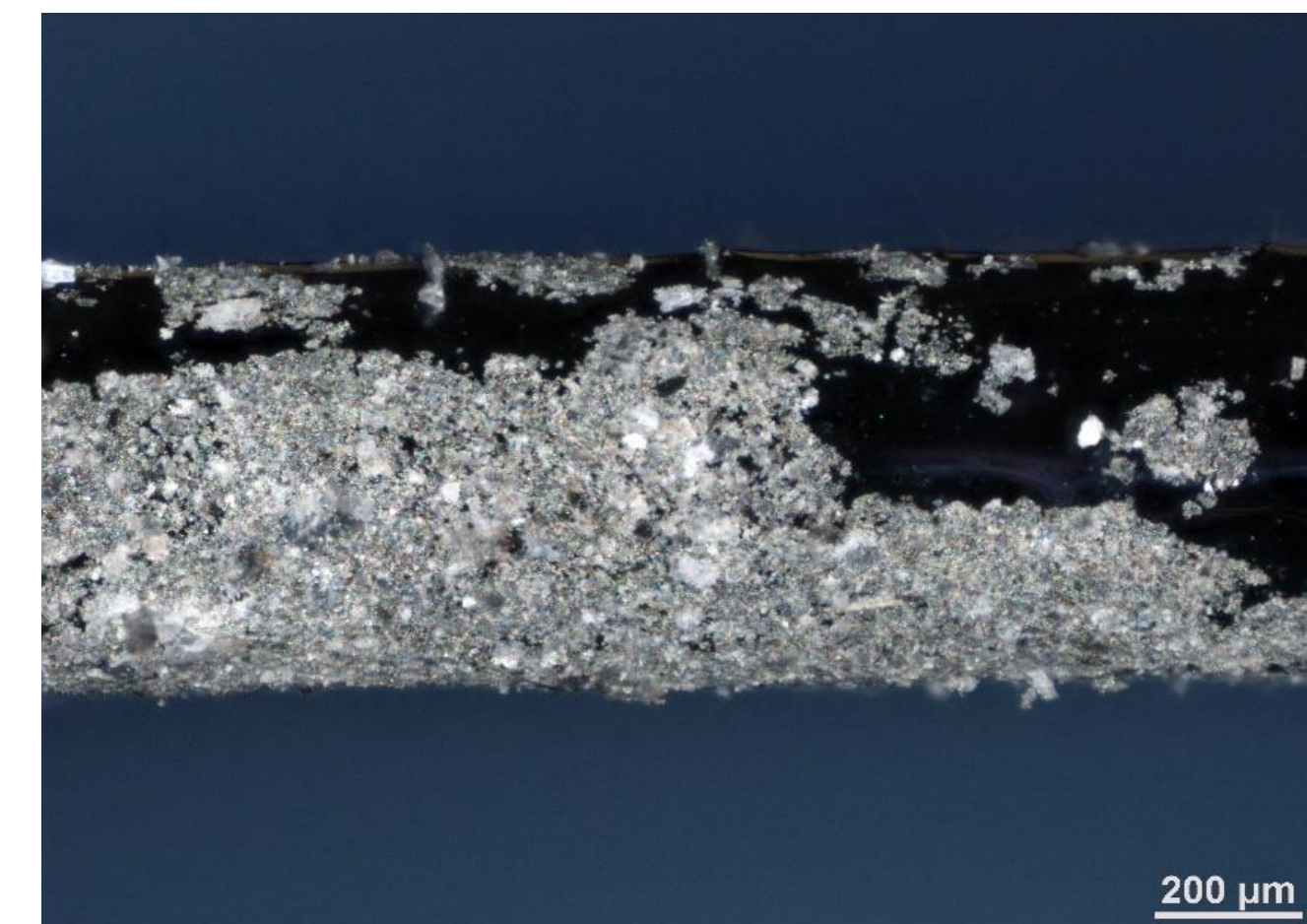

Fig.2. The surface of the R-AgLAFE electrode imaged using a Nikon Eclipse MA200 optical microscope with a "Nikon Lu Plan Fluor 10x/0.30A" objective [7].
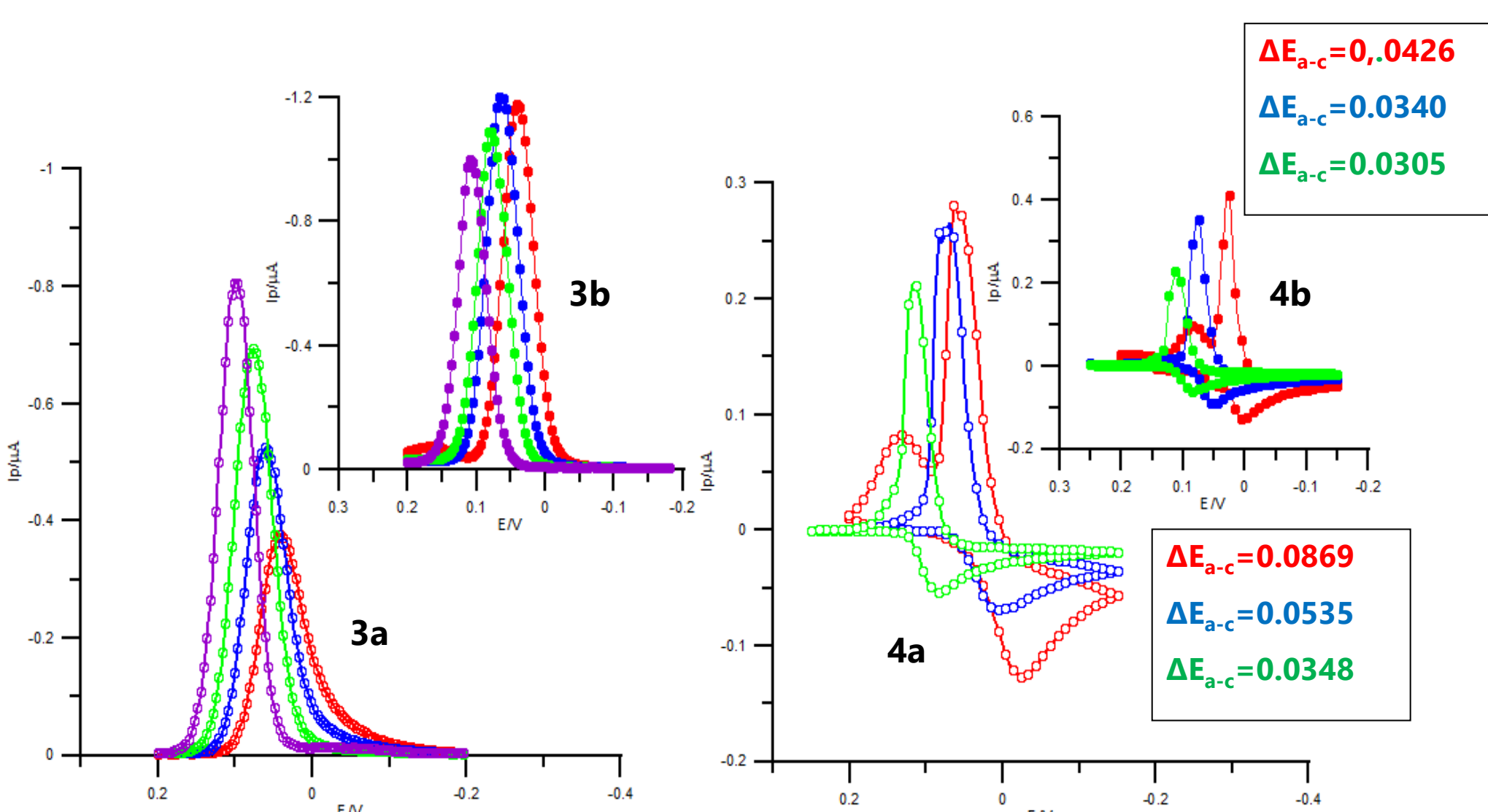

Fig. 3 (a) SWV peaks of electroreduction of $1 \cdot 10^{-3}$ mol·dm^{-3} Bi(III) in 2 mol·dm^{-3} (o); 4 mol·dm^{-3} (o); 6 mol·dm^{-3} (o); 8 mol·dm^{-3} (o) chlorates(VII); **3 (b)** and with the addition of $1 \cdot 10^{-3}$ mol·dm^{-3} 2-thiocytosine for the same chlorates(VII) concentrations.

Fig.4 (a) CV curves of electroreduction of $1 \cdot 10^{-3}$ mol·dm^{-3} Bi(III) in 2 mol·dm^{-3} (o); 4 mol·dm^{-3} (o); 6 mol·dm^{-3} (o); **4 (b)** and with the addition of $1 \cdot 10^{-3}$ mol·dm^{-3} 2-thiocytosine for the same concentrations of chlorates(VII); electrode polarization rate v = 50 mV·s^{-1}

The small changes in ΔEa-c with the change in polarization rate (especially at low electrode polarization rates (Table 1) indicate that the step controlling the rate of the electroreduction process of Bi(III) ions in the presence of 2-thiocytosine, with varying water activity, is the chemical reaction of the formation of Bi-TC active complexes [8].

Table 2a. Values of cathodic transition factors α and standard reaction rate constants ks for the electroreduction process of $1 \cdot 10^{-3}$ mol·dm^{-3} Bi(III) w 1-8 mol·dm^{-3} chlorate(VII) and **2b** in the presence of $1 \cdot 10^{-3}$ mol·dm^{-3} 2-thiocytosine.

2a

$C_{chlorates(VII)}$/ mol·dm^{-3}	α	$10^4 k_s$ /cm·s^{-1} CV
1	0.23	0.35
2	0.28	0.75
3	0.29	0.93
4	0.33	1.47
5	0.35	2.98
6	0.47	3.03
7	0.48	3.28
8	0.50	5.07

2b

$C_{chlorates(VII)}$/ mol·dm^{-3} +$1 \cdot 10^{-3}$ mol·dm^{-3} TC	α	$10^4 k_s$ /cm·s^{-1} CV
1	0.38	0.80
2	0.42	1.91
3	0.39	26.0
4	0.50	27.4
5	0.57	27.2
6	0.50	29.3
7	0.51	30.7
8	0.53	29.4

Based on cyclic voltammetric curves recorded with CV technique, the values of kinetic parameters such as cathodic transition coefficients (α) and standard reaction rate constants (ks) were determined. The kinetic parameters determined indicate the catalytic effect of 2-thiocytosine in solutions with varying water activity and its magnitude (Table 2 a,b). The standard rate constants for the electroreduction of Bi(III) ions in chlorates (VII) and in the presence of TC increase with increasing the concentration of the basic electrolyte up to 6 mol·dm^{-3}, in 7 and 8 mol·dm^{-3} chlorates (VII) a slight decrease in values is observed.

Results

As can be seen from Figure 3a, as the chlorate(VII) concentration increases, the SWV peaks of electroreduction of Bi(III) ions definitely increase and shift towards positive potentials. This indicates that the reversibility of the electroreduction process increases with decreasing water activity [6]. A similar relationship was observed by studying the electroreduction process of Bi(III) ions on a mercury electrode [6]. The addition of $1 \cdot 10^{-3}$ mol·dm^{-3} 2-thiocytosine to the electrolyte solution causes a further increase in the currents of the Bi(III) ion electroreduction peaks as well as a decrease in the width of the SWV peaks at half their height, which also indicates an increase in the reversibility of Bi(III) ions. With increasing chlorate(VII) concentration, no significant changes in the heights of the Bi(III) electroreduction SWV peaks are observed. Only for solutions with much lower water activity the peaks slightly decrease. The course of cyclic voltammetry curves confirms the fact that the presence of 2-thiocytosine, as well as water activity, affect the changes in the reversibility of electroreduction of Bi(III) ions (Fig. 4 a, b). The addition of $1 \cdot 10^{-3}$ mol·dm^{-3} 2-thiocytosine to the basic electrolyte solution causes a decrease in the distance between the anodic and cathodic peaks (ΔEa-c) compared to the distance recorded for the Bi(III) ion solution in all chlorate(VII) solutions, confirming an increase in the reversibility of the electroreduction processes of Bi(III) ions [6].

Table 1. Changes of ΔEa-c for the electroreduction process of $1 \cdot 10^{-3}$ mol·dm^{-3} Bi(III) w 1-8 mol·dm^{-3} chlorates(VII) and in the presence of $1 \cdot 10^{-3}$ mol·dm^{-3} 2-thiocytosine from the polarization rate v.

$C_{chlorates(VII)}$/ mol·dm^{-3}	ΔE/V							
	v/mV·s^{-1}							
	5	10	20	50	100	200	500	1000
1	0.0425	0.0429	0.0450	0.0454	0.0410	0.0382	0.0579	0.0607
2	0.0407	0.0409	0.0410	0.0426	0.0425	0.0309	0.0286	0.0276
3	0.0400	0.0400	0.0401	0.0350	0.0333	0.0313	0.0348	0.0409
4	0.0389	0.0386	0.0365	0.0340	0.0301	0.0383	0.0326	0.0438
5	0.0356	0.0359	0.0306	0.0300	0.0321	0.0427	0.0434	0.0450
6	0.0338	0.0330	0.0384	0.0305	0.0304	0.0360	0.0364	0.0403
7	0.0335	0.0334	0.0335	0.0346	0.0355	0.0440	0.0438	0.0484
8	0.0379	0.0367	0.0340	0.0354	0.0367	0.0434	0.0446	0.0421

Conclusions

This study indicates that the rate of electroreduction of Bi(III) in chlorate(VII) is affected by the presence of 2-thiocytosine as well as by water activity. Decreasing the water activity gives a similar effect as increasing the concentration of 2-thiocytosine. The Bi-TC active complex, which mediates electron transfer, will play an important role [9]. The fact of the formation of the complex in the adsorption layer of the R-AgLAFE electrode is related to the adsorption of 2-thiocytosine on the electrode, which increases the activity of the electrode without limiting its surface area [9].

References

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