

Catalytic influence of acetazolamide on the electroreduction process of In(III) in chlorates(VII) with varied water activity; the application of nanostructured cyclic renewable liquid silver amalgam film electrode (R-AgLAFE)



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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 In(III) ions in the presence of acetazolamide(ACT) under conditions of varying water activity.

Methods

The investigations were carried out using an electrochemical analyser Autolab/GpES (version 4.9) 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. 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 In(III) ions ($1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ In(III)) while the basic electrolyte consisted of chlorate(VII) solutions in the concentration range from $1 \text{ mol} \cdot \text{dm}^{-3}$ to $8 \text{ mol} \cdot \text{dm}^{-3}$. As a catalyst for the analysed process of electroreduction of In(III) ions, acetazolamide was used at a concentration of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$.

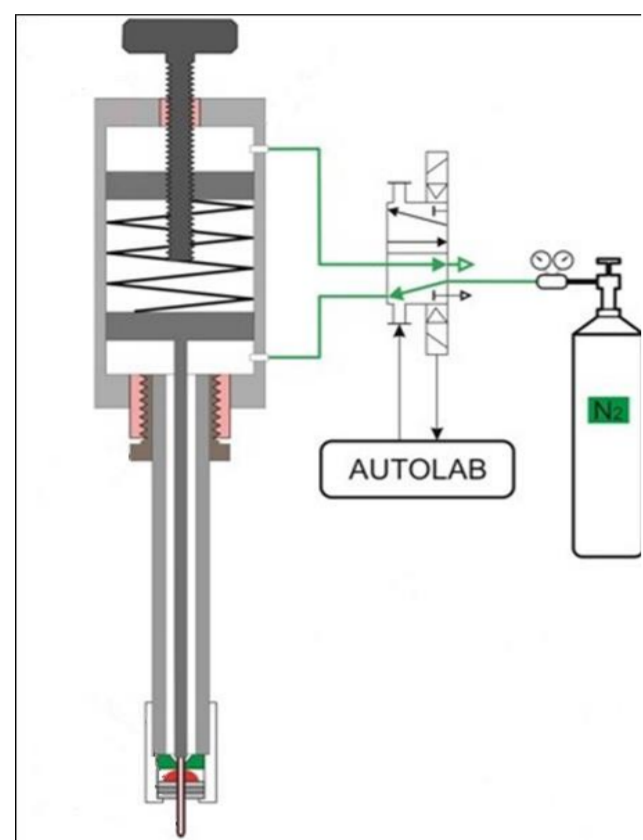


Fig. 1. Vertical axial section of the R-AgLAFE electrode including power and control components [7].

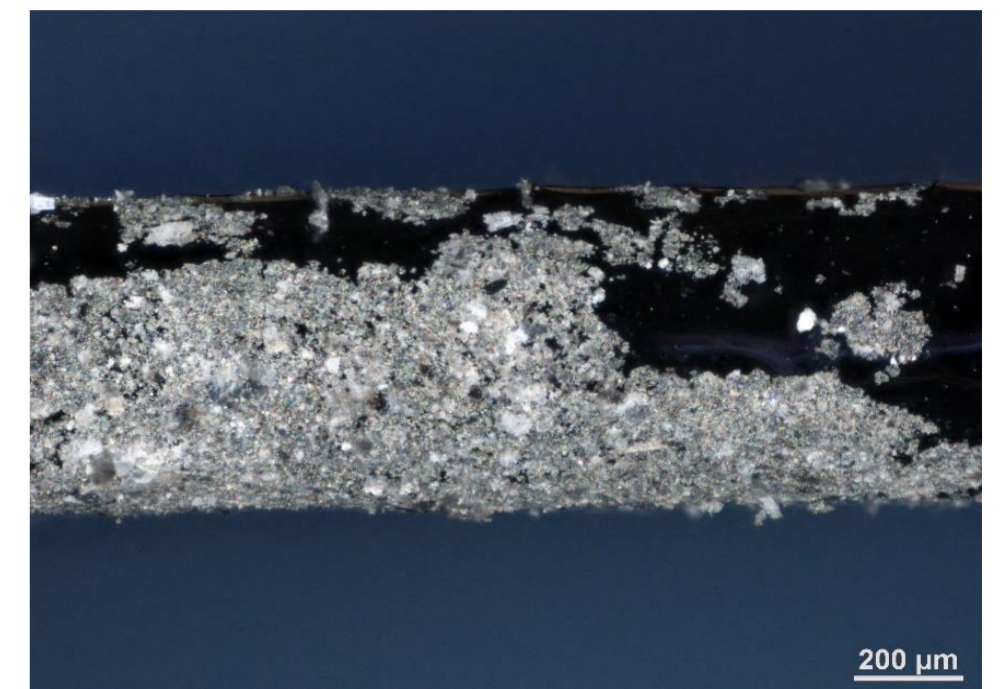


Fig. 2. The surface of the R-AgLAFE electrode imaged using a Nikon Eclipse MA200 optical microscope with a "Nikon Lu Plan Fluor 10x/0.30A" objective [7].

Results

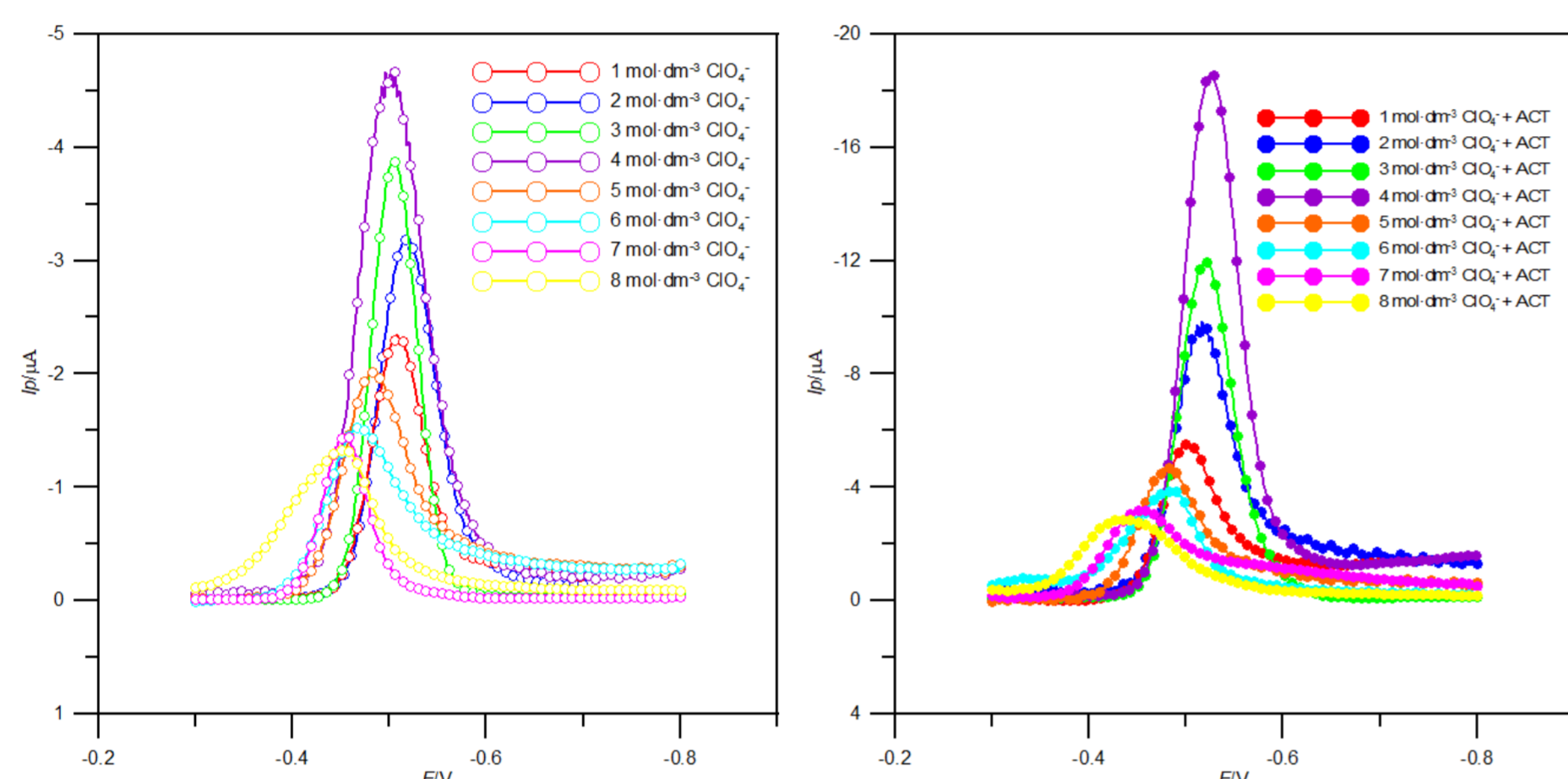


Fig. 3 (a) SWV peaks of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ In(III) ions electroreduction in 1-8 chlorates(VII); 3 (b) and with the addition of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ acetazolamide for the same chlorates(VII) concentrations.

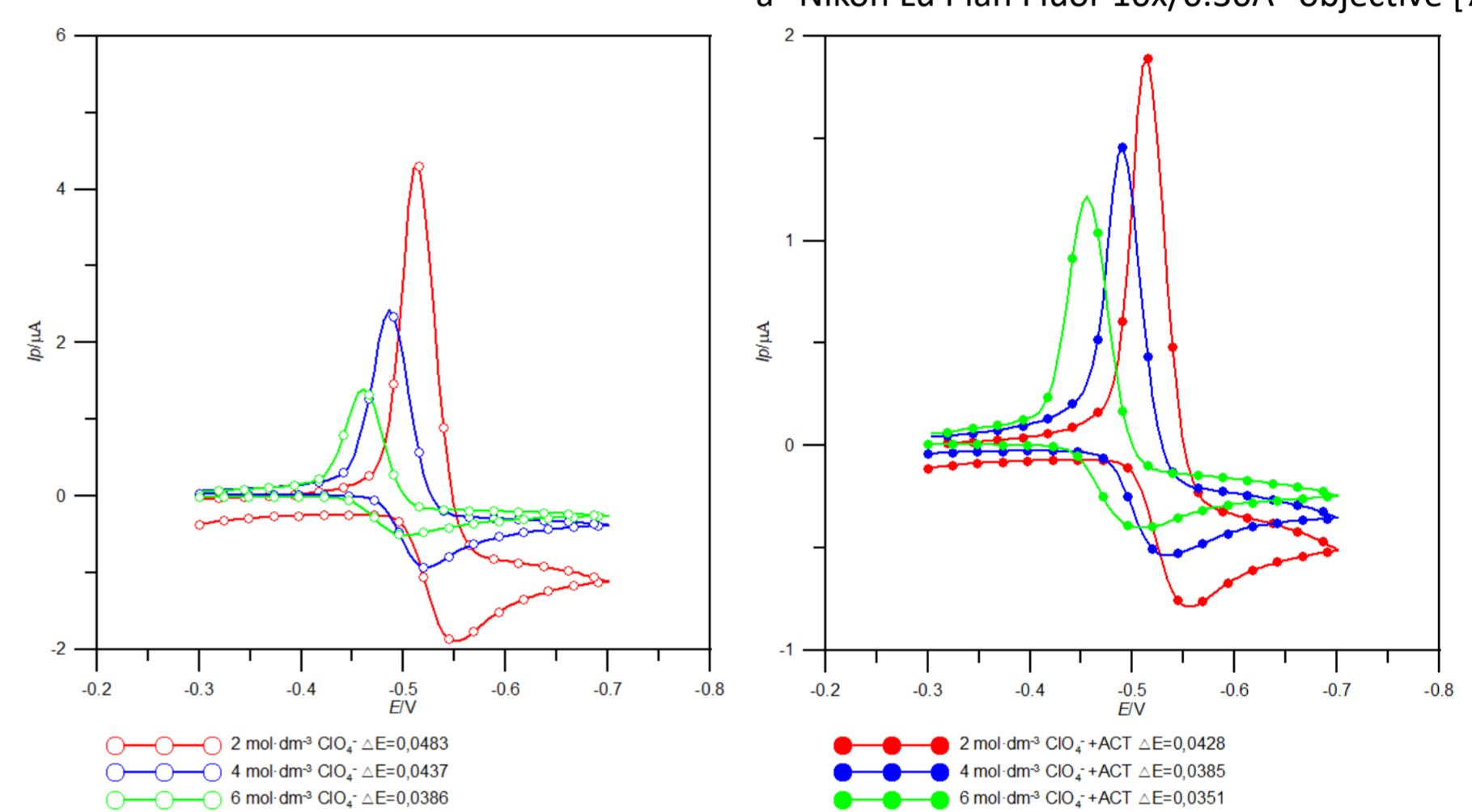


Fig. 4 (a) CV curves of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ In(III) ions electroreduction in 1-8 chlorates(VII); 4 (b) and with the addition of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ acetazolamide for the same chlorates(VII) concentrations; electrode polarization rate $v = 50 \text{ mV} \cdot \text{s}^{-1}$

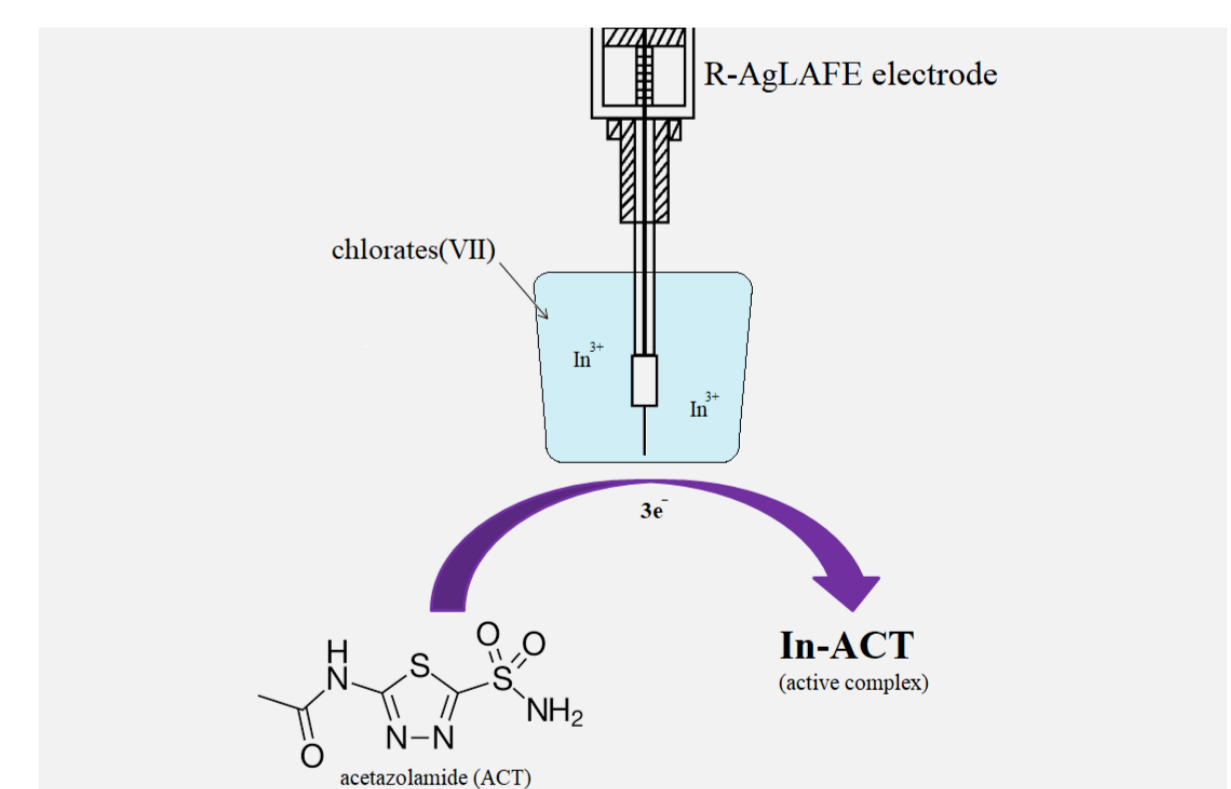
As can be seen from Figure 3a and 3b, as the basic electrolyte concentration increases, a significant increase in the height of the SWV peak currents up to a concentration of 4 M is observed. This indicates an increase in the reversibility of In(III) ions electroreduction process. In contrast, above this concentration and with an increase in chlorate(VII) concentration, the opposite situation is observed. Introduction of acetazolamide into chlorates(VII) solutions results in an increase in the SWV peak current for all chlorates(VII) concentrations tested. At the same time, we observe a decrease in their width at mid-height, which indicates an increase in the reversibility of In(III) ions electroreduction process. It was also observed that above a 4 M concentration of chlorates(VII) the SWV peak currents decrease with decreasing water activity, suggesting a decrease in the reversibility of the electroreduction process.

Confirmation of the changes in the kinetics of In(III) ions electroreduction process with decreasing water activity is provided by the relationships obtained from cyclic voltammetry curves. An increase in chlorates(VII) concentration causes a decrease in the potential difference between the anodic and cathodic peaks ΔE , indicating an increase in the reversibility of In(III) ions electroreduction process. Of course, such a relationship is observed up to a concentration of 4 M chlorates(VII), above this concentration there is an increase in the potential difference between ΔE_{a-c} [6].

Table 1. Changes of ΔE_{a-c} for the electroreduction process of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ In(III) w $1-8 \text{ mol} \cdot \text{dm}^{-3}$ chlorates(VII) and in the presence of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ acetazolamide from the polarization rate v .

$C_{\text{chlorates(VII)}} + \text{ACT} / \text{mol} \cdot \text{dm}^{-3}$	$\Delta E / V$							
	$v / \text{mV} \cdot \text{s}^{-1}$							
	5	10	20	50	100	200	500	1000
1	0.0343	0.0349	0.0354	0.0474	0.0674	0.0921	0.1487	0.1761
2	0.0326	0.0337	0.0348	0.0428	0.0556	0.0823	0.1217	0.1657
3	0.0305	0.0325	0.0344	0.0417	0.0530	0.0747	0.1011	0.1535
4	0.0292	0.0317	0.0329	0.0385	0.0493	0.0701	0.0937	0.1468
5	0.0278	0.0306	0.0324	0.0368	0.0466	0.0603	0.0873	0.1292
6	0.0272	0.0295	0.0318	0.0351	0.0438	0.0545	0.0677	0.1050
7	0.0267	0.0278	0.0303	0.0347	0.0417	0.0504	0.0635	0.0777
8	0.0243	0.0250	0.0272	0.0333	0.0343	0.0486	0.0575	0.0645

The small changes in ΔE_{a-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 In(III) ions in the presence of acetazolamide, with varying water activity, is the chemical reaction of the formation of In-ACT active complexes [8].



Scheme 1. Scheme of In(III) ions electroreduction in chlorates(VII) including the mediating role of active complexes in the charge (electron) transfer.

Table 2a. Values of cathodic transition factors α and standard reaction rate constants k_s for the electroreduction process of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ In(III) w $1-8 \text{ mol} \cdot \text{dm}^{-3}$ chlorates(VII) and 2b in the presence of $1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ acetazolamide.

2a			2b		
$C_{\text{chlorates(VII)}} / \text{mol} \cdot \text{dm}^{-3}$	α	$10^4 k_s / \text{cm} \cdot \text{s}^{-1}$	$C_{\text{chlorates(VII)}} / \text{mol} \cdot \text{dm}^{-3} + 1 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3} \text{ ACT}$	α	$10^4 k_s / \text{cm} \cdot \text{s}^{-1}$
		CV			CV
1	0.40	0.53	1	0.59	6.23
2	0.42	0.65	2	0.62	19.1
3	0.50	0.70	3	0.65	21.5
4	0.62	0.84	4	0.71	33.8
5	0.53	0.50	5	0.57	12.5
6	0.45	0.39	6	0.47	9.75
7	0.35	0.37	7	0.41	8.85
8	0.27	0.29	8	0.35	5.37

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 (k_s) were determined. The kinetic parameters determined indicate the catalytic effect of acetazolamide in solutions with varying water activity and its magnitude (Table 2 a,b). The standard rate constants for the electroreduction of In(III) ions in chlorates (VII) and in the presence of ACT increase with increasing the concentration of the basic electrolyte up to $4 \text{ mol} \cdot \text{dm}^{-3}$, in $5-8 \text{ mol} \cdot \text{dm}^{-3}$ chlorates (VII) a slight decrease in values is observed.

Conclusions

- the rate of the multi-step electroreduction process of In(III) ions in chlorates(VII) was shown to be influenced by both the presence of ACT and the varying activity of the water
- the equilibrium reaction of the formation of In - ACT active complexes mediating electron transfer determines the magnitude of the catalytic effect of ACT,
- varying water activity suggests changes in the composition of active complexes following the passage of successive electrons, which influenced the kinetics and mechanism of electroreduction of In(III) ions [9],
- in solutions with high water activity, there is probably an optimisation of the state of the electrode layer for more efficient acceleration of the electroreduction of In(III) ions by the ACT molecule,
- the highest catalytic activity was observed in 4 M chlorates(VII).

References

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