Catalytic activity of acetazolamide on electroreduction of In(III) in chlorates(VII); use of a cyclic renewable film of liquid silver amalgam electrode (R-AgLAFE)

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Introduction

Hitherto, the effect of „cap – pair" [1] has only been studied on mercury drop electrodes. The use of an innovative electrode with a cyclic renewable film of liquid silver amalgam R-AgLAFE is an excellent alternative to HDME, as it guarantees similar quality and performance parameters to HMDE [2,3] and fits into the current trend of green chemistry.

Acetazolamide is one of the most important drugs used in the treatment of secondary glaucoma. Acetazolamide also accelerates acclimatization in high mountain conditions by counteracting respiratory alkalosis and drug-induced oedema and in patients with heart failure [4]. Therefore, there is a need to study the mechanisms of action of this drug or search for new systems of controlled release.

The influence of acetazolamide (ACT) on multi-step In(III) ion electroreduction was investigated using both voltammetry and impedance methods. It was observed that acetazolamide catalyzes the electroreduction of In(III) ions. Since the „cap – pair" effect provides a significant increase in the sensitivity of the quantification of both the depolarizer (In(III) and the ligand (ACT) hence the proposed procedure may be of paramount importance for evaluating the progress of treatment and building a mechanistic model of the effects of this drug on the human body.

Methods

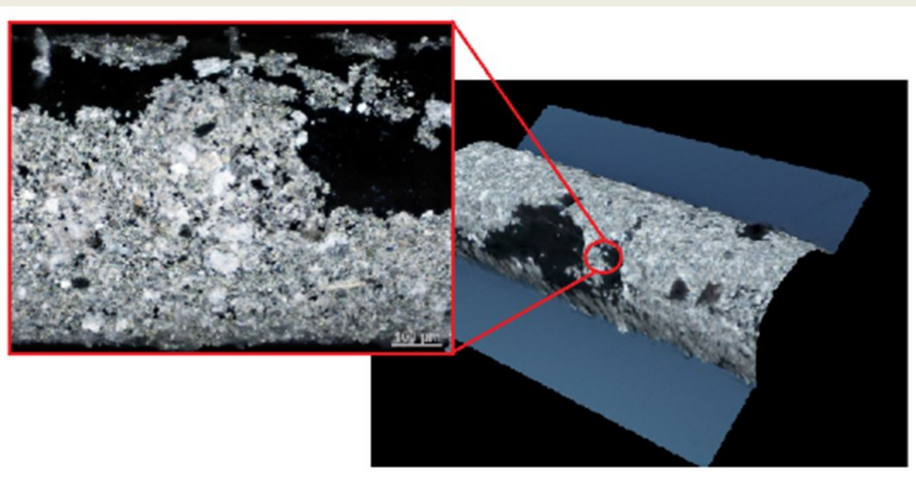

Fig. 1 Surface of the R-AgLAFE electrode imaged using a Nikon Eclipse MA200 optical microscope with a "Nikon Lu Plan Fluor 10x/0.30A" objective.

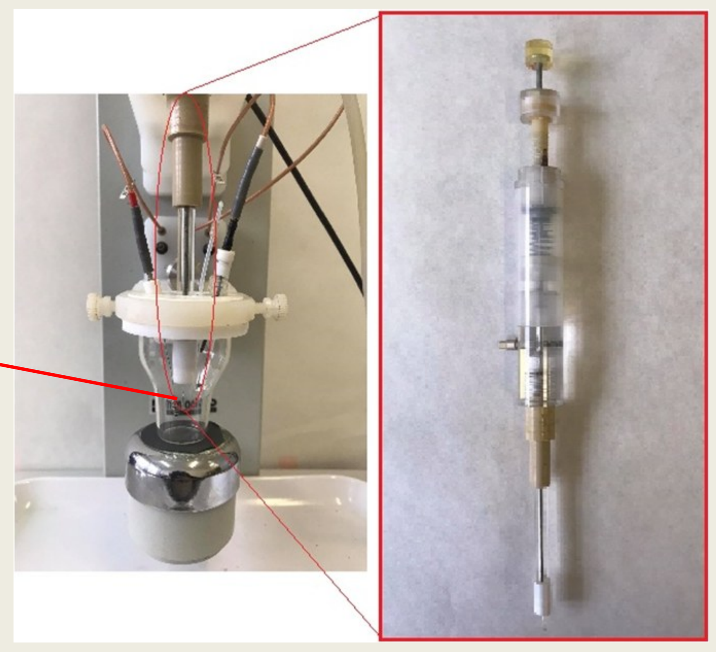

Fig. 2 R-AgLAFE sensor mounted in the mtm-anko M165 tripod.

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Fig. 3 µAutolab/GpES.

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Application of electrochemical techniques:

- DC polarography,
- CV voltammetry and SWV voltammetry

allowed the determination of kinetic parameters determining the catalytic effect of acetazolamide and its magnitude.

Results

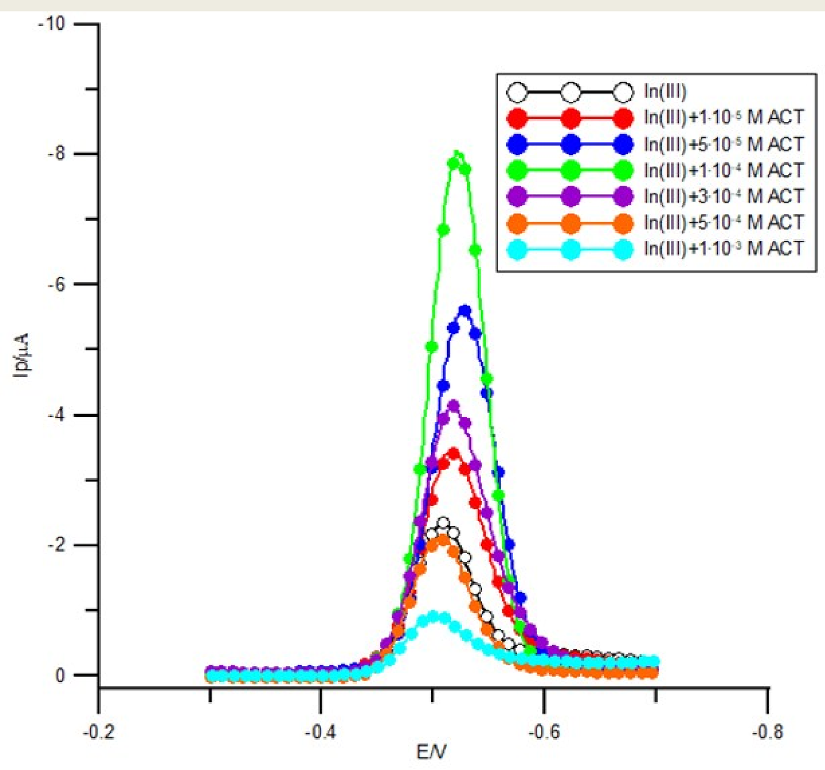

Fig. 4 SWV peaks of electroreduction of In(III) ions in 1 M chlorate(VII) with increasing acetazolamide concentration included in the legend.

Addition (ACT) to the chlorate(VII) solution causes an increase in the SWV peak current

this indicates an increase in the reversibility of the electroreduction process of In(III) ions

Above the concentration of $1 \cdot 10^{-4}$ $mol \cdot dm^{-3}$ ACT, SWV peak currents decrease, which suggests a decrease in the reversibility of the electrode process.

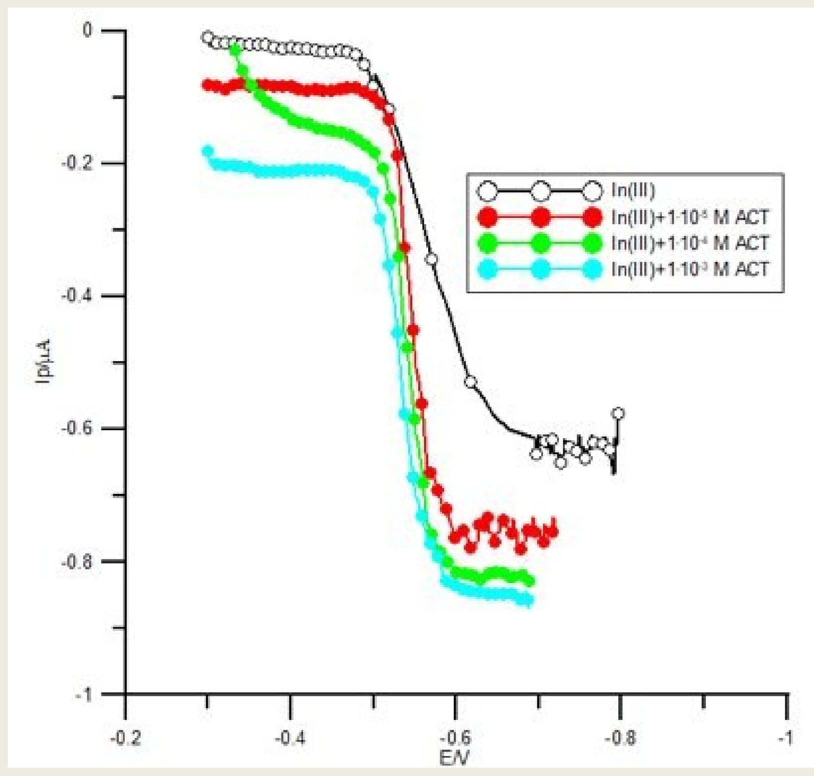

Fig. 5 DC polarographic waves of electroreduction of In(III) ions in 1 M chlorate(VII) with increasing concentration of acetazolamide included in the legend.

An increase in the slope of the polarographic waves of the electroreduction of In(III) ions in the presence of ACT also indicates an increase in the reversibility of the electrode process.

Introduction and increase of ACT concentration causes decrease of ΔE difference, which indicates the increase of reversibility of the process of electroreduction of In(III) ions

also only up to the concentration of $1 \cdot 10^{-4}$ $mol \cdot dm^{-3}$ ACT.

Above this concentration values of ΔE increase, which confirms the change of dynamics of catalytic action of ACT on the process of electroreduction of In(III) ions.

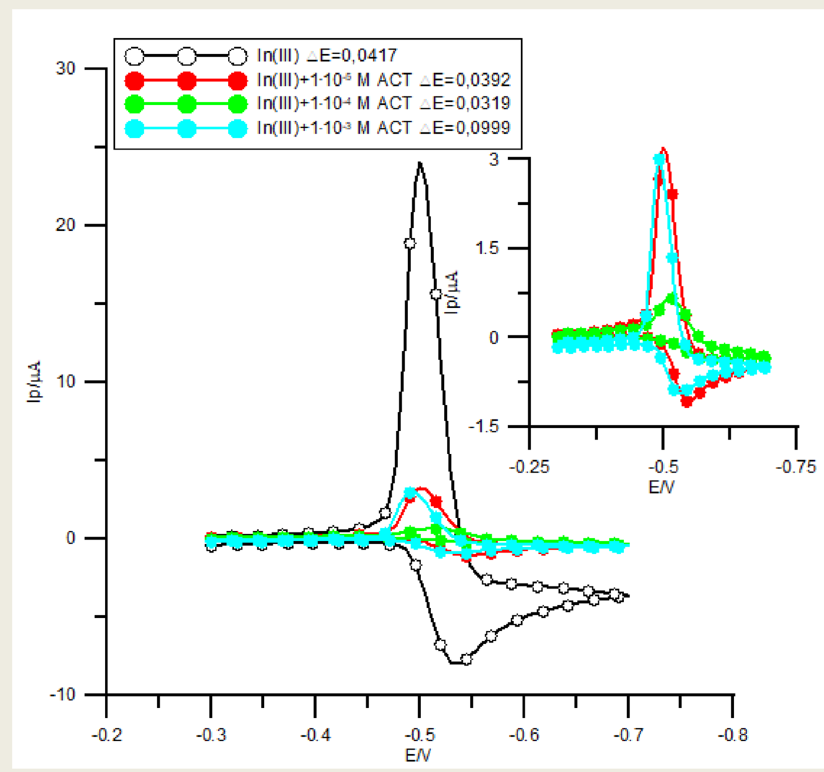

Fig. 6 Voltammetric CV curves of electroreduction of In(III) ions in 1 M chlorate(VII) with increasing concentration of acetazolamide included in the legend.

Table 1. Changes in ΔE of the electroreduction process of $1 \cdot 10^{-3}$ $mol \cdot dm^{-3}$ In(III) and in the presence of acetazolamide in 1 $mol \cdot dm^{-3}$ chlorate(VII) at polarization rate v.

$10^3 c_{In(III)} + 10^4 c_{ACT}$ /mol·dm^{-3}	ΔE/V							
	v/mV·s^{-1}							
	5	10	20	50	100	200	500	1000
0.00	**0.0292**	**0.0313**	**0.0324**	**0.0333**	**0.0417**	**0.0504**	**0.0625**	**0.0645**
0.10	0.0260	0.0265	0.0273	0.0321	0.0392	0.0468	0.0571	0.0592
0.30	0.0230	0.0232	0.0238	0.0310	0.0368	0.0440	0.0520	0.0558
0.50	0.0222	0.0226	0.0230	0.0297	0.0343	0.0381	0.0457	0.0501
1.00	0.0207	0.0211	0.0218	0.0281	0.0319	0.0340	0.0398	0.0472
3.00	0.0541	0.0547	0.0555	0.0613	0.0648	0.0710	0.0768	0.0910
5.00	0.0602	0.0608	0.0614	0.0690	0.0789	0.1141	0.1268	0.1373
10.0	0.0758	0.0762	0.0767	0.0878	0.0999	0.1257	0.1358	0.1411

No significant changes in ΔE were observed with the change in electrode polarization rate, suggesting a stepwise nature of the electrode process and an intermediate step, which may be a chemical reaction. She may also be the stage that controls the rate of the electroreduction process of In(III) ions in the presence of ACT. This is probably a reaction for the formation of active In- ACT complexes on the electrode surface, which may mediate electron transfer.

The lack of occurring changes in the value of the formal potential E_f^0 with increasing ACT concentration in chlorate(VII) solutions confirms that the mentioned complexes do not form in the solution of the basic electrolyte. ACT adsorbs on the electrode, therefore, the place of active complexes is probably in the adsorption layer.

Table 2. Formal potential values of electroreduction of $1 \cdot 10^{-3}$ $mol \cdot dm^{-3}$ In(III) ions in 1 $mol \cdot dm^{-3}$ chlorate(VII) and in the presence of acetazolamide.

$10^3 c_{In(III)} + 10^4 c_{ACT}$ /mol·dm^{-3}	E_f^0/V
0.00	**0.520**
0.10	0.540
0.30	0.530
0.50	0.550
1.00	0.540
3.00	0.560
5.00	0.560
10.0	0.580

Table 3. Values of cathodic transition coefficients (α) and standard rate constants (ks) of electroreduction of $1 \cdot 10^{-3}$ $mol \cdot dm^{-3}$ In(III) ions in 1 $mol \cdot dm^{-3}$ chlorate(VII) and in the presence of acetazolamide.

$10^3 c_{In(III)} + 10^4 c_{ACT}$ /mol·dm^{-3}	α	k_s 10^4/cm·s^{-1}
0.00	0.40	0.53
0.10	0.44	0.89
0.30	0.48	1.23
0.50	0.51	3.29
1.00	0.59	6.23
3.00	0.49	6.17
5.00	0.35	5.93
10.0	0.27	5.72

The increasing values of the α transition coefficients upon addition of acetazolamide to chlorate(VII) solution indicate an increase in the reversibility of the electroreduction process of In(III) ions in the presence of the organic substance under study. It should be noted that the dynamics of the catalytic action of ACT above $1 \cdot 10^{-4}$ $mol \cdot dm^{-3}$ ACT concentration changes towards inhibition. Standard rate constants also confirm such relationships. The changes in the kinetics of the electrordeduction process of In(III) ions in the presence of ACT should be related most probably to the changes occurring in the adsorption layer of the R-AgLAFE electrode. Which may suggest, for example, a different arrangement of complexes or even a blockade of the electrode.

Conclusions

- the catalytic effect of acetazolamide on the multistep electroreduction process of In(III) ions according to the cap-pair rule was demonstrated,
- the magnitude of the catalytic effect is related to the formation of active complexes mediating the electron transfer,
- the formation of active complexes on the electrode surface enables the adsorption of ACT at the R-AgLAFE/solution interface,
- "cap-pair" studies on the R-AgLAFE electrode also for the In(III) electroreduction process proved to be valid and yielded satisfactory results.

References

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