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Influence of temperature on the reduction kinetics of Bi(III) ion in the presence of cystine in chlorate (VII) solutions of decreased water activity

Research Article

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Abstract: The results of the kinetic measurements of Bi(III) electroreduction on a mercury electrode in 1–8 mol dm^{-3} chlorate (VII) solutions and in the presence of cystine demonstrate a dependence of the process on the temperature. The applied electrochemical techniques (DC polarography, cyclic and SWV voltammetry) allowed for the determination of the kinetic and thermodynamic parameters and their correlation with water activity. The catalytic activity of cystine was confirmed by the decrease in overall enthalpies of activation. The changes in the values of $\Delta H^{\neq}$ and ΔS^{0} for Bi(III) electroreduction in the presence of cystine with the increase of chlorate (VII) concentration showed that the mechanism is different in solutions with low water activity as compared to those with high water activity. Probably it is connected with a different structure of the activated complexes (Bi – Hg(SR)$_2$), mediating electron transfer.

Keywords: *Bi(III) electroreduction • L-cystine • Activation energy • Standard reaction entropy • Electrochemistry*

1. Introduction

The electrochemical properties of metal ions depend on the type of supporting electrolyte, the type of electrode and the presence of organic substances. These properties are directly connected with metal electrodeposition, corrosion, protection, the functioning of batteries and increasing the accuracy of depolarizer determinations [1-5]. In accordance with the cap – pair effect, organic substances introduced to the supporting electrolyte may catalyze [6,7] some electrode processes while they have a neutral or inhibitory effect on others [8].

The reversibility of Bi(III) electroreduction in 1–8 mol dm^{-3} chlorates (VII) increases with decreasing water activity [9]. It has been found that in solutions with high water activity the mechanism of Bi(III) electroreduction is different from that in solutions with low water activity.

It has been also shown that a decrease in water activity gives the same effect as an increase in the concentration of catalytic organic substances, *e.g.* methionine or cysteine [10,11].

The temperature dependence of the kinetics parameters has been discussed in the literature [12–17]. Marczak *et al.* [15] analysed the temperature dependence of transfer coefficients for cathodic and anodic electrode reactions of two different types of systems, namely Cr(III)/Cr(II) and Cr(II)/Cr(Hg) in 5 mol dm^{-3} $NaClO_4$ solutions. In the case of the Cr(III) to Cr(II) and Cr(II)/Cr(Hg) electroreduction, a temperature dependence of α exists what results from the double layer changes.

Also, the change of the Tafel slope with temperature was observed for the Ba(II)/Ba(Hg) system in DMF in 0.1 mol dm^{-3} TEAP [18] what is connected with some adsorption of cations of the background electrolyte.

Changes in the rates of electrode reactions are strictly connected with changes in the activation energy ($\Delta H^{\neq}$) or standard reaction entropy (ΔS^{0}) of the process [11,15,17].

The presence of thiourea in mixed water - organic solutions [17] decreased the value of activation energy of the electroreduction process of Zn(II) thus confirming

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the catalytic activity of thiourea. The catalytic activity of sodium 1 – decanesulfonate was confirmed as well by the decrease of overall enthalpies of activation which means the decrease of the activation barrier of the first electron transfer [19].

In previous papers, it was found that the process of Bi(III) ion electroreduction is catalyzed by methionine [10], cysteine [11] and cystine [20]. The changes of enthalpies of activation $\Delta H^{\neq}$ confirms the catalytic activity of methionine [10] and cysteine [11]. Additionally, the presence of 1×10^{-3} mol dm^{-3} cysteine in the 1–8 mol dm^{-3} chlorate (VII) solutions decreased the value of ΔS^0 at all the examined chlorate (VII) concentrations and suggested changes in the dynamics of the process of Bi(III) ion electroreduction. The catalytic activity of cystine [20,21] clearly depends on water activity.

This paper presents the analysis of the temperature dependences of the kinetic parameters of the electrode reactions in the Bi(III)/Bi(Hg)/1–8 mol dm^{-3} chlorates (VII) + cystine systems.

The applied electrochemical techniques (DC polarography, cyclic and SWV voltammetry) allowed to determine the kinetic and thermodynamic parameters as well as their correlation with water activity.

2. Experimental procedure

Polarographic and voltammetric measurements were performed by employing an AUTOLAB electrochemical analyzer controlled by GPES software, version 4.9 (Eco Chemie, Utrecht Netherlands). The experiments were performed in a three – electrode cell with a hanging controlled-growth mercury drop electrode (CGMDE, electrode area = 0.009487 cm^2, drop time = 3 s) (Entech, Cracow, Poland), and the reference electrode was Ag/AgCl/saturated NaCl. The auxiliary electrode was a platinum spiral.

Prior to measurements, the solutions were deaerated using high purity nitrogen. Furthermore, nitrogen was passed over the solutions during measurements.

All experiments were carried out in the temperature range of 288–303 ± 0.1 K.

Chemicals of analytical grade from Fluka were used. The supporting electrolytes were x mol dm^{-3} $NaClO_4$ + 1 mol dm^{-3} $HClO_4$ (where $0 \le x \le 7$). The concentration of Bi(III) ions in the solutions studied was always 1×10^{-3} mol dm^{-3}. Due to the weak solubility of $Bi(NO_3)_3$ in chlorates(VII), the solutions were sonicated. Cystine solutions (1×10^{-2} mol dm^{-3}) were prepared just before the measurements.

3. Results and discussion

3.1. Voltammetric measurements

The introduction of cystine to solutions of 1×10^{-3} mol dm^{-3} Bi(III) in 1–8 mol dm^{-3} chlorates (VII) causes an increase in the SWV peak current of Bi(III) ion electroreduction [20,21]. The magnitude of this effect depends on cystine and supporting electrolyte concentrations but as well on the temperature (Fig. 1, 1a).

With an increase of chlorate (VII) concentration from 1 to 4 mol dm^{-3}, the peak currents of Bi(III) electroreduction in the presence of cystine decrease, while with an increase of chlorate (VII) concentration from 4 to 6 mol dm^{-3} the peak currents increase. For higher concentrations of supporting electrolyte the decrease of the SWV peaks height is observed.

With the temperature increase 288 K < 293 K < 298 K < 303 K the values of peak currents increase (Fig. 1), and the peaks potentials are shifted simultaneously towards the positive potentials. These dependences are observed for all the supporting electrolyte concentrations studied.

Fig. 2 presents DC polarograms of 1×10^{-3} mol dm^{-3} Bi(III) electroreduction in 3 mol dm^{-3} chlorate (VII) in the presence 1×10^{-2} mol dm^{-3} cystine registered for different temperatures. With the increase of temperature the DC wave increases and half – wave potentials ($E_{1/2}$) are shifted towards the positive potentials. Similar relations of temperature dependences are represented by the determined values of the diffusion coefficients (D_{ox}) of Bi(III) ions in 1–8 mol dm^{-3} chlorates (VII) in the presence of 10^{-2} mol dm^{-3} cystine (Fig. 2a). This effect was also observed for the reduction of Zn(II) in the $NaClO_4$ systems [16] and was related to the temperature dependence of different kinetic or thermodynamic parameters.

Using the method of cycling voltammetry the curves $I_p = f(E)$ of Bi(III) ions electroreduction were registered at different temperatures in the 1–8 mol dm^{-3} chlorates (VII) in the presence of 10^{-2} mol dm^{-3} cystine. Some examples of voltammetric curves are shown in Fig. 3.

The temperature dependence of the height of the cathodic peak remains in agreement with the changes of the diffusion coefficients. It should be emphasized here that the temperature increase decreases the overpotential accompanying the cathodic process of reduction of Bi(III) ions [19]. In order to perform a more detailed analysis of the effect of temperature and concentration of supporting electrolyte in the presence of cystine on Bi (III) ions electroreduction, Table 1 includes the values of $\Delta E = E_a - E_c$, for all the investigated systems.

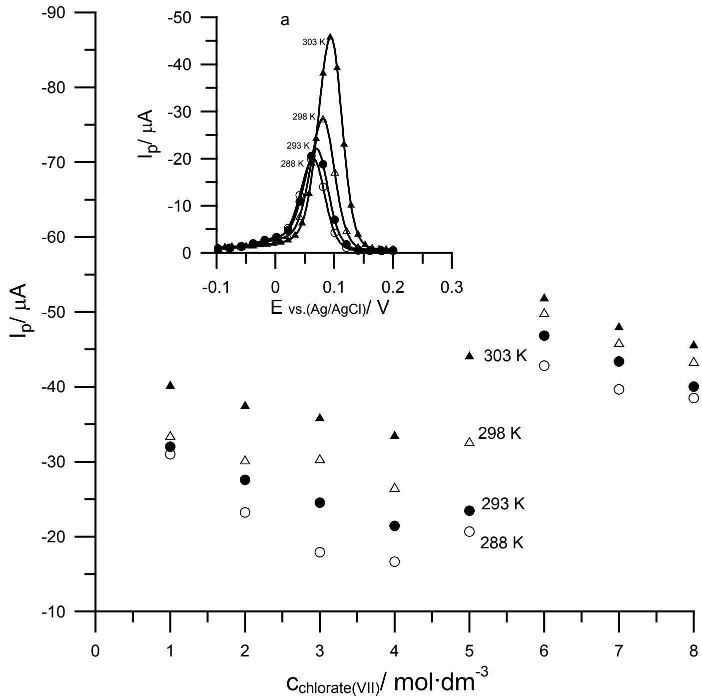

Figure 1. Dependence of the SWV peak current of 1×10^{-3} mol dm^{-3} Bi(III) in chlorates (VII) in the presence 1×10^{-2} mol dm^{-3} cystine on chlorate (VII) concentration, in the studied temperature range: (○) 288 K, (●) 293 K, (Δ) 298 K, (▲) 303 K. Fig. 1a.: SWV peaks of 1×10^{-3} mol dm^{-3} Bi(III) electroreduction in 4 mol dm^{-3} chlorates (VII) in the presence of 1×10^{-2} mol dm^{-3} cystine, in the studied temperature range: (○) 288 K, (●) 293 K, (Δ) 298 K, (▲) 303 K

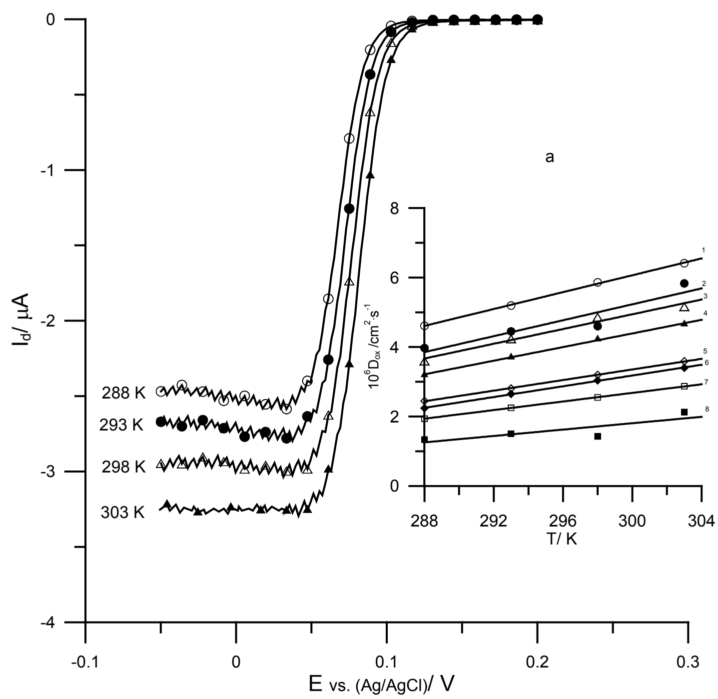

Figure 2. DC polarograms of 1×10^{-3} mol dm^{-3} Bi(III) in 3 mol dm^{-3} chlorates (VII) in the presence of 1×10^{-2} mol dm^{-3} cystine, in the studied temperature range: (○) 288 K, (●) K, (Δ) 298 K, (▲) 303 K. Fig. 2a.:Temperature dependence of the diffusion coefficients D_{ox} of Bi(III) ions in 1–8 mol dm^{-3} chlorates (VII) in the presence of 10^{-2} mol dm^{-3} cystine. The concentration of chlorates (VII) in mol dm^{-3} is indicated at each curve.

$D_{\alpha x}$

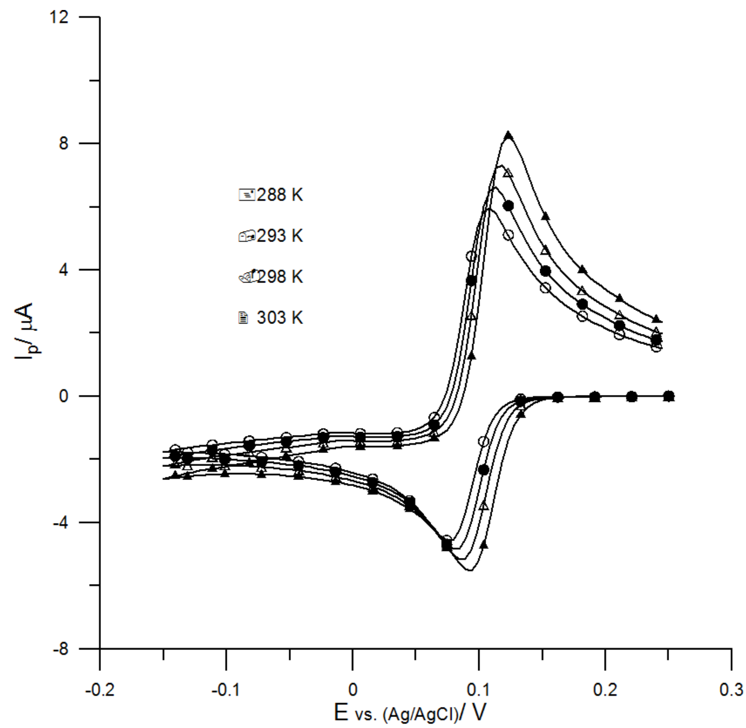

Figure 3. Cyclic voltammetric curves for the Bi(III)/Bi(Hg) system in 5 mol dm^{-3} chlorate (VII) in the presence of 10^{-2} mol dm^{-3} cystine at scan rate of 100 mV s^{-1}, in the studied temperature range: (○) 288 K, (●) 293 K, (Δ) 298 K, (▲) 303 K.

Table 1. Changes in the difference between the anodic peak potential and the cathodic peak potential ($\Delta E = Ea - Ec$) for the process of 1×10^{-3} mol dm^{-3} Bi(III) ion electroreduction in 1–8 mol dm^{-3} chlorates(VII) in the presence of 1×10-2 mol dm^{-3} cystine *vs*. temperature at scan rate of v= 100 mV s^{-1} and v= 1000 mV s^{-1}

c chlorate (VII)/ mol dm^{-3}	ΔE/ V							
	v= 100 mV s^{-1}				v= 1000 mV s^{-1}			
	T = 288 K	*T* = 293 K	*T* = 298 K	*T* = 303 K	*T* = 288 K	*T* = 293 K	*T* = 298 K	*T* = 303 K
1	0.032	0.032	0.032	0.032	0.068	0.056	0.050	0.042
2	0.034	0.032	0.033	0.033	0.100	0.075	0.060	0.056
3	0.043	0.040	0.035	0.033	0.105	0.090	0.070	0.082
4	0.041	0.039	0.037	0.031	0.119	0.098	0.084	0.065
5	0.037	0.035	0.033	0.029	0.081	0.065	0.055	0.048
6	0.034	0.032	0.030	0.030	0.040	0.038	0.037	0.035
7	0.030	0.030	0.029	0.030	0.032	0.032	0.032	0.031
8	0.030	0.030	0.031	0.032	0.032	0.032	0.033	0.034

As can be seen from Table 1, the values of ΔE for v = 100 mV s^{-1} do not practically depend on temperature in 1, 2 as well as 6, 7 and 8 mol dm^{-3} chlorates (VII). In 3, 4 and 5 mol dm^{-3} chlorates (VII) the distinct decrease of ΔE values with the increase of temperature can be observed. The similar dependences are observed for the polarization rates in the range of 5 to 200 mV s^{-1}. For greater polaryzation (>200 mV s^{-1}) (Table 1) the values of ΔE decrease with the increase of temperature in particularly for the solutions of 4 and 5 mol dm^{-3} chlorates (VII). For the solutions of 7 and 8 mol dm^{-3} chlorates (VII) the changes in the values of ΔE are practically imperceptible. These observations testify to the changes of the dynamics of the acceleration process which seems to be the highest in 3, 4 and 5 mol dm^{-3} chlorates (VII).

Table 2. The values of standard rate constants *ks* of 1×10^{-3} mol dm^{-3} Bi(III) ion electroreduction in 1–8 mol dm^{-3} chlorates(VII) in the presence of 1×10^{-2} mol dm^{-3} cystine *vs*. temperature.

c chlorate (VII)/ mol dm^{-3}	$10^3\,k_s$/cm s^{-1}			
	T = 288 K	T = 293 K	T = 298 K	T = 303 K
1	7.28	7.00	8.00	8.10
2	7.07	7.05	7.10	7.40
3	7.40	7.20	7.99	7.76
4	7.60	7.70	7.36	8.00
5	6.90	7.75	8.64	10.1
6	8.30	8.90	11.0	12.5
7	7.87	8.99	8.97	11.1
8	7.70	7.79	8.64	10.9

The values of the ks of 1×10^{-3} mol dm^{-3} Bi(III) ion electroreduction in 1–8 mol dm^{-3} chlorates(VII) in the presence of 1×10^{-2} mol dm^{-3} cystine at the temperature of 298 K are taken from [21].

3.2. Standard rate constants

The values of standard rate constants k_s of 1×10^{-3} mol dm^{-3} Bi(III) electroreduction in 1 – 8 mol dm^{-3} chlorate (VII) in the presence of 1×10^{-2} mol dm^{-3} cystine in the temperature range of 288–303 K were calculated using the Nicholson method. The details of calculations are described elsewhere [9].

As can be seen from Table 2, the values of k_s increase with the temperature and concentration of supporting electrolyte (decrease of water activity) to 6 mol dm^{-3}. At lower water activities the values of k_s decrease slightly.

3.3. Real enthalpies of activation and standard reaction entropy

From the temperature dependence of standard rate constants k_s, the enthalpies of activation $\Delta H^{\neq}$ were determined according to Eq. 1 [9]:

$$\Delta H^{\neq} = R\frac{d\ln k_s}{d\frac{1}{T}} \quad (1)$$

As it results from Table 3, for electroreduction of Bi(III) in 1–8 mol dm^{-3} chlorates (VII) the values of $\Delta H^{\neq}$ decrease with the decrease of water activity. These changes are minute in 1–5 mol dm^{-3} chlorates (VII) and more noticable in the solutions of 6–8 mol dm^{-3} chlorates (VII). Following the addition of cystine to the supporting electrolyte, the values of activation energy in all the examined chlorate (VII) solutions significantly decrease. The upward tendency of $\Delta H^{\neq}$ with the decrease of water activity should be noticed as well as the fact that in 7 and 8 mol dm^{-3} chlorates (VII) (*ergo* at very low water activity), $\Delta H^{\neq}$ does not differ practically from this value of $\Delta H^{\neq}$ in the presence of cystine. It points that as the value of a_{H_2O} decreases in the solution, cystine plays a diminishing role in the kinetics of Bi(III) electroreduction.

The values of the formal potentials (E_f^0) for electrode processes at different temperatures were computed from the equation [9]:

$$E_{f^0}=\frac{1}{2}\left[E_{a/4}+E_{c/4}+\frac{(E_{a/4}+E_{c/4})-(E_{3a/4}+E_{3c/4})}{g-1}\right] \quad (2)$$

where:

$$g=\frac{(E_{3a/4}-E_{3c/4})}{(E_{a/4}-E_{c/4})}$$

$E_{a/4}$ or $E_{3a/4}$ - the potentials of accordingly one fourth or three fourth of the anodic peaks height

$E_{c/4}$ or $E_{3c/4}$ - the potentials of accordingly one fourth or three fourth of the cathodic peaks height

The values of E_f^0 (Fig. 4) are shifted towards the higher potentials, both as a result of the temperature increase and the concentration increase of chlorate (VII).

The slopes of the plots in Fig. 4 provide values of the standard reaction entropy (ΔS^0) for the reduction of Bi(III) and in the presence of cystine [16]:

$$\Delta S^0_{Bi(III)/Bi(Hg)}=2\mathrm{F}\frac{dE_f^0}{dT} \quad (3)$$

As can be seen from Fig. 4, the value of the standard reaction entropy for the reduction of Bi(III) in the presence of cystine is independent on chlorate (VII) concentrations and is equal $\Delta S^0_{Bi(III)/Bi(Hg)}$ = 221.95 ± 10 J mol^{-1} K^{-1}. Whereas in Bi(III) solutions without cystine

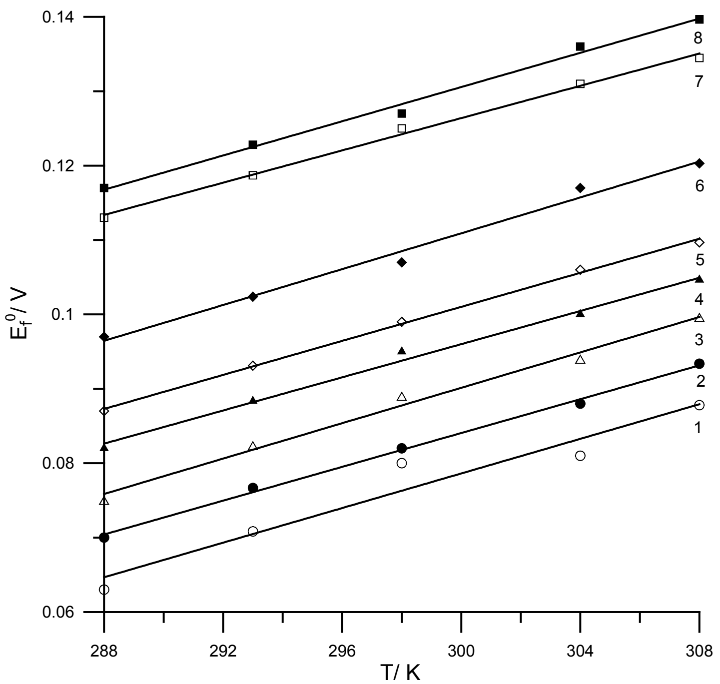

Figure 4. Temperature dependence of the formal potential of 1×10^{-3} mol dm^{-3} Bi(III) electroreduction in 1–8 mol dm^{-3} chlorates (VII) in the presence 1×10^{-3} mol dm^{-3} cystine. The concentration of chlorates (VII) in mol dm^{-3} is indicated at each line.

Table 3. The values of standard activation energy ($\Delta H^{\neq}$) for Bi(III) ion electroreduction and for Bi(III) ion electroreduction + 1×10^{-2} mol dm^{-3} cystine in 1–8 mol dm^{-3} chlorates (VII).

c chlorate (VII)/ mol dm^{-3}	$\Delta H^{\neq}$/ KJ mol^{-1}	
	Bi(III)	Bi(III)+cystine
1	31.69	0.91
2	31.68	0.89
3	31.59	0.87
4	31.00	3.10
5	30.64	11.44
6	28.72	20.89
7	21.06	19.92
8	22.40	21.80

The values of $\Delta H^{\neq}$ for Bi(III) ion electroreduction are taken from [11].

the values of $\Delta S^0_{Bi(III)/Bi(Hg)}$ = 335.82 ± 10 J mol^{-1} K^{-1} in 1 to 4 mol dm^{-3} chlorates (VII) and $\Delta S^0_{Bi(III)/Bi(Hg)}$ = 193 ± 10 J mol^{-1} K^{-1} in 5 to 8 mol dm^{-3} chlorates (VII) [11]. It suggests the increase of arrangement in the system for chlorate (VII) solutions with the higher water activity comparing to these ones with low water activity.

The presence of 1×10^{-2} mol dm^{-3} cystine changes the dynamics of the process of Bi(III) ion electroreduction. The lower values of the standard reaction entropy in the solutions with high water activity point to the higher arrangement of system, what implicates the higher changes in reversibility and the mechanism of the process of Bi (III) ions electroreduction in 1–4 mol dm^{-3} chlorates (VII) comparing with the solutions of 5–8 mol dm^{-3} chlorates (VII).

4. Conclusions

The presented measurements concerning the process of the electroreduction of Bi(III) ions in the presence of cystine in the 1–8 mol dm^{-3} chlorates (VII) demonstrate a dependence of the process rate on the temperature. It was found that the influence of temperature on the kinetics of the process of Bi(III) ions electroreduction in the presence of cystine is slightly higher in the solutions with high water activity as compared to those with low water activity. In all the examined systems the presence of cystine decreases the value of activation energy thus confirming the catalytic activity of cystine (Table 3).

As results from the foregoing studies [9–11,20–21] the catalytic influence of the amino acids on the electroreduction of Bi(III) ions in chlorates (VII) is connected with the formation of active complexes Bi – amino acids.

Based on literature, it is well-known, that the cystine (RSSR) is electrochemically active and in aqueous solutions it reacts with mercury forming cysteine mercuric thiolate $Hg(SR)_2$ and cysteine mercurous thiolate $Hg_2(SR)_2$, which are both strongly adsorbed at the electrode [22,23]. The multistep Bi(III) electroreduction process is controlled by the kinetics of the formation of active Bi – $Hg(SR)_2$ complexes preceding the transfer of consecutive electrons. Cystine is a mediator in the formation of these complexes, which are located inside the adsorbate layer [21]. This kind of mechanism explains the catalytic role of cystine in the investigated system.

The changes of $\Delta H^{\neq}$ for Bi(III) electroreduction in the presence of cystine with the increase of chlorates (VII) concentration point that the mechanism is different in solutions with low water activity as compared to those with high water activity. Probably it is connected with a different structure of the activated complexes (Bi – $Hg(SR)_2$), mediating electron transfer what was suggested before [21]. The obtained regularities confirm as well the changes of the values of the standard reaction entropy (ΔS^0) for the reduction of Bi(III) in the presence of cystine.

As water activity decreases, the contribution of H_2O molecules to the adsorbate layer declines, which facilitates the deposition of Bi-$Hg(SR)_2$ complexes in this layer. After exceeding a certain limit of activity (6–8 mol dm^{-3} chlorate(VII) solutions), there is practically no further acceleration of the process of Bi(III) electroreduction in chlorates(VII) by cystine. This indicates that H_2O molecules and Bi-$Hg(SR)_2$ complexes compete in the deposition of the near-electrode layer and that the composition of active complexes depends on water activity.

Similar regularities were obtained in the system Zn(II)/ $NaClO_4$ – DMSO – H_2O in the presence of thiourea [17].

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