Polish J. Chem., **75**, 1493–1504 (2001)

Influence of the Silver Electrode Surface Structure on Electrochemical Adsorption of Thiourea in Perchloric Acid Solution

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(Received April 9th, 2001)

Electrosorption of thiourea (TU) on single crystal electrodes: Ag(111), Ag(100) and Ag(110) was studied using electrochemical and radiochemical methods. A radiotracer method, with TU labeled with C-14 in 0.1 M $HClO_4$, was used to determine the surface concentration of the adsorbate. From radiometric data it follows that adsorption of TU is reversible with respect to the bulk concentration and the potential in the range of ideal polarizability of electrodes. The maximum surface concentration of TU, determined radiometrically, follows the sequence: Ag(111) > Ag(100) > Ag(110), which is in agreement with the atom surface density of the silver planes. The simple Langmuir adsorption equation describes experimental data up to 80% of surface coverage. The Gibbs energy of adsorption is similar (25.5 ± 1 kJ/mol) for all planes studied.

Key words: silver electrode, monocrystalline, thiourea, adsorption, radiometry

Thiourea (TU) is often used in electrochemistry as a brightener and levelling additive in the deposition of metals [1,2]. It is also known as an inhibiting and depolarizing agent in many electrochemical processes. In the fundamental electrochemistry TU is used as the probe dipole to evaluate the electrostatic parameters of the inner double layer structure of metal – solution interface [3]. Hence, there are many papers dealing with the adsorption of TU on different metals. The electrosorption of TU on polycrystalline silver electrode was studied using various methods like cyclic voltammetry, surface enhanced Raman spectroscopy (SERS) [4–11] differential capacity measurements [6,12], and radiometric methods [14–15].

Macomber and Furtak [4] found that TU is bound to the surface of Ag electrode through the sulphur end. The intensity of the C=S mode (715 cm^{-1}) increases as the potential becomes more negative, however, its influence is inconsistent with a simple charge-transfer mechanism. El Hajbi *et al.* [5] studied the SERS spectra in acidified sulphate media (pH = 2) and noticed that in the potential range 0.0 ÷ –0.4 V *vs* SCE the Raman signals arised from insoluble silver complexes, whereas at more negative range the spectra of adsorbed TU and sulphates anions occurred. The influence of roughening of electrodes in sulphate or chloride media on the SERS spectra was ob-

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served. The coadsorption of TU and ClO_4^- ion was observed by Tian *et al.* [6]. The study of TU adsorption in acidic and neutral solutions showed a different orientation of adsorbed molecules. In neutral solution the evolution of hydrogen on silver electrode is catalysed by TU molecules parallely adsorbed to the surface, whereas in acid media H_2 evolution is inhibited by TU molecules adsorbed perpendicularly. Kim [7] observed a strong SERS band of TU in the acidic solutions, where protonation of NH_2 groups and coadsorption of anions enhance the surface stability of TU. In contrast only a weak SERS signals in neutral media were observed. The influence of TU on H_2 evolution at silver electrode was studied by Bukowska and Jackowska [8] by electrochemical and SERS methods. The previous observation [6] of catalytic and inhibiting effects of TU adsorption on H_2 evolution in neutral and acid media, respectively, was confirmed. However, no evidence of reorientation of TU molecules, perpendicularly oriented to the silver surface in perchloric acid solution was found. Also, no evidence of the protonation of NH_2 groups in acidic TU solution was observed. It was concluded that the inhibiting effect of H_2 evolution in perchloric acid solution is due to thiourea adsorbed at Ag electrode, which interacts with ClO_4^- ions through NH_2 groups. Reents *et al.* [9] confirmed the potential-dependent TU adsorption and ClO_4^- coadsorption, but no evidence for the adsorption of Ag–TU complexes, regardless of TU bulk concentration, was found. Joy and Srinivasan [10] studied the SERS spectra of TU and some substituted thioureas adsorbed on silver films and observed, in all these systems, a strong band assigned to Ag–S stretch. The frequencies and bandwidths of benzene ring were unaffected by adsorption, which indicates that the benzene ring does not interact with the silver surface. Yao *et al.* [11] observed the time-dependent SERS spectra of TU and ClO_4^- coadsorbed on silver electrodes. After polarization to very negative potential (–2.0 V) all band intensities show the fast response characteristics. This was explained in terms of co-existence of two types adsorption sites, neutral and partially charged Ag atoms. It reveals the nature and structural dynamics of adsorption sites formed by chemical interaction.

Miłkowska [12] measured the differential capacity of a polycrystalline silver electrode in aqueous KF solution containing TU. The experimental adsorption isotherm can be described by the Frumkin model of adsorption. The isotherm parameters (the saturated concentration of TU and Gibbs energy of adsorption) as well as the inner layer parameters (dielectric constant and inner layer thickness) were determined [13].

The adsorption of TU on silver electrode was studied by radiometric method, too. Horanyi *et al.* [14] found that in the range of potential, where neither hydrogen evolution nor the oxidation of silver electrode occur, the adsorption process of TU is reversible with respect to the potential. The mobility of adsorbed TU was demonstrated by the exchange of labeled TU with non-labeled species added in great excess to the solution. Szklarczyk *et al.* [15] studied the adsorption of TU on rough silver electrode in acidic and neutral solutions of perchlorates. From the plot of surface concentration *vs* electrode potential it was concluded, that near the onset of silver oxidation potential the reorientation of TU molecules from perpendicular to parallel occurs. The drop of the surface concentration of adsorbed TU labeled with C-14 at potentials close to Ag oxidation was observed, which was caused likely owing to the blocking of the electrode surface by products of TU decomposition containing sulphur.

The above review shows that the influence of various agents on the mechanism of TU adsorption on silver electrode is not satisfactorily clear, as yet. In this work the results of TU adsorption on monocrystalline silver electrodes, studied by electrochemical and radiometric methods, are presented. Though the radiometric method cannot give the information about the structure of adsorbed species, however, it allows to observe the number of adsorbed molecules on the electrode surface. As far as we know, the influence of the silver electrode surface structure on the TU adsorption has not been studied yet.

EXPERIMENTAL

Materials: All reagents were of analytical grade and prepared from ultra pure water obtained from a Millipore system. The measurements were carried out at ambient temperature (*ca.* 20°C) and in 0.1 M $HClO_4$ as a supporting electrolyte. Thiourea labeled with carbon-14 (β^- emitter, maximum energy 0.156 MeV) of specific activity 20 mCi/mmol (Amersham), diluted to an appropriate concentration, was used. The Ag | AgCl | 1M Cl^- electrode was applied as a reference electrode in all experiments.

Electrode preparation: The poly- and monocrystalline silver electrodes as discs of 1.25 cm in diameter ($S = 1.23$ cm^2) were prepared in the Crystal Growth Laboratory of the Institute of Atomic Energy, Poland. The orientation of monocrystalline electrodes (±0.5°) was checked by neutron scattering. The cleaning procedure of the electrodes was described in detail, previously [16]. After the cleaning, the electrode was immediately transferred to the electrochemical cell under protection of a drop of water. The real surface area of the electrode was determined in two ways: (i) from the charge involved in the underpotential deposition (upd) of Pb on Ag electrodes and (ii) from the voltammetric curves taken for differ-

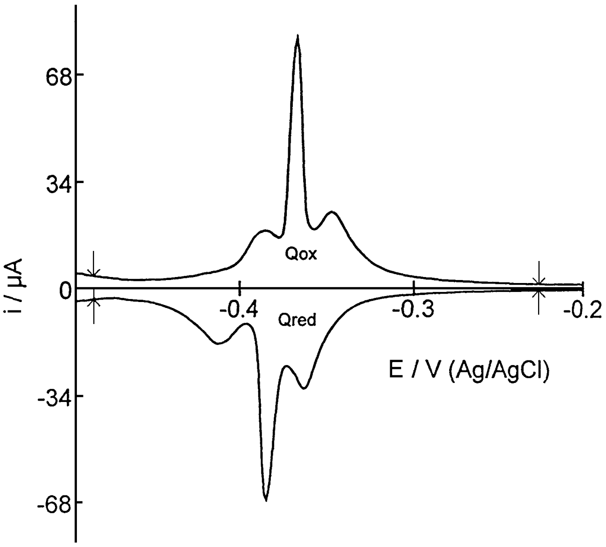

Figure 1. The upd of Pb on Ag(111) electrodes. Solution: 0.1 M $HClO_4 + 10^{-3}$ M Pb^{2+}. $Q_{red} = Q_{ox} = 407 \pm 15$ μC. The roughness factor: $R = (407 \pm 15)/(302\times1.23) = 1.10\pm0.04$.

ent scan rates, in the double layer range of potential. The obtained voltammetric curves on individual planes of Ag electrodes in the presence of Pb^{2+} in the solution were similar to those reported in [17,18] and they proved that monocrystalline Ag electrodes used in this study were properly prepared. It was assessed that if the atoms deposited are larger in size than the atoms of the substrate, a close packed monolayer is formed, independently of the substrate surface structure [19]. This is the case for Pb deposited on Ag. As an example, the run of voltammetric curve for the Ag(111) face in the presence of Pb^{2+} ions in the solution is given in Fig. 1. It is seen that the process of upd is reversible. The charge of Pb monolayer deposited on Ag(111) electrode is equal to 302 $\mu C/cm^2$ [18]. Hence, the real electrode surface area and the roughness factor (*i.e.* the ratio of the real to the geometric areas of the electrode) can be easily estimated. A similar procedure was used for other monocrystalline Ag electrodes. The voltammetric curves, taken for different scan rates *v*, in the double layer range of potentials, for Ag(111) electrode given as an example, are presented in Fig. 2. From the *i vs v* plot (see insert) the total capacity of the electrode can be calculated. Assuming that the differential capacity of the double layer per 1 cm^2 is equal to 28 $\mu F/cm^2$ [20], the real area of the electrode surface was estimated. Both procedures give similar results. The same procedures were used for all studied silver electrode planes. The roughness factor of the electrodes was calculated as 1.1 ± 0.05. The inaccuracy of the roughness factor determination is the main source of error in the surface concentration calculation.

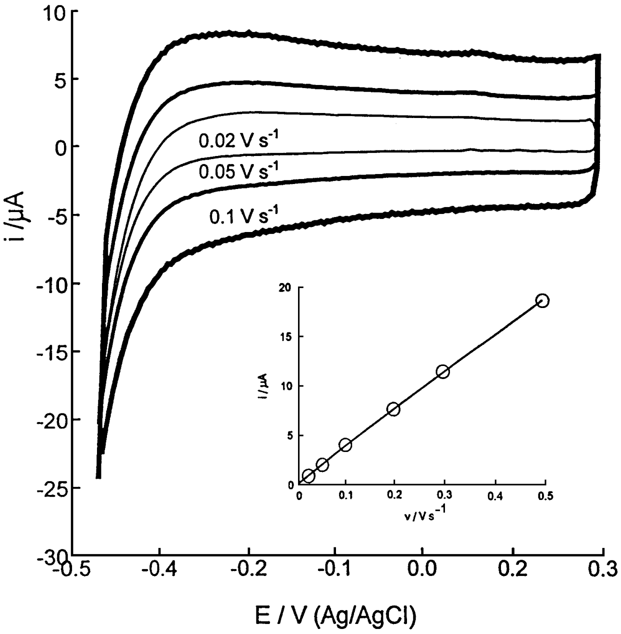

Figure 2. The voltammetric curves of Ag(111) in 0.1 M $HClO_4$ at different scan rates. Only 3 cv curves are shown for the sake of clarity. Insert: *i vs* v at –0.1 V. di/dv = dq/dE = C = 37±1 μF. R = 1.07±0.03.

Methods: Two methods were used for the adsorption study: cyclic voltammetry, to characterize the surface state of the electrodes, and radiometry to determine the surface concentration of thiourea. The voltammetric measurements were restricted only to the range of potential, where no oxidation of the silver surface occurred. The hanging-meniscus contact technique described by Dickertmann *et al.* [21] was used. The modified radiometric method, called *electrode lowering method* [22], was applied. The disc-shape electrode was placed into the cell, in the bottom of which the glass scintillator as a radiation detector was fixed. To the supporting electrolyte (0.1 M $HClO_4$) a desired amount of thiourea solution, labeled with carbon-14, was added. The counting rate was measured when the electrode was far from the detector and then after pressing it down towards the detector. In the first step only the counting rate from solution, while in the second step the counting rate from adsorbed species and from the thin layer of the solution between the electrode and the detector, are measured. The method was described in [23].

The surface concentration of adsorbed species can be calculated from [22,23]:

$$\Gamma = \frac{N_a}{N_b} \frac{cN_{AV}}{\mu_s R f_b \exp(-\mu_s x)}$$

where: N_a – the counting rate from adsorbed species, N_b – the counting rate when the electrode is far from the detector, c – the bulk solution concentration of the adsorbate, mol cm^{-3}, N_{AV} – Avogadro's constant, μ_s – the linear attenuation coefficient of the β^- radiation in water (300 cm^{-1} for ^{14}C [24]), f_b – the backscattering factor, calculated from Zumwalt relationship [22], (for Ag equal to 1.69), R – the roughness factor of the electrode, x – the thickness of the solution layer between the electrode and the detector, cm.

The error in Γ determination is due to systematic errors (μ_s, R, f_b) as well as random errors (N, c, x). The absolute values of Γ are determined with accuracy about 10% ÷ 15%.

RESULTS AND DISCUSSION

The voltammetric curves recorded for three basal planes and polycrystalline silver electrodes in 0.1 M $HClO_4$ are shown in Fig. 3.

The lowest onset potential of hydrogen evolution can be observed for Ag(111) and the highest for Ag(110). The silver activity for hydrogen ions discharge decreases in the sequence Ag(111) > Ag(poly) > Ag(100) > Ag(110), which is consistent with the Ag surface atom concentration on the individual planes (see Table 1). An addition

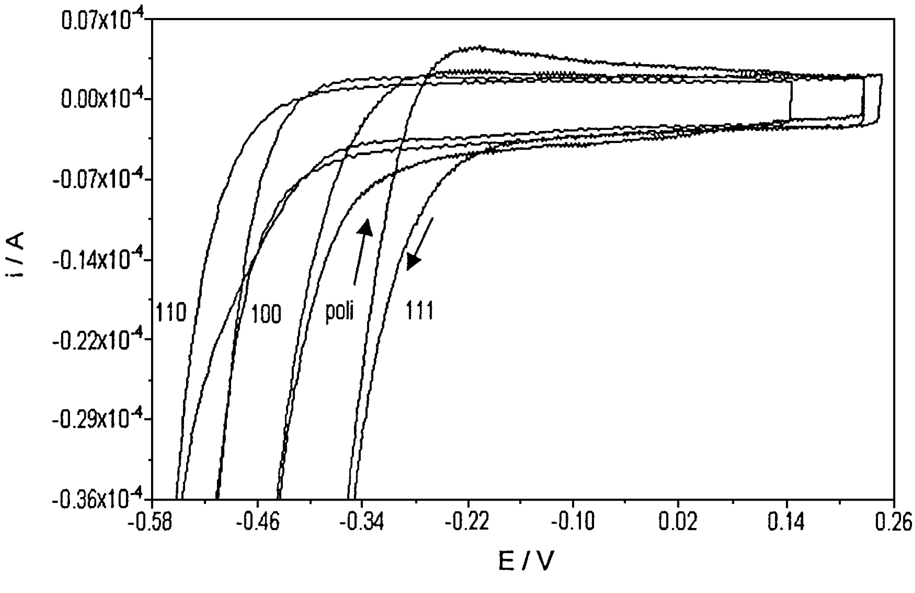

Figure 3. The voltammetric curves of silver electrodes. Solution: 0.1 M $HClO_4$, ν = 0.1 V/s.

of TU causes the appearance of the oxidation and reduction peaks on the voltammogram. An example for Ag(110) is shown in Fig. 4.

Table 1. Thermodynamic parameters of TU adsorption on Ag electrodes.

	Ag(111)	Ag(100)	Ag(110)
10^{-15} σ_{Ag}/atom cm^{-2}	1.388	1.202	0.850
10^{-14} Γ_{max}/molec cm^{-2}	6.0±0.5	4.6±0.4	3.9±0.4
σ_{Ag}/Γ_{max} atom molec^{-1}	2.4±0.2	2.6±0.2	2.2±0.2
10^{-3} β_L/dm^3 mol^{-1}	24.2±0.3	50.2±0.4	36.7±0.4
ΔG^o_L/kJ mol^{-1} (293 K)*	–24.6±0.5	–26.4±0.5	–25.6±0.5

σ_{Ag} – surface atom density.
*The standard state: $\Gamma^o = 0.5\ \Gamma_{max}$, $c^o = 1$ mol dm^{-3}.

The higher bulk concentration of TU the greater the inhibition of hydrogen evolution and the higher the current of anodic oxidation of TU, which is common for all Ag planes investigated. Similar effects in acidic solution were observed earlier for polycrystalline electrode [6,8,15]. Comparing the data for different planes of Ag electrodes we found that the most active one, in respect to TU oxidation, is Ag(111). This phenomenon is likely related to the highest surface density of Ag atoms of this plane. The potential ranges of ideal polarizability of Ag electrodes were as follows: –0.2 V ÷ +0.25 V, –0.40 V ÷ +0.23 V, –0.44 ÷ +0.15 V and –0.30 V ÷ +0.23 V for Ag(111), Ag(100), Ag(110) and Ag(poly), respectively. The further experiments on

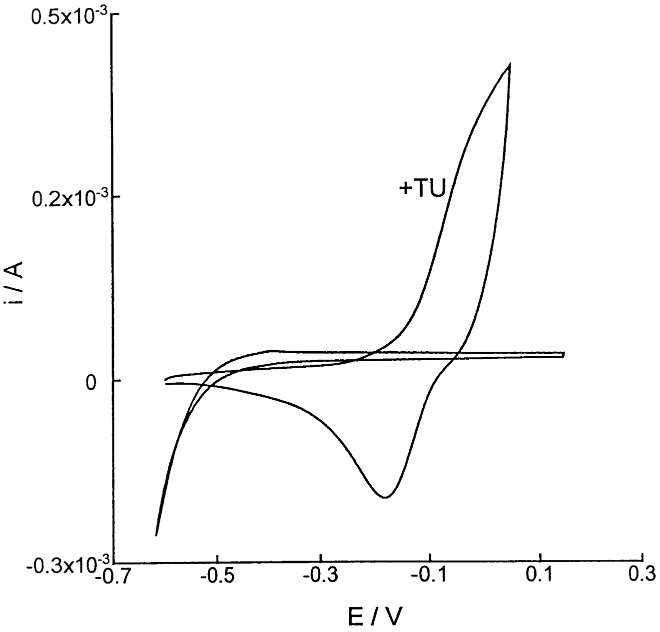

Figure 4. The influence of thiourea (10^{-3} M) on the voltammetric curve of the (110) silver electrode.

TU adsorption on Ag electrodes were restricted only to the range of potential, where neither the H^+ reduction nor the TU (or surface) oxidation occurred.

To examine the reversibility of adsorption, potentiostatically controlled surface-to-bulk exchange experiments were carried out. After the adsorption was completed, the 100-fold excess of nonlabeled TU was added to the solution. The procedure was described in [25]. The exchange process of labeled TU by nonlabeled one leads to the displacement of as much as 95% of the labeled surface species (Fig. 5).

Hence, the adsorption can be considered as reversible with respect to the bulk concentration of thiourea, though a small amount of thiourea may still exist on the electrode surface. It should be noted that during anodic-cathodic polarization of TU labeled with C-14 and S-35 on the gold electrode [26], the TU molecule is partly decomposed at the anodic range of potential. However, during cathodic cycle, the product of destruction labeled with C-14 is easier desorbed than the one, labeled with S-35. It means that a small part of chemisorbed product of TU, containing sulphur, can remain on the electrode surface even at cathodic polarization. Adsorption of TU on all silver surfaces takes place in the entire range of the potential of ideal polarizability of Ag electrodes. The surface concentration of TU increases with the potential rise (Fig. 6).

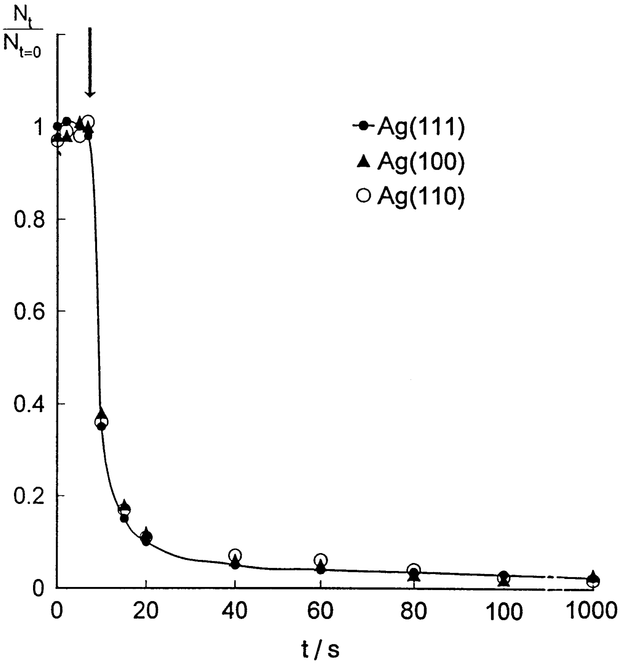

Figure 5. The exchange of adsorbed TU species by the TU molecules from the bulk of the solution. Solution: 0.1 M $HClO_4 + 5\cdot10^{-5}$ M TU. The arrow shows the moment of addition of nonlabeled TU solution to the cell in 100-fold excess. N_t – the counting rate, $N_{t=0}$ – the counting rate at the moment of addition of nonlabeled TU.

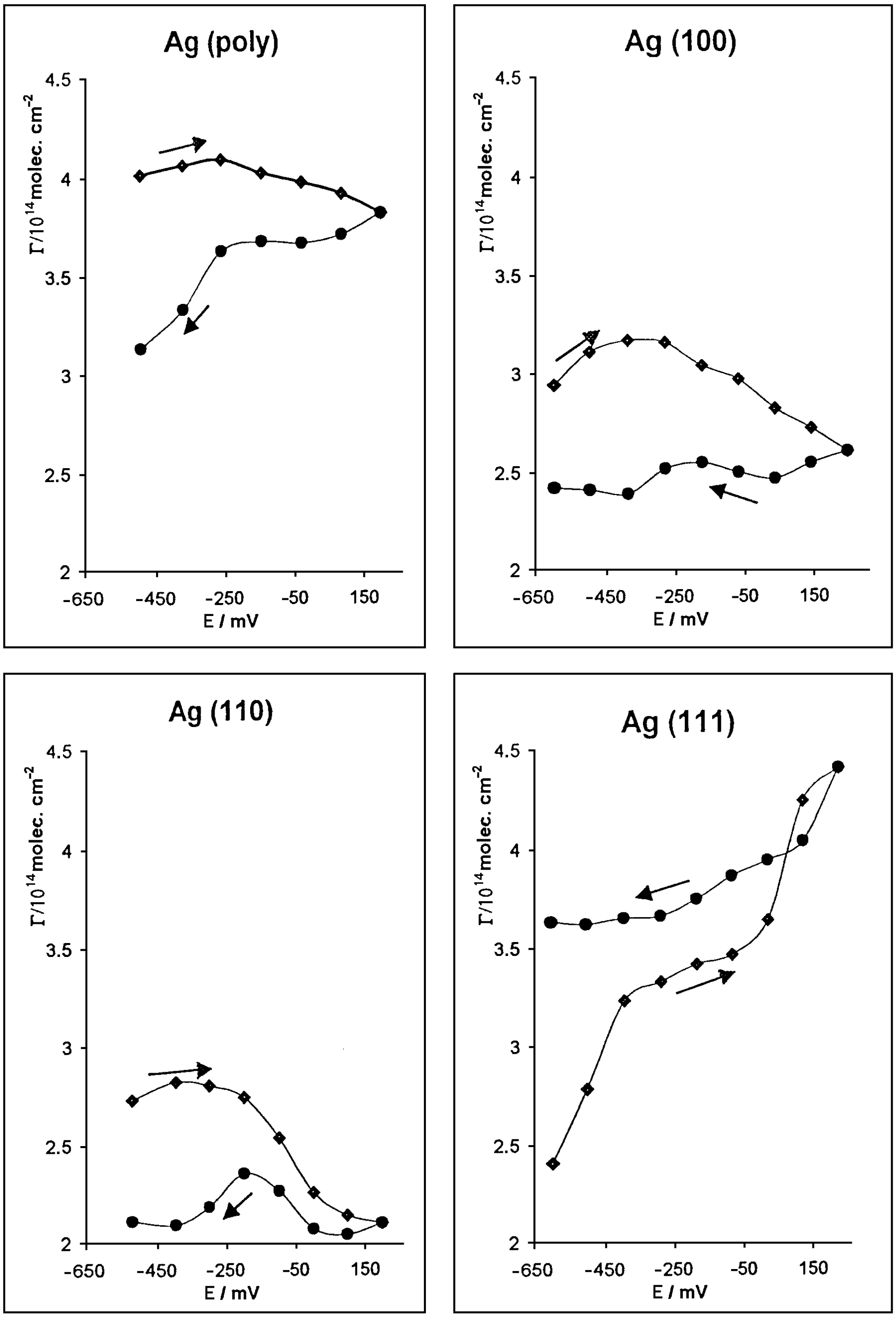

Figure 6. The dependence of TU surface concentration on the electrode potential. Solution: 0.1 M $HClO_4$ + 10^{-5} M TU.

The dependence Γ *versus E* is different for every plane of the Ag electrode. The hysteresis is likely due to the slight oxidation of the surface, which is not visible on voltammograms owing to the lower sensitivity of cv than the radiometric method. The isotherms of TU adsorption obtained by radiometric measurements, at –0.2 V *vs* Ag | AgCl electrode, are presented in Fig. 7.

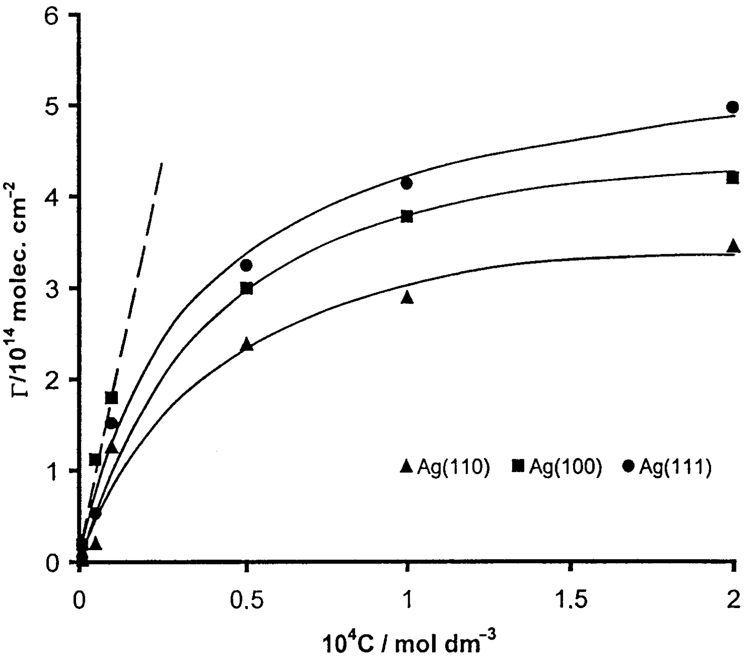

Figure 7. The isotherms of TU adsorption for Ag(111), Ag(100) and Ag(110). Points represent the experimental data, solid lines were calculated using the isotherm parameters given in Table 1. Solution: 0.1 M $HClO_4$, E_{ads} = –0.2 V.

Taking into account the fact that adsorbed TU molecules are easily exchanged by TU molecules from the bulk, *i.e.* the adsorption process is generally reversible, the data presented in Fig. 8 were inspected by fitting several isotherms. The linear test of Frumkin isotherm, ln $\Gamma/[(\Gamma - \Gamma_{max})c]$ *vs* Γ/Γ_{max}, often used for describing the adsorption process, is nearly parallel to the Γ/Γ_{max} axis, which means that the interaction coefficient is close to zero. Hence, the Langmuir isotherm in the form:

$$c/\Gamma = 1/(\beta_L\Gamma_{max}) + c/\Gamma_{max}$$

was used to fit the experimental data. The plots of c/Γ *vs c* are presented in Fig. 8. From the slopes of the plots c/Γ *vs c* and the intercepts of the ordinate, the values of Γ_{max} and the adsorption equilibrium constants β_L have been calculated, respectively. The pertinent data are given in Table 1.

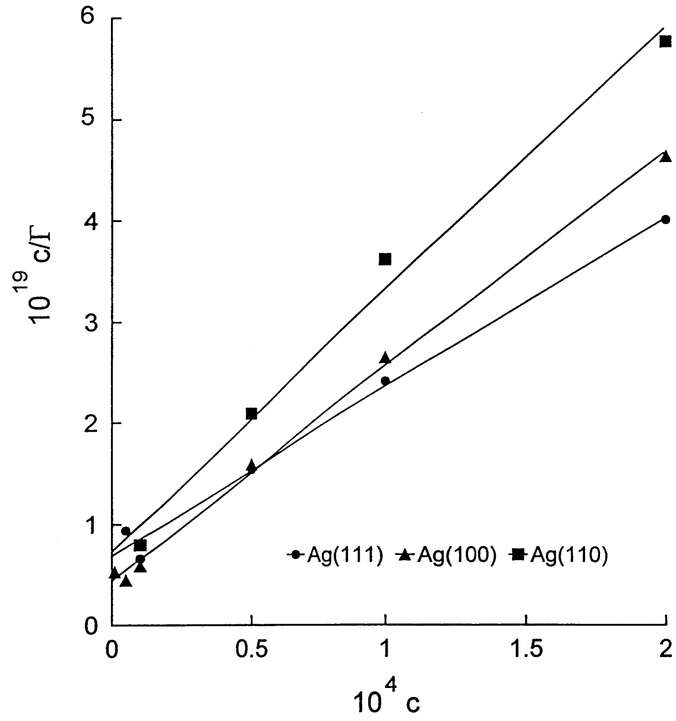

Figure 8. The plots of $1/\Gamma$ *vs* $1/c$ to determine the values of Γ_{max} and equilibrium constant β. The values of thermodynamic parameters of adsorption process are given in Table 1.

From these data it follows that the number of adsorbed TU molecules is proportional to the surface concentration of silver atoms. Though the Γ_{max} values are different for each plane of Ag electrodes, the ratio of the surface density of Ag atoms and the number of TU molecules is near the same for all planes of the electrodes and amounts to *ca.* 2 ÷ 3. It means that two or three atoms of Ag bound one TU molecule. It is worth to note that Ag^+ ion in the solution bounds three or even four TU molecules, which replace the water molecules from the coordination sphere of Ag^+ ion [27].

From the β values, the Gibbs energies, ΔG^o, of TU adsorption on the individual planes of Ag electrodes were calculated (see Table 1). The values of the Gibbs energy differ slightly for each electrode studied. Since the experimental ΔG includes the energy of water desorption from the surface, the observed small differences of ΔG can be caused by the different hydrophilicity of the Ag planes. For low bulk concentration of TU and thus the small surface coverage of the electrodes, the Henry isotherm, $\Gamma = \beta c$, can be used for β and ΔG evaluation. As it is seen (Fig. 7 – dashed line), the slope of Γ *vs* *c* is similar for all planes of Ag electrodes, which means that β_H and thus ΔG_H do not differ essentially for all planes studied. The maximum surface concentration of TU for closed-packed monolayer can be estimated from the cross-section area of TU obtained from crystallographic data [28]. Assuming the rigid structure and perpendicular orientation of the molecule with sulphur atom towards the electrode surface, the calculated Γ_{max} equals $6.1 \cdot 10^{14}$ molec·cm^{-2}. The experimentally determined Γ_{max} for Ag(111) is nearly equal to the calculated one and indicates the perpendicular orientation of TU on this plane. For Ag(100) and Ag(110) the Γ_{max} values are lower and for these planes a parallel or tilted orientation of TU molecules towards the electrode surface is possible. The SERS data show that the coadsorption of ClO_4^- with TU molecules is possible. The comparison of Γ_{max} with the ClO_4^- ion size indicates that the latter cannot be coadsorbed besides the TU molecule. However, the coadsorption of ClO_4^- ions on the top of TU molecules layer is possible.

Some experiments were performed also for higher ($>2\times10^{-4}$ M) TU concentrations. The data, presented for Ag(111) electrode as an example (Fig. 9), show that the surface concentration of TU increases above the Γ_{max} given in Table 1. Likely, in such a case a multilayer adsorption of TU molecules occurs.

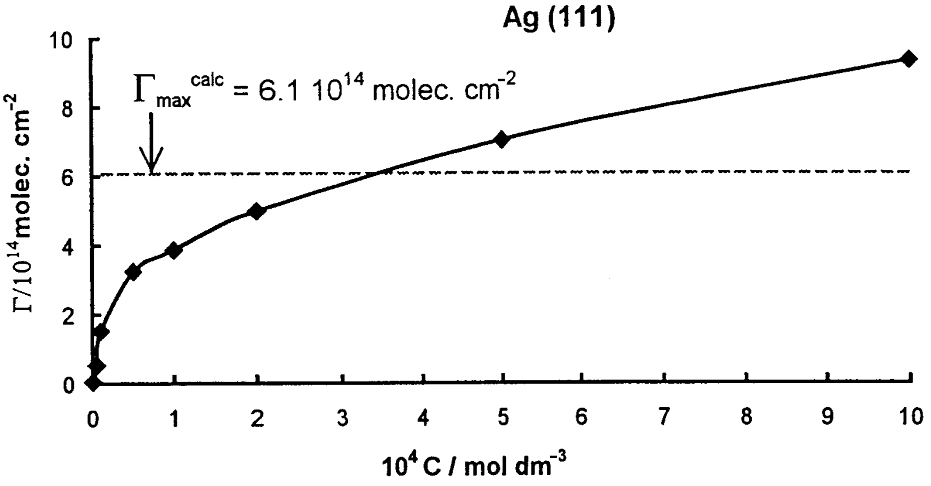

Figure 9. The bulk-concentration dependence of TU adsorption on Ag(111) electrode. The dashed line represents the calculated maximum surface concentration.

The main conclusions of the electrochemical adsorption of TU on monocrystalline silver electrodes are:

(*i*) The surface activity of silver monocrystalline electrodes in respect to hydrogen evolution and TU oxidation increases in the sequence: Ag(111) > Ag(poly) > Ag(100) > Ag(110) and is related to the atom surface density.

(*ii*) The energy of interaction of TU molecules with adsorption sites on Ag electrodes is slightly dependent on the surface structure; it can be connected with the different hydrophilicity of the electrode planes.

(*iii*) The maximum surface concentration of TU on individual planes of Ag electrodes depends on the number of adsorption sites (Ag atoms) on the surface. TU molecules on Ag(111) surface are perpendicularly oriented, whereas on Ag(100) and Ag(110) they are parallel or tilted in respect to the electrode surface.

(*iv*) For higher solution concentration of TU a multilayer adsorption of TU on the electrode surface is possible.

Acknowledgment

This work was financially supported by the Polish State Committee for Scientific Reasearch under grant number 3 T09A 067 17.

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