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The Comparison of Electrochemical and Radiochemical Methods in Adsorption Study of Thiourea on the Polycrystalline Silver Electrode in Neutral Solution*

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Radiometry and impedance spectroscopy have been compared in the study of thiourea (TU) adsorption on polycrystalline silver electrode. Differential capacity of silver electrode in 0.01 M $NaClO_4$ solution containing TU of concentrations from 10^{-6} to 5×10^{-4} M has been measured. The isotherms of TU adsorption, θ *vs* c determined from the capacitance and radiometric measurements have been compared and the Gibbs energy of adsorption was calculated. The experimental data were described by the Langmuir isotherm. The radiometric method allowed us to determine the surface concentration of TU. It was found that TU adsorption takes place in the entire range of the applied potential. The process of adsorption is reversible with respect to the electrode potential and the bulk concentration of TU, though the desorption process is not completed and small amounts of TU remain on the surface of Ag electrode.

Key words: adsorption, thiourea, silver electrode, radiometry, impedance spectroscopy

The aim of this work was to compare the electrochemical and radiometric methods in the study of adsorption of thiourea on the silver electrode. The link between the surface excess of the adsorbed species determined by thermodynamic and radiotracer methods has been discussed although the conclusions were different [1,2]. The surface excess of sulphate ions on the monocrystalline gold electrode Au(111) were determined from the charge density data and compared with the data of radiochemical measurements using ^{35}S-labeled sulphate solution. A good agreement of the obtained results by the two methods was reported [3]. The problem of surface concentration determination by radiometric method was the subject of some controversial opinions [4,5].

Numerous works deal with the adsorption of thiourea on silver electrodes because of its practical application and interesting behaviour in the study of metal/solution interface. The review of the literature on the subject was given previously [6].

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

The described earlier impedance [7] as well as the radiometric [8] measurements of thiourea adsorption were carried out on polycrystalline silver electrode under the same experimental conditions to be able to compare the results obtained by both methods.

EXPERIMENTAL

Materials: All reagents were of analytical grade. Solutions were prepared from ultra pure water obtained using Millipore system fed with twice distilled water and boiled off to a third of its initial volume to remove traces of organic impurities. The specific resistivity of water was at least 18.2 MΩ cm. Its purity was verified with a GC-MS system. The experiments were carried out in $NaClO_4$ solution deaerated with purified nitrogen at ambient temperature. The Ag| AgCl, 1 M Cl^- electrode was used as a reference electrode in all experiments.

Thiourea was labeled with carbon-14 (β^- emitter, E_{max} = 0.156 MeV) of specific activity 20 mCi/mmol (Amersham).

Electrode preparation: The surface of polycrystalline silver electrode**,** in the form of disc of 1.25 cm in diameter, was prepared using a variety of polishing grits and diamond pastes from 30 to 0.25 μm in grain size (Buehler) followed by chemical treatment described earlier [9]. After the cleaning, the electrode was immediately transferred to the electrochemical cell under protection of a drop of water to avoid the contact with air. The proper run of the voltammetric curve was the test of cleanness of the electrode and solution. In all voltammetric experiments, meniscus-contact technique [10] was employed.

The real surface area of silver electrode was estimated from the double layer capacitance (C) calculated from the scan rate (v) dependence of voltammetric current (i) at constant potential (E) ($C = (i/v)_E$) and from the charge involved in the upd of Pb on silver electrode. The detailed description of both methods was given elsewhere [6]. The roughness factor of Ag electrode used in experiments was equal to 1.15±0.05.

Methods: Two methods were applied for the study of TU adsorption, *i.e.*, impedance spectroscopy (i) and radiometry (ii).

(i) The impedance was measured at frequencies from 1 to 100 Hz in 25 mV steps using an AUTOLAB electrochemical system equipped with a frequency response analyzer (FRA, ECO Chemie, Netherlands). The applied potential was limited only to the range of ideal polarizability of the electrode to avoid the silver surface oxidation. Silver oxide cannot be reduced electrochemically [11].

The impedance spectrum is described by the equation [12]:

$$Z(\omega) = R_S + [R_F + Y_{CPE}]^{-1} \tag{1}$$

where Y_{CPE} is the admittance defined as:

$$Y_{CPE} = Q_a(j\omega)^n \tag{2}$$

where Q_a is constant, $j = \sqrt{-1}$, ω – angular frequency, R_S – ohmic resistance of the solution, R_F – faradaic resistance and n is a fractional exponent. For $n = 1$ $Y_{CPE} = j\omega C_d$, where C_d is a double layer capacitance. The term $Y_{CPE}^{-1} = Q_a'(j\omega)^{-n}$ is called the constant phase element. The origin of *CPE* behaviour at the interface has been the subject of discussions and may be a result of several phenomena, such as roughness and heterogeneity of the electrode surface, concentration of the solution *etc.* [13]. In the absence of faradaic process $R_F \approx 0$ and

$$Z(\omega) = R_S + Q_a'(j\omega)^{-n} \tag{3}$$

Because the capacitance is independent of time, so if the fractional exponent $n < 1$, the impedance spectra deviates from the capacitive behaviour and $Q_a^{'}$ cannot be identified with the capacitance. However, when $n > 0.9$ the measurement errors are greater than the error of approximation and $Q_a^{'} \approx C_\mathrm{d}$ [12]. It should be noticed that the impedance diagram Z'' *vs* Z' for solid electrodes is often complex because the part of energy can be dissipated [13].

(ii) A radiometric thin gap method [5] (called also the „electrode lowering method" [4]) was used to determine the surface concentration of the adsorbate.

The disc-shaped electrode was placed in the cell, in the bottom of which the glass scintillator as a radiation detector was fixed. A desired amount of thiourea solution, labeled with C-14 was added to the supporting electrolyte (0.01 M $NaClO_4$). The counting rate was measured when electrode was far from the detector, and then after pressing it down towards the detector. In the first case, only the counting rate from the solution alone is measured. In the second case the measured signal corresponds to the counting rate from the adsorbed species on the surface of the electrode and from the thin layer of the solution trapped between the electrode and the detector. The surface concentration of the adsorbate in molec.´cm-2 was calculated from the equation [14]:

$$\Gamma = \frac{N_a}{N_b} \frac{10^{-3} c N_A}{\mu R f_b \exp(-\mu x)} \tag{4}$$

N_a and N_b denote the measured counting rates from the labeled compound on the surface of the electrode and the bulk of the solution, respectively, c – the bulk concentration of the adsorbate in mol dm^{-3}, N_A – the Avogadro number, R – the roughness factor of the electrode, f_b – the backscattering factor of β^- radiation, μ – the linear absorption coefficient of β^- radiation in the solution in cm^{-1} and x is the distance between the electrode and detector (the gap) in cm.

The counting rate coming from the solution trapped in the gap has to be taken into account. It can be determined by counting rate in the potential range where no adsorption occurs or when the labeled adsorbate at the electrode surface can be displaced by the non-labeled one. When such conditions are not fullfiled (*e.g.* in the case of irreversible adsorption) the calibration procedure has to be done. In this work we used the solution of $Na_2^{14}CO_3$ of the same specific activity as studied $(NH_2)_2^{14}CS$. The CO_3^{2-} ions are not adsorbed on the silver electrode surface.

The backscattering factor f_b accounts for β^- radiation reflected by the electrode back towards the scintillator. Its value depends on the kind of the metal and can be calculated from the empirical formula (see *e.g.* [14]):

$$f_b = 2 - \exp(-Z/40) \tag{5}$$

where Z is the atomic number of a metal. For silver it is equal to 1.69 and differs slightly from f_b determined experimentally (1.81 [5]). The gap thickness can be estimated from the equation (6), assuming that there is no adsorption on the electrode surface:

$$\frac{N\downarrow}{N\uparrow} = [1 - \exp(-\mu x)][1 + (f_b - 1)\exp(-\lambda x)] \tag{6}$$

where N$\downarrow$ and N$\uparrow$ denote the downward (lowered) and upward position of the electrode to the radiation detector, respectively. The value 1 - N$\downarrow$/N$\uparrow$ is called squeezing efficiency [14]. λ is the linear absorption coefficient of the backscattered radiation. Because the energy of backscattered radiation is lower than that coming directly from the radionuclide the absorption coefficient λ is higher than μ. It can be calculated from the empirical formula [14]:

$$\lambda = \mu \frac{225}{106 + Z} \tag{7}$$

where Z is the atomic number of the metal. The absorption coefficient of ^{14}C radiation in water is $\mu = 300$ cm^{-1} [15] while the value of λ ($Z_{Ag} = 47$) is equal to 441 cm^{-1}. The relation between the squeezing efficiency and the gap thickness for silver and β^- radiation of ^{14}C is shown in Fig. 1.

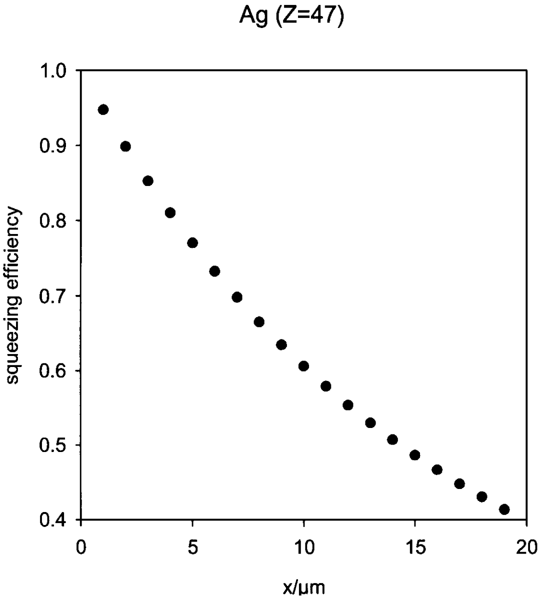

Figure 1. The squeezing efficiency, $1 - N{\downarrow}/N{\uparrow}$ for $^{14}C\ \beta^-$ radiation and Ag. x – thickness of the gap.

It can be seen that the smaller the gap the better accuracy of the adsorption measurement. The errors in the estimation of the values of parameters in equations (4) and (6) as well as the semiempirical character of formulas (5) and (7) make the uncertainty of Γ determination not lower than 10%.

RESULTS AND DISCUSSION

The electrode potential at open circuit, after addition of thiourea to 0.01 M $NaClO_4$ solution, practically does not change, in the concentration range studied in this work, which means that there is no reactions at the electrode surface.

The voltammetric curves for increasing concentration of thiourea are presented in Fig. 2. From the data of Fig. 2 it follows that thiourea acts as a catalyst for hydrogen ions discharge in neutral solution. This effect was observed earlier [16,17] and explained by the formation of hydrogen bonds between $-NH_2$ in thiourea and water molecules which mediate the proton discharge at the surface of the electrode. The range of so called – ideal polarizability – decreases with increase of thiourea concentration.

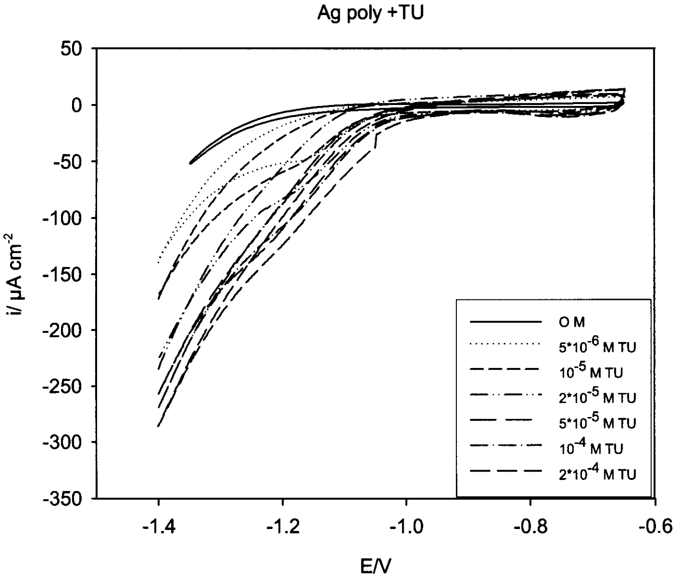

Figure 2. The voltammetric curves of silver electrode for different TU concentrations.

(i) Impedance measurements. Typical impedance spectra for Ag in 0.01 M $NaClO_4$ solution and with addition of TU for the frequency range 1–100 Hz at –0.93 V, considered as the potential of zero charge (*pzc*) [18], is presented in Fig. 3.

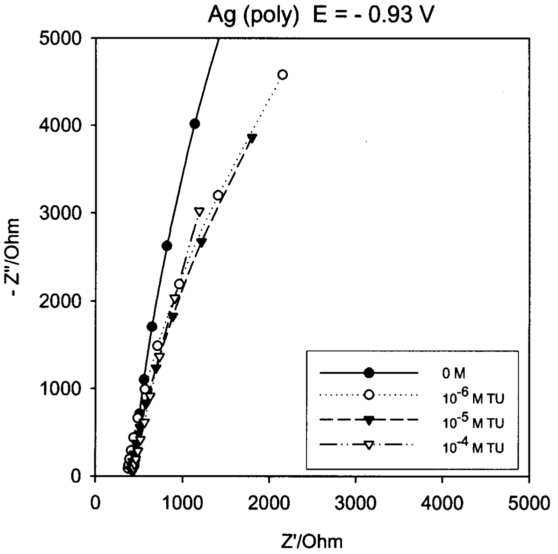

Figure 3. Complex plane plots for Ag electrode with addition of TU at E = –0.93 V.

As it can be seen, the plots Z′′ *vs* Z′ show downward bending rather than straight lines even for the supporting electrolyte. This means that the system has *CPE* behaviour. The smaller angle values were observed at the negative potentials, where faradaic processes are more pronounced (see Fig. 2). The experimental results were fitted employing $R_S - CPE$ with parallel R_F as the equivalent circuit and the values of n and Q_a were calculated from experimental data using ZView for Windows, version 1.8 software. The value of n is practically independent of the electrode potential in the region of ideal polarizability. It is equal to 0.95±0.01 in the supporting electrolyte and decreases with the increase of TU concentration for each potential studied.

Beside the $R_S - C$ system with constant phase element (*CPE*) including the term R_F representing the faradaic process, the simple $R_S - C$ in series circuit was also tested. The difference in treating the system as a simple equivalent circuit R_sC in series, as well as by a *CPE* element with parallel R_F resistance, increases with TU concentration but the position of the minimum on the curves is the same for both cases and is equal to –0.93 V, reported as the *pzc* of polycrystalline Ag electrode [18]. For the sake of simplicity, further presentation of results will be restricted only to the $R_S - C$ in series circuit, the more so as the difference in $Q_a^{'}$ and C has only unsignificant influence in the calculation of surface coverage by the adsorbate.

The plots *C vs E* for various concentration of thiourea (from 10^{-6} M to 5×10^{-4} M) are shown in Fig. 4.

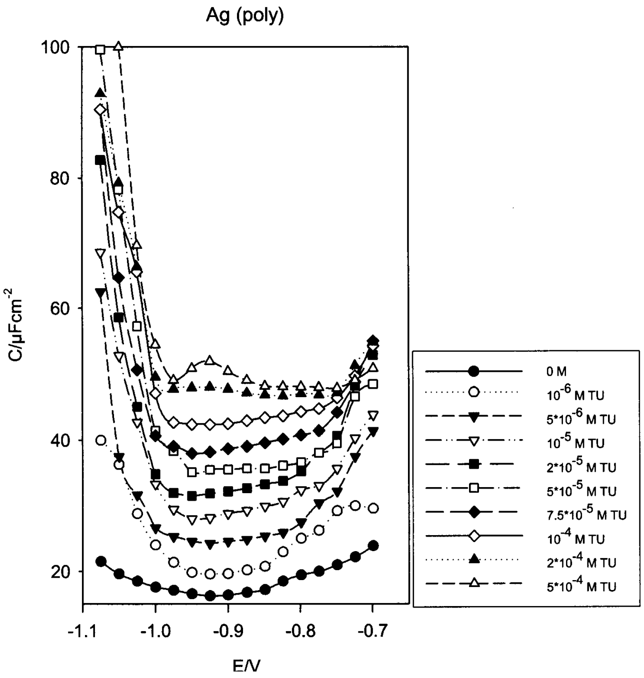

Figure 4. Plots of capacity *vs* potential for silver electrode in 0.01 M $NaClO_4$ and with addition of thiourea to the solution.

We observe some characteristic features common to all the curves like increase of the capacitance resulting from the onset of the hydrogen evolution reaction (the cathodic branch) and due to silver and/or TU oxidation (the anodic branch), as well as shallow diffuse layer minima. The minima of capacitance are shifted slightly towards negative potentials with the rise of TU concentration as it is observed for anions. Also, the increase of capacitance in the presence of TU is not typical for adsorption of organic molecules.

As can be seen in Fig. 4 the capacity curves of the studied system do not overlap the corresponding curve of supporting electrolyte solution even at negative potential. This fact unables the application of the back integration method for surface charge determination. Therefore the classical analysis for adsorption parametres determination is not possible.

Assuming that the maximum of TU adsorption is situated at the *pzc* or near this potential, the surface coverage θ can be calculated [19] from the equation (8):

$$\theta = \frac{C_0 - C_\theta}{C_0 - C_1} \tag{8}$$

where C_0, C_1 and C_θ are capacitances at $\theta = 0$, $\theta = 1$ and given θ, respectively. Firstly, the Frumkin isotherm was tested:

$$\frac{\theta}{1-\theta} = \beta \times c \times \exp(-2a\theta) \tag{9}$$

where β and a are adsorption equilibrium constant and the coefficient of lateral interactions of the adsorbate on the electrode surface, respectively. The plot of $\ln[\theta/(1-\theta)c]$ *vs* θ is linear and the slope is near 0 what means that $a \approx 0$ and the Langmuir isotherm can be used for the calculation of the Gibbs energy of adsorption, ΔG:

$$\frac{\theta}{1-\theta} = \beta \times c = c \times \exp\left(-\frac{\Delta G}{RT}\right) \tag{10}$$

The values of β and ΔG are given in Table 1. The adsorption isotherms of TU for two potentials are given in Fig. 9.

(ii) Radiometric measurements. The kinetics of adsorption of TU on a silver electrode is presented in Fig. 5. The results show that adsorption process is slower at the more positive potential. The surface concentration attains constant value after 300 s for each potential studied and does not change for a long time.

To examine the reversibility of adsorption, potentiostatically controlled surface-to-bulk experiments were carried out. After the adsorption was completed, a large excess of unlabeled TU was added to the cell (Fig. 5). The exchange process is slow and depends on the electrode potential. The more negative potential the higher the degree of the exchange process. For $E_{pzc} = -0.93$ V the exchange process leads to displacement as much as 80% of the labeled surface species during 20 minutes. For

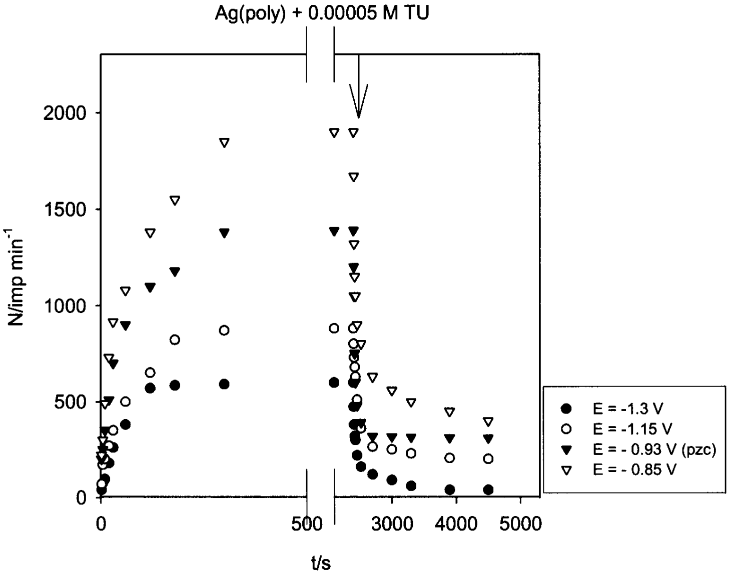

Figure 5. Surface/bulk exchange of thiourea on Ag electrode at large excess of unlabeled TU. Starting point for the exchange is marked with an arrow.

more negative potentials the exchange between labeled and unlabeled TU molecules is better and equal to 95% and is probably facilitated by the hydrogen deposition on the electrode.

The dependence of the surface concentration of adsorbed TU *vs* potential is presented in Fig. 6. It can be seen that the adsorption process takes place in the entire range of potential range studied and is practically reversible with respect to the potential. The small hysteresis shows that a small amounts of TU (or products of its oxidation) remains on the surface after anodic step of polarization.

The dependence of Γ *vs* bulk concentration for different potentials is given in Fig. 7. As it can be seen, the surface concentration of adsorbed TU increases when the potential shifts towards the anodic range. It confirms the conclusion that TU molecule behaves like an anion at the Ag electrode.

Considering the adsorption process of TU on silver electrode as a reversible process, at least near the potential of zero charge, we used the data of Γ *vs* bulk concentration to calculate thermodynamic parameters of adsorption process. The Langmuir isotherm in the form:

$$\frac{c}{\Gamma} = \left(\frac{1}{\beta \times \Gamma_{\max}}\right) + \frac{c}{\Gamma_{\max}} \tag{11}$$

was used to describe the adsorption. The plots of c/Γ *vs* c for different potentials are presented in Fig. 8.

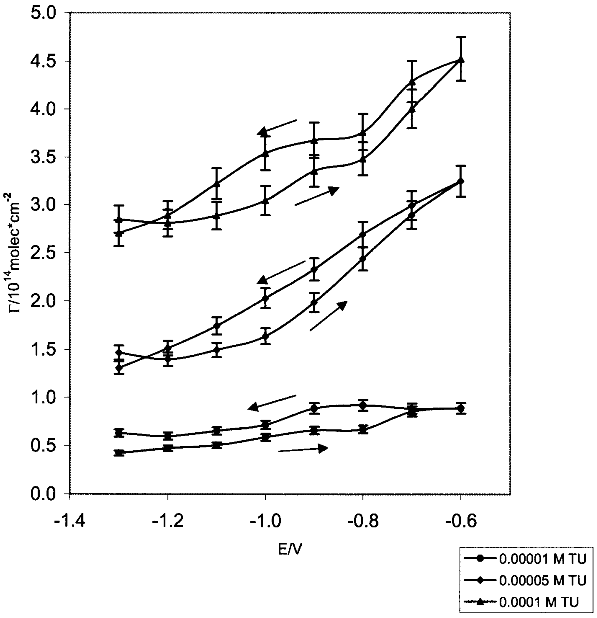

Figure 6. Potential dependence of TU adsorption in the presence of 10^{-5} M, 5×10^{-5} M, and 10^{-4} M TU in 0.01 M $NaClO_4$.

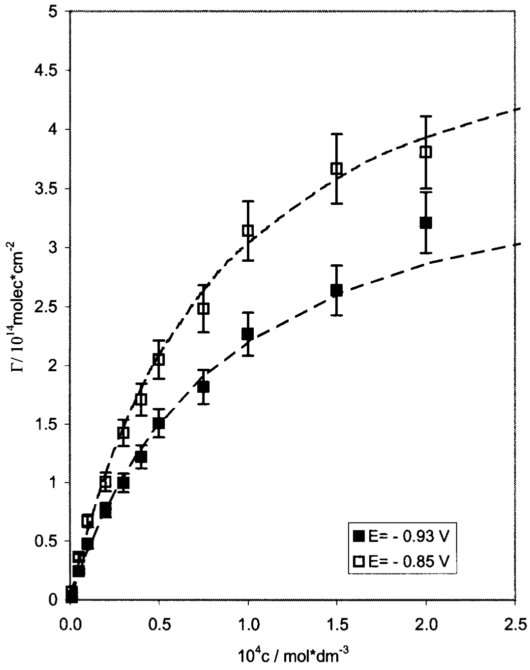

Figure 7. The isotherms of TU adsorption for silver electrode obtained radiometrically. The points represent the experimental values, solid lines were calculated using the values of β and Γ_{max} taken from Table 1.

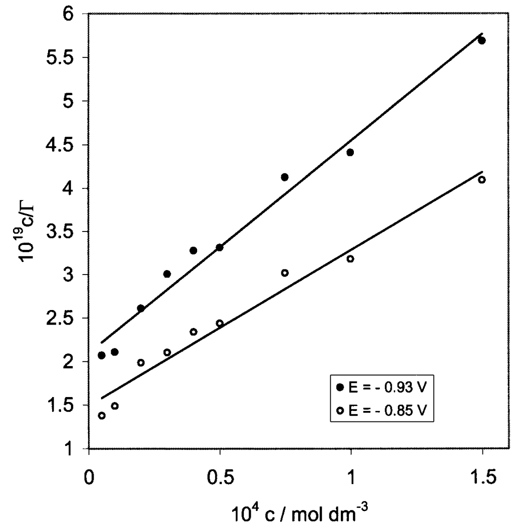

Figure 8. The plots of c/Γ *vs c* for Γ_{max} and β determination The values of thermodynamic parameters of adsorption process are given in Table 1.

From the slope of the plots c/Γ *vs c* and the intercept of the ordinate, the values of Γ_{max} and the adsorption equilibrium β have been calculated. The results of fitting the experimental data to the Langmuir isotherm are presented in Fig. 8 (solid lines). From the β values, the Gibbs energy of adsorption of TU was calculated. The pertinent data are given in Table 1.

Table 1. The Gibbs energy of TU adsorption on silver electrode obtained from capacitance and radiometric measurements. The maximum surface concentration was determined radiometrically.

	Capacitance measurements		Radiometry	
	E = –0.93 V	E = –0.85 V	E = –0.93 V	E = –0.85 V
Γ_{max}/molec.× cm^{-2}	–	–	4.1×10^{14}	5.5×10^{14}
lnβ	9.8	10.1	9.4	9.4
ΔG^0/kJ× mol^{-1} (293 K)	–23.9 ±1.0	–24.6±1.0	–22.9±0.5	–22.9±0.5

standard state: $\theta = 0.5$, $c = 1$ mol×dm^{-3}.

The maximum surface concentration of TU for closed-packed monolayer can be estimated from the cross-section area of the molecule obtained from crystallographic data [20]. Assuming the rigid structure of the molecule, the Γ_{max} are equal to 4.3×10^{14} and 6.1×10^{14} molec.×cm^{-2} for parallel and perpendicular orientation of TU on Ag electrode, respectively [17]. Comparing these values with the experimentally obtained data (Table 1) one can suppose that at *pzc* TU molecules are parallely situated on the surface. With the change of the potential towards the anodic direction the Γ_{max} increases, as if the part of TU molecules change the orientation to tilted position.

The surface of polycrystalline Ag can be considered as a sum of randomly distributed monocrystals of basal indices. If so, the surface atom density on polycrystalline Ag electrode, equivalent to the adsorption sites, is equal to 1.1×10^{14} atom$\times$cm^{-2}. Hence, one can conclude that one TU molecule occupies *ca* 4 adsorption sites on the Ag electrode surface.

(iii) Comparison of capacitance and radiometric data. The isotherms θ *vs* c, obtained from capacitance and radiometric measurements are shown in Fig. 9.

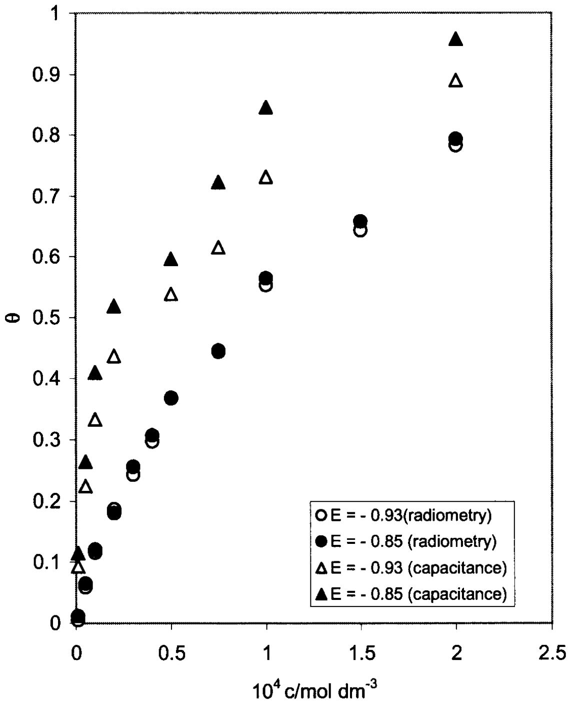

Figure 9. The comparison of the adsorption isotherms of TU on Ag electrode obtained radiometrically and from capacitance measurements for E = –0.93 V and E = –0.85 V.

One can notice that there is a difference in the plots of the isotherms though the values of the Gibbs energy of adsorption does not differ significantly. The main reason of the divergence in the results obtained by two methods is the low rate of the adsorption process. In impedance spectroscopy the frequency of the alternating current imposed on the polarized electrode is likely too high to attain the adsorption equilibrium, though the results have been extrapolated to zero angular frequency. The back integration of the capacity curves, applied for calculation of the surface charge and surface concentration of the adsorbate, could not be used because the TU desorption process overlaps the faradaic current that occurs due to the hydrogen ions discharge on the electrode. Moreover, the desorption process of TU is not completed even after a long time so the reversibility of the adsorption process is limited (see Fig. 5). Hence, the radiometric data seems to be more unfailing.

The more reliable comparison of impedance and radiometric methods would be possible if the adsorption process were quick, fully reversible and the desorption process were not disturbed by other surface reactions. However, it should be noticed that both methods have some limitations. The charge density obtained from electrochemical measurements follows from the surface excess of the adsorbate and the contribution of ions in the diffuse layer. Hence, the measurements should be done in the excess of non-adsorbing electrolyte. The radiometric measurements provide direct information about the surface excess of the adsorbate but not about the location of this excess on the potential scale. Moreover, the bulk concentration of the labeled adsorbate can not be higher than 10^{-2} M because the signal coming from the solution trapped in the gap between the electrode and detector can be too high compared with the signal coming from the adsorbed species on the electrode surface. So, impedance and radiometry can be considered rather as complementary and not competitive methods.

CONCLUSIONS

1. The adsorption of TU on polycrystalline silver electrode in neutral solution is a reversible process in the narrow range of potentials, close to the *pzc*.
2. The hydrogen ions discharge is catalyzed owing to the presence of TU at the electrode.
3. The process of TU adsorption on Ag determined by impedance and radiometric methods can be described by the Langmuir isotherm.
4. The full thermodynamic analysis of TU adsorption studied by impedance methods cannot be applied because of the presence of hydrogen discharge current in the potential range of TU desorption.
5. Small discrepancies in the Gibbs energy of adsorption calculated from impedance and radiometric data can be explained within the limitations of both methods.
6. From radiometric data it follows that the TU molecule at *pzc* is parallely situated towards the electrode surface and occupies four adsorption sites.

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REFERENCES

1. Lang G., Aramata A., Seo M. and Horanyi G., *J. Electroanal. Chem.,* **484**, 93 (2000).
2. Parsons R., *J. Electroanal. Chem.,* **484**, 97 (2000).
3. Shi Z., Lipkowski J., Gamboa M., Zelenay P. and Wieckowski A., *J. Electroanal. Chem.,* **366**, 317 (1994).
4. Poskus D., *J. Electroanal. Chem.*, **442,** 5 (1998).
5. Więckowski A. and Kolics A., *J. Electroanal. Chem.*, **464**, 118 (1999).

6. Smoliński S. and Sobkowski J., *Polish J Chem*., **75**, 1493 (2001).
7. Łukomska A. and Sobkowski J., *J. Electroanal. Chem*., **567**, 95 (2004).
8. Sobkowski J., *Nukleonika*, **43**, 399 (1998).
9. Smoliński S., Zelenay P. and Sobkowski J., *J. Electroanal. Chem*., **44**, 41 (1998).
10. Dickertmann D., Koppitz F.D. and Schulze J.W., *Electrochim. Acta*, **21**, 967 (1976).
11. Hamelin A., in: Modern Aspects of Electrochemistry, Eds. Conway B.E., White R.E. and Bockris J.O'M., vol. 16, p. 1, Plenum Press, NY 1985.
12. Zoltowski P., *J. Electroanal. Chem*., **443**, 149 (1998).
13. Bidoia E.D., Bulhoes L.O.S. and Roha-Filho R.C., *Electrochim. Acta*, **39**, 763 (1996).
14. Krauskopf E. and Wieckowski A., in: Adsorption of Molecules at Metal Electrodes, Eds. Lipkowski J. and Ross P.N., VCH Publishers, NY 1992.
15. Lerch P., *Anal. Chem*., **27**, 921 (1955).
16. Bukowska J. and Jackowska K., *J. Electroanal.Chem*., **367**, 41 (1994).
17. Szklarczyk M., Hoa N.N. and Zelenay P., *J. Electroanal.Chem*., **405**, 111 (1996).
18. Valette G. and Hamelin A., *J. Electroanal. Chem*., **45**, 301 (1973).
19. Damaskin B.B., Survila A.A. and Rybalka L.E., *Elektrokhimiya*, **3**, 146 (1967).
20. Takahashi I., Ondera A. and Shiozaki Y., *Acta Cryst.*, **B46**, 861 (1990).