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Adsorption of urea on a polycrystalline silver electrode; comparison of electrochemical and radiometric methods

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Abstract The adsorption of urea on a polycrystalline silver electrode was studied by radiometry and impedance spectroscopy. The differential capacity of the silver electrode in 0.01 M NaClO₄ solution containing urea in concentrations from 10⁻⁶ to 5×10⁻⁴ M has been determined. The isotherms of urea adsorption, found from the capacitance and radiometric measurements have been compared. The experimental data were described by the Langmuir isotherm, and the Gibbs energy of adsorption was calculated. The urea adsorption takes place in the entire range of the applied potential. The process is reversible with respect to the electrode potential and the bulk urea concentration.

Keywords Urea · Silver electrode · Adsorption · Radiometry · Impedance spectroscopy

Introduction

The electrochemical adsorption of urea on different metals was a subject of numerous works. Parsons et al. [1] studied the urea adsorption on mercury electrode in nitrate solution. The double layer capacities and electrocapillary curves were measured. It was found that the process could be described by the Langmuir isotherm. The area occupied by urea molecule under conditions of saturation was equal to 24 Å² with maximum at a charge of +8 μC cm⁻². It was concluded that the urea dipole tends to the parallel orientation towards the

electrode surface. The contribution of water dipoles and nitrate ions in the adsorption process was considered.

The adsorption of urea on platinized platinum (from perchloric acid as a supporting electrolyte) was studied by Horanyi et al. [2] using the radiometric method, described earlier [3]. The reversibility of the adsorption process on the electrode potential, in the range up to 0.7 V versus reversible hydrogen electrode (RHE), was observed. The surface concentration increased monotonically with the potential and the urea bulk concentration. The decrease of adsorption above 0.8 V versus RHE was explained by the slow oxidation of chemisorbed species and/or surface oxidation of Pt electrode. Upon addition of different anions to the solution, the decrease in urea surface concentration, as a result of competition in adsorption, was observed. In the presence of organic compounds, the irreversible chemisorption of organic molecules prevented the adsorption of urea. The study of adsorption of urea on monocrystalline platinum electrodes Pt(111), Pt(110) and Pt(100) showed that this process depends on the electrode structure [4]. More detailed study was carried out on the Pt(100) electrode using various methods such as voltammetry, radiometry, LEED and Auger electron spectroscopy [5]. The radiochemically determined surface concentration was equal to 3.4×10¹⁴ molecules cm⁻², which corresponds to 0.26 monolayer on Pt(100) surface. As was evidenced by the Auger electron spectroscopy, the urea molecule did not decompose on the platinum surface, contrary to the theoretical study of urea adsorption on Pt(100) electrode [6]. The adsorption of urea on the Pt(111) electrode from perchloric acid solution was studied by cyclic voltammetry, charge displacement and FTIR spectroscopy [7]. Below 0.5 V versus RHE the adsorbed urea species were bonded through only one of the nitrogen atoms, but at higher potentials the O-bonded species predominated. The saturation of the surface by urea molecules was attained at ca. 0.70 V. The absolute coverage of the Pt(111) electrode was 0.45. The infrared spectroscopy and voltammetry study [8] of urea adsorption on platinum

Dedicated to Professor Gyorgy Horanyi on the occasion of his 70th birthday

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single-crystal stepped surfaces indicated that urea molecules behaved like anions on platinum electrodes. The orientation of molecules on Pt(110) and Pt(111) changed with the electrode potential. By application of the lattice-gas modelling technique it was demonstrated [9] that the specific adsorption of small molecules, like urea, on the single-crystal electrodes is characterized by a good fit between the adsorbate geometry and the electrode surface structure.

The structural effects of urea adsorption on the single-crystal rhodium electrodes (studied by voltammetry and in-situ FTIR spectroscopy) were observed [10]. It was found that the surface orientation of urea molecules depended on the plane of the Rh electrode.

The electrosorption of urea and thiourea on a polycrystalline gold electrode was studied by voltammetry, tensammetry and SER-spectroscopy [11]. The SER-spectra indicated the adsorption of urea with the oxygen atom in the coordinating position. The adsorption of urea from acidic solution could not be studied because of urea hydrolysis, resulting in the formation of carbon dioxide and ammonium ions. The adsorption of urea on single-crystal electrodes Au(100) and Au(111) was studied by cyclic voltammetry and FTIR spectroscopy [12]. The FTIR data indicated that urea was adsorbed on Au(100) with a molecular plane normal to the electrode surface. On the Au(111) electrode, two kinds of adsorbate were located—one nitrogen-terminated, and the other one oxygen-terminated. In the presence of sulphate ions in the solution, owing to their strong adsorption on Au(111), the adsorption of urea was not observed.

The aim of this work was to study the adsorption of urea on an Ag electrode by impedance spectroscopy and radiometry and also to compare the results obtained by these two different techniques. As far as we know, the adsorption of urea on a silver electrode was not yet studied. The number of papers concerning both comparative electrochemical and radiometric study is very limited. Fair agreement between surface concentrations determined from chronocoulometric experiments and radiochemical measurements was observed for adsorption of sulphate ions on Au (111) [13], and pyridine on Au (poly) [14] electrodes. The link between the relative surface excess determined by thermodynamics and radiotracer methods was the subject of discussion [15, 16]. According to Horanyi et al. [15], in the presence of a great excess of supporting electrolyte the surface excess determined by the radiotracer method can be used as a good approximation in thermodynamic calculations.

Experimental

Materials

All reagents were of analytical grade. Solutions were prepared from ultra-pure water obtained using the

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 M Ω cm. Its purity was verified with a GC-MS system. The experiments were carried out in a NaClO₄ solution deaerated with purified nitrogen at ambient temperature.

The Ag|AgCl, 1 M Cl⁻ electrode was used as a reference electrode in all experiments.

Urea labeled with carbon-14 (β^- emitter, $E_{\max} = 0.156$ MeV) of specific activity 15 mCi mmol⁻¹ (Amersham) was used in radiometric experiments.

Electrode preparation

The surface of a polycrystalline silver electrode, in the form of disc 1.25 cm in diameter, was prepared using a variety of polishing grits and diamond pastes from 30 to 0.25 μ m in grain size (Buehler) followed by chemical treatment described earlier [17]. After the cleaning, the electrode was immediately transferred to the electrochemical cell under protection of a drop of water to avoid contact with the air. The proper run of the voltammetric curve was the test of cleanness of the electrode and solution. In all voltammetric experiments, the meniscus-contact technique [18] was employed.

The real surface area of the silver electrode was estimated from the double-layer capacitance (C) calculated from the dependence of the voltammetric current (i) on the scan rate (v) at constant potential (E) ($C = (i/v)_E$) as well as from the charge involved in the upd of Pb on the silver electrode. A detailed description of both methods has been given elsewhere [19]. The roughness factor of the Ag electrode used in the experiments was 1.15 ± 0.05 .

Methods

Two methods were applied for the study of urea adsorption: impedance spectroscopy (1) and radiometry (2).

1. 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 precision of the data obtained was the best for 25 Hz. The phase angle was close to 90°, thus the constant phase element could be neglected and the simple RC circuit in series was used for capacity calculation. 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 [20].
2. The radiometric thin gap method [21] (also called the "electrode lowering method" [22]) was used to determine the surface concentration of the adsorbate.

The disc-shaped electrode was placed into the cell, in the bottom of which the glass scintillator as a radiation detector was fixed. To the supporting electrolyte (0.01 M NaClO₄) a desired amount of urea solution, labeled with carbon-14, was added. The radiometric method used in this work was described in detail by Zelenay and Wieckowski [23].

The surface concentration of adsorbed species Γ (molecules cm⁻²) can be calculated from the equation [23, 24]:

$$\Gamma = \frac{N_a}{N_b} \frac{10^{-3} c N_{AV}}{\mu_s R f_b \exp(-\mu x)} \quad (1)$$

where 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 centimeter.

The counting rate contributed from the solution trapped in the gap between the electrode and scintillator has to be taken into account. A detailed description of the gap thickness determination has been given elsewhere [25]. The backscattering factor f_b accounts for β^- radiation reflected by the electrode back towards the scintillator. For silver, it is equal to 1.69, and differs slightly from f_b determined experimentally 1.81 [21]).

Results and discussion

The electrochemical measurements

The voltammetric curves of the polycrystalline silver electrode in the supporting electrolyte, i.e., 0.01 M NaClO₄, and in the presence of increasing urea concentration in this solution are shown in Fig. 1

The voltammetric curves reveal catalytic properties of urea in neutral solution in respect to hydrogen evolution. It is likely due to the formation of hydrogen bonding between -NH₂ in urea and water molecules, which mediates the proton discharge. The similar effect was observed for the thiourea-silver system [25, 26].

The double-layer capacitance of the supporting electrolyte and solutions of different urea concentration are presented in Fig. 2

The capacitance minimum in 0.01 M NaClO₄ solution corresponds to the potential of zero charge of silver electrode [27] and equals to -0.93 V. In the presence of urea, the minimum of capacitance moves slightly towards negative potentials. The maximum adsorption occurs at a charge of +2 $\mu\text{C cm}^{-2}$. Apparently, the urea molecule is O-bonded to the surface of the silver electrode. The similar orientation of the urea molecule on a gold electrode was observed by SER-spectroscopy [11].

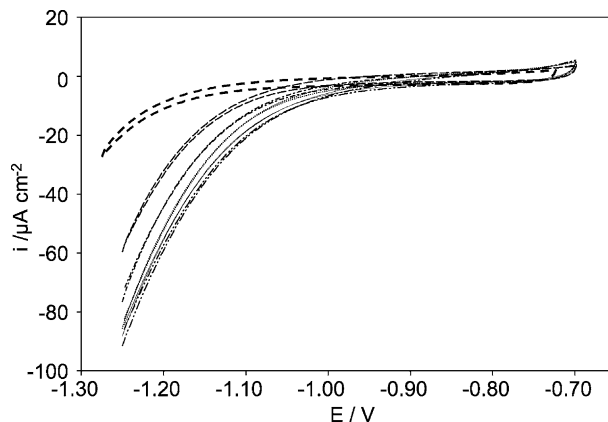


Fig. 1 The voltammetric curves of the silver electrode for different urea concentrations: - - - 0 M, - - - 10⁻⁶ M, - · - · 5 × 10⁻⁶ M, · · · · 10⁻⁵ M, — 5 × 10⁻⁵ M, - · - · 10⁻⁴ M; $\nu = 100$ mV/s

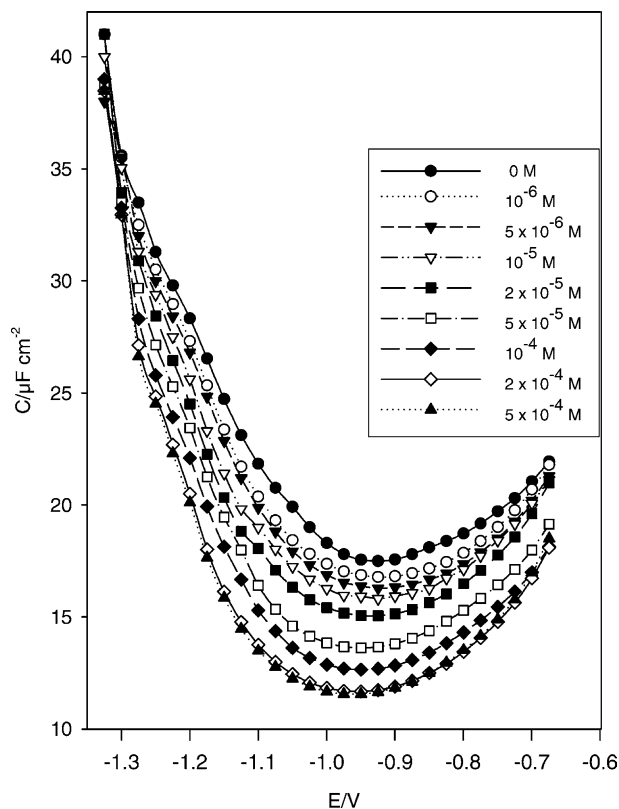


Fig. 2 Plots of capacity versus potential for silver electrode in 0.01 M NaClO₄ and with addition of urea to the solution

All the curves merge at about -1.33 V, thus indicating that at this potential the urea molecule does not adsorb. The surface concentration was calculated by double integration and one differentiation step of capacitance curves. The first integration provided the charge density—potential curves. The required integration constant was determined by integration of the capacitance curve corresponding to the supporting electrolyte, starting from the potential of zero charge. Since only the relative values of surface energy (surface

tension) π are necessary to calculate the surface concentration of the adsorbate, the electrocapillary equation: $\Gamma = -c/(RT) \times (d\pi/d \ln c)_E$ can be used to calculate the surface concentration (the surface excess) of urea. The isotherms for different electrode potentials are presented in Fig. 3.

From Fig. 3 it results that the adsorption of urea on a silver electrode increases with the increase in urea bulk concentrations and with the potential rise.

The maximum concentration of urea molecules at full coverage of the electrode can be estimated from the cross section area of urea molecule, calculated from crystallographic data [28]. Assuming the hexagonal, closed packed structure and the perpendicular orientation of the molecule towards the electrode surface, the maximum concentration of monomolecular layer of urea is equal to $\Gamma_{\max} = 4.8 \times 10^{14}$ molecules cm^{-2} . Since the experimentally determined surface concentration of urea on an Ag electrode is much lower, the mutual interaction of adsorbed molecules can be neglected and the simple Langmuir equation: $\Gamma/(\Gamma - \Gamma_{\max}) = \beta \times c$ (β is the equilibrium constant of adsorption) can be used to describe the adsorption process, as it was observed for the urea adsorption on mercury electrode [1]. To calculate the values of Γ_{\max} and β the Langmuir equation was transformed to the form: $c/\Gamma = c/\Gamma_{\max} + 1/(\beta \times \Gamma_{\max})$. From the linear plot of c/Γ versus c the values of Γ_{\max} , and β were calculated. The pertinent data are given in Table 1.

The surface concentration as well as β values increase with the polarization in anodic direction and confirm the presumable orientation of urea molecule with its oxygen

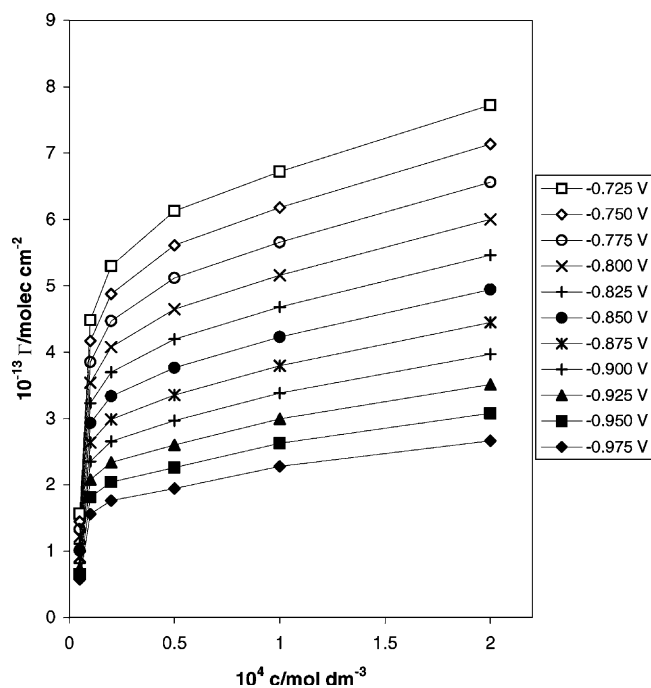


Fig. 3 Surface concentration of urea against the concentration in the bulk at constant electrode potentials

Table 1 The values of Γ_{\max} and β for various electrode potentials

E (V)	Γ_{\max} 10^{-13} (molecules cm^{-2})	β 10^{-4} ($\text{mol}^{-1} \text{dm}^3$)
-0.97	2.8	6.8
-0.95	3.2	6.9
-0.93	3.7	7.0
-0.90	4.2	7.1
-0.87	4.7	7.3
-0.85	5.2	7.4
-0.82	5.7	7.5
-0.80	6.3	7.7
-0.77	7.0	7.6
-0.75	7.4	7.9
-0.72	8.0	8.0

The accuracy of Γ_{\max} and β determination is within $\pm 10\%$

atom directed towards the electrode surface. The value of Gibbs energy of adsorption: $\Delta G = -RT \ln \beta$, which is much less sensitive parameter than β , only weakly depends on the electrode potential and its value at -0.93 V is equal to -27.1 ± 0.5 kJ mol^{-1} .

Since the surface concentration calculated from capacity data is not reliable enough, the surface coverage near the *pzc* has been estimated from the equation [29]:

$$\theta = \frac{C_{\theta=0} - C_{\theta}}{C_{\theta=0} - C_{\theta=1}} \quad (2)$$

where $C_{\theta=0} = 17.50$ $\mu\text{F cm}^{-2}$ and $C_{\theta=1} = 11.56$ $\mu\text{F cm}^{-2}$ are the capacitances at $\theta=0$ and $\theta=1$, respectively (see Fig. 2). No further decrease of double-layer capacity was observed when the urea concentration was higher than 0.5 mM. The test of Frumkin isotherm i.e., the plot $\ln[\theta/(1-\theta)c]$ vs. θ shows (Fig. 4) that the interaction parameter, a , is close to zero.

The intercept of the ordinate provides the Gibbs energy of adsorption which is practically independent of the surface coverage. The value of ΔG at the potential of maximum adsorption calculated from the data of Fig. 4 is equal to -26.1 ± 0.5 kJ mol^{-1} , and is practically independent of the surface coverage. This value can be

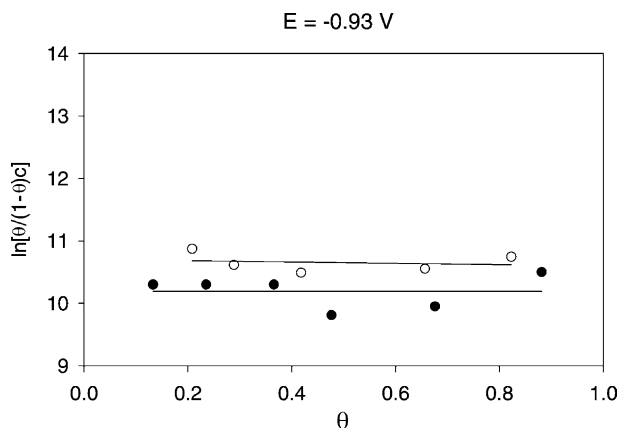


Fig. 4 Test of Frumkin isotherms of urea adsorption at -0.93 V obtained from impedance measurements (open circle) and radiometry (filled circle)

compared with the data for a polycrystalline gold electrode $\Delta G = -24 \pm 0.2 \text{ kJ mol}^{-1}$ [11].

The radiochemical measurements

In the first step, the reversibility of urea adsorption process was tested. Thus, the potentiostatically controlled surface-to-bulk exchange experiments were carried out. After the constant rate counting was attained, a large excess of unlabeled urea was added to the solution. The exchange of adsorbed, labeled urea by the unlabeled one was observed. The results are shown in Fig. 5.

It can be seen that the urea adsorption (in the studied potential range) is a nearly reversible process (the adsorbed species are movable [30]). The exchange is not a fast process. It could be explained by the slowness of desorption process or the slowness of diffusion of labeled molecules from the electrode surface. It should be noticed that the maximum coverage of the Ag electrode is observed at a very low bulk concentration of urea (see Fig. 2).

In the next step, the dependence of the surface concentration of urea versus potential was determined. The relevant plots are presented in Fig. 6.

It is seen that the adsorption takes place in the entire potential range studied, increases with the anodic polarization, and is reversible with respect to the potential. The small hysteresis suggests that likely for higher urea concentrations, insignificant amounts of urea (or products of its oxidation) can remain on the surface after an anodic step of polarization.

The isotherm of urea adsorption was determined by the addition of increasing amounts of labeled urea solution to the supporting electrolyte. The results for $E_{pzc} = -0.93 \text{ V}$ are presented in Fig. 7.

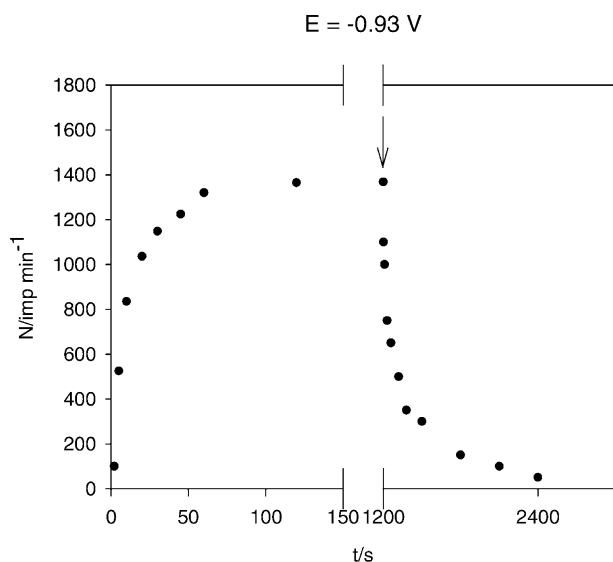


Fig. 5 Surface/bulk exchange of urea on Ag electrode at large excess of unlabeled urea molecules. Starting point for the exchange is marked with an arrow

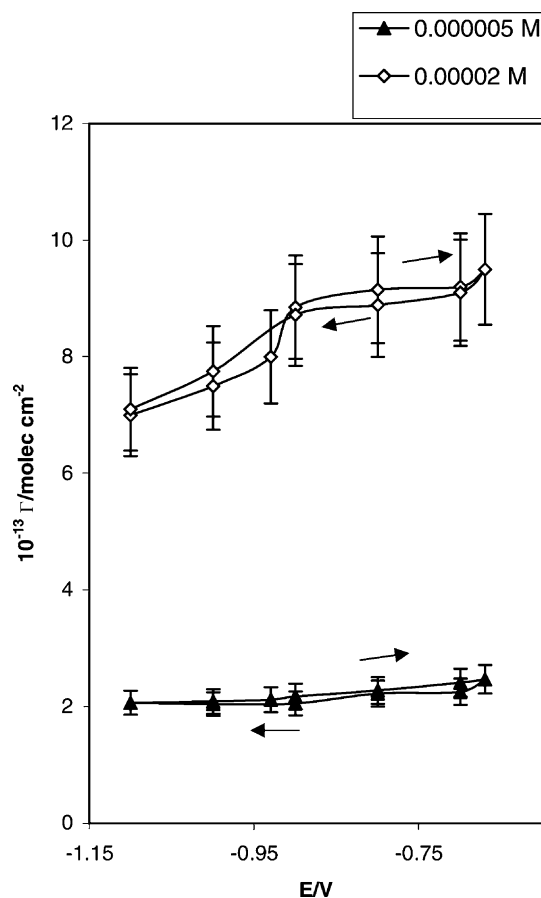


Fig. 6 The surface concentration of urea on a silver electrode determined radiometrically versus electrode potential

The maximum surface concentration was determined by extrapolation of the plot $1/\Gamma$ vs. $1/c$ to $1/c \rightarrow 0$ and is equal to $\Gamma = (1.10 \pm 0.15) \times 10^{14} \text{ molecules cm}^{-2}$, so it is higher than that calculated from electrochemical measurements. Comparing this value with the surface concentration, calculated from the cross section area of urea molecule, it follows that only about 20% of the electrode surface is covered by urea molecules.

Using the values of counting rates at given urea concentration N_c and under saturation condition N_{\max} , the surface coverage $\theta = N_c/N_{\text{sat}} = \Gamma/\Gamma_{\max}$ and the adsorption isotherm can be determined. The linear test of Frumkin isotherm, at the potential near the potential of maximum of adsorption (see Fig. 4), shows that the interaction coefficient of adsorbed molecules can be neglected and the Langmuir isotherm describes the adsorption process satisfactorily (see Fig. 8). The calculated value of $\Delta G = -24.8 \pm 0.5 \text{ kJ mol}^{-1}$ is a little lower than that obtained from capacitance measurements but is close to the data of Holze and Schomaker for an Au electrode [11]. The precision of ΔG calculation is limited owing to the errors in counting rate, calibration procedure, backscattering factor and in estimation of roughness factor of the electrode.

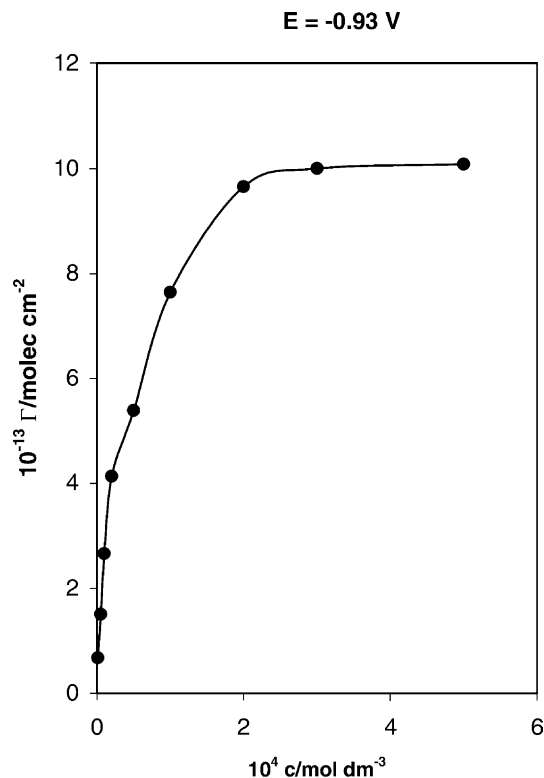


Fig. 7 The adsorption isotherm of urea, determined by radiometric method, at -0.93 V

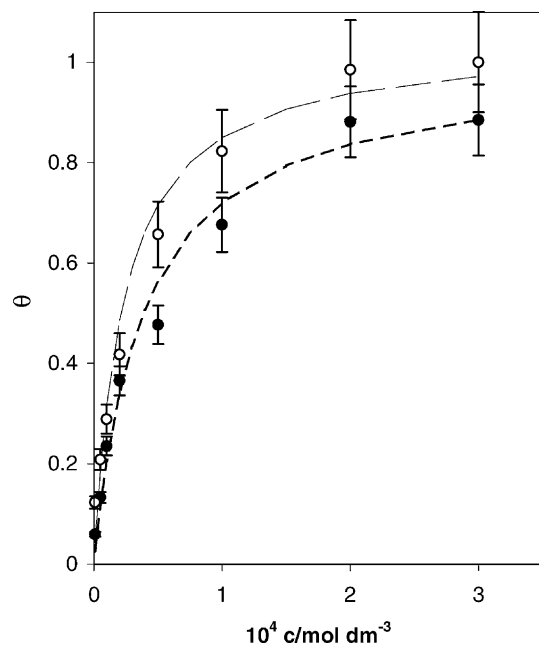


Fig. 8 A comparison of the adsorption isotherms of urea on an Ag electrode obtained radiometrically (filled circle) and from impedance measurements (open circle) at $E = -0.93$ V. The points represent the experimental values; solid lines were calculated using the values of β determined from the isotherm

The comparison of electrochemical and radiochemical methods

The isotherms θ versus c , obtained from impedance and radiometric measurements are shown in Fig. 8.

Note that there are some differences in the plots of the isotherms, even though the values for the Gibbs energy of adsorption do not differ significantly. The main reason for the divergence in the obtained results is the limitations of both methods. In impedance spectroscopy, the frequency of the alternating current imposed on the polarized electrode is likely too high to attain the equilibrium when the adsorption process is not fast enough (see Fig. 5). Moreover, two integration and one differentiation steps used to calculate the surface concentrations of adsorbate limit the precision of the Γ values determination. However, the electrochemical methods enable to find e.g. the dependence of adsorption on the surface charge, or the influence of adsorbate on the change of surface energy i.e., the relations which are unattainable by radiometry. In radiometric measurements, the reproducibility of the gap thickness between the electrode and detector (squeezing efficiency) is not very high, which restricts the precision of surface concentration determination to ca. 10–15%. Various aspects of the thin gap technique were the subjects of discussion [21, 22]. It was shown that even the kind of radiation detector can influence the obtained results [21]. Nevertheless, the surface concentration of adsorbed species determined by radiometric methods is more reliable than that obtained by impedance method because of direct measurements of signals coming from labeled adsorbate molecules. Hence, the impedance and radiometry can be considered as complementary rather than competitive methods.

Conclusions

1. Urea adsorbed on a silver electrode catalyzes the process of hydrogen ion discharge.
2. The adsorption of urea on a polycrystalline silver electrode in neutral solution within the double layer range of potentials is a reversible process with respect to the bulk concentration of the adsorbate and electrode potential.
3. The surface coverage of a silver electrode by urea molecules is lower than that on other metals, i.e., platinum.
4. The adsorption process can be described by the Langmuir isotherm.
5. The Gibbs energy of adsorption indicates the strong physisorption of urea molecules on a silver electrode.
6. The surface concentration values of urea calculated from impedance measurements are lower than the surface concentration determined from direct and more precise radiometric measurements. However, the electrochemical measurements provide more information on the thermodynamic parameters of the adsorption process.

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