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Adsorption of urea on a polycrystalline copper electrode

Abstract The adsorption of urea on a polycrystalline copper electrode from 0.01 M $NaClO_4$ solution has been studied by impedance spectroscopy and radiometric method. The dependence of the surface concentration of urea on the electrode potential and the bulk concentration was determined. From radiometric data, it follows that the adsorption of urea on the copper electrode takes place in the entire range of studied potentials where no faradaic processes occur. In this range, the process of adsorption is practically reversible with respect to the potential and the bulk concentration of urea. The experimental data were described by the Langmuir and the virial isotherms and the Gibbs energy of adsorption were calculated. The data of the urea adsorption on different electrodes have been compared and the role of the kind of the metal on the adsorption process was discussed.

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

Introduction

Because urea participates in many bioelectrochemical processes, the electrochemical adsorption of urea on different metals was a subject of numerous works [1–18]. A detailed review of the literature on the electrosorption of urea was given earlier [4].

The aim of this work was to study the adsorption of urea on the copper electrode by electrochemical and radiometric methods. The work is a continuation of the study of urea adsorption on silver electrode [4]. As far as we know, the data on the adsorption of urea on a copper electrode have not been reported yet. The earlier data on the adsorption of

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urea on mercury [1], gold [2, 3], silver [4], and platinum electrodes [5–8] give possibility to discuss the role of the kind of metal on the adsorption process.

Experimental

Materials

All reagents were of analytical grade. Solutions were prepared from ultra pure water obtained using the Millipore system. To avoid the slow decomposition of urea in acidic media [2], the experiments were carried out in an $NaClO_4$ solution deaerated with purified nitrogen at ambient temperature.

Urea labeled with carbon-14 (β^- emitter, E_{max}=0.156 MeV) of specific activity 15 mCi/mmol (ARC) diluted to appropriate concentration was used in radiometric experiments.

The Ag | AgCl, 1 M Cl⁻ (0.227 V vs SHE) electrode was used as a reference electrode in all experiments.

Electrode preparation

The working electrode was a polycrystalline copper electrode, in the form of disc of 1.15 cm in diameter. It was prepared using a variety of polishing grits and diamond pastes from 30 to 0.25 μm in grain size (Buehler) followed by the chemical treatment described earlier [19]. After the cleaning, the electrode was immediately transferred to the electrochemical cell under the protection of a drop of water to avoid the contact with air. The voltametric measurements were restricted only to the range of the potential where no oxidation of the copper surface occurred. Even a small amount of surface copper-oxidized species cannot be completely reduced by cathodic polarization. In all voltammetric experiments the meniscus-contact technique [20] was employed. To compare the electrochemical and radiometric results of measurements, the same electrodes were used in both types of experiments. The large area of electrodes

(1.04 cm^2) was necessary to get the better accuracy of radiometric measurements.

The roughness factor of Cu electrode used in the experiments was 1.15±0.05. The detailed description of the real surface area determination was given elsewhere [19].

Methods

The adsorption of urea on the copper electrode was studied by two methods: (1) impedance spectroscopy and (2) radiometry. The impedance was measured at frequencies from 1 to 100 Hz in 25 mV steps using the AUTOLAB electrochemical system equipped with the response analyzer (FRA, ECO Chemie, Netherlands). The differential capacity was calculated on the base of ac impedance measurements assuming the simplest RC equivalent circuit representing the electric double layer model. Because of a small frequency dispersion of capacitance, the obtained data were extrapolated to zero angular frequency. Furthermore, to verify whether the energy supplied to the system is used only for charging of the double layer and is not involved in the faradaic processes or dissipated in another way, the experimental data were fitted to the equivalent circuit with ohmic resistance, constant phase element, and faradaic process resistance. The procedure of impedance measurements was described in details previously [19]. It was found that in the ideal polarizability potential range of the Cu electrode, replacing simple equivalent RC circuit by the equivalent circuit with ohmic resistance, constant phase element, and faradaic process resistance did not influence significantly the results of capacitance determination. So, the assumed RC equivalent circuit as a good description of a double layer region is justified.

The radiometric thin gap method [21] (also called the "electrode lowering method" [22]) was used to determine the surface concentration of the adsorbate. The details of the method and the surface concentration calculation of adsorbed species Γ were given elsewhere [23, 24]. It was assumed that the linear absorption coefficient of β^- radiation in the solution is equal to 314 cm^{-1} for C-14 and the backscattering factor of β^- radiation for Cu f_b=1.52 [24]. Though, from radiometric data, no information about the double layer structure can be obtained, it allows to determine the surface concentration (Γ) more directly. Hence, the radiometric data of Γ are more reliable than that calculated from double layer capacitance measurements which require two integrations and one differentation steps.

Results and discussion

Electrochemical measurements

The voltammetric curves of polycrystalline copper electrode in 0.1 M NaClO$_4$, and in the presence of increasing concentration of urea are shown in Fig. 1.

From the data found in Fig. 1, it follows that urea acts as catalyst for the hydrogen ions discharge on the copper
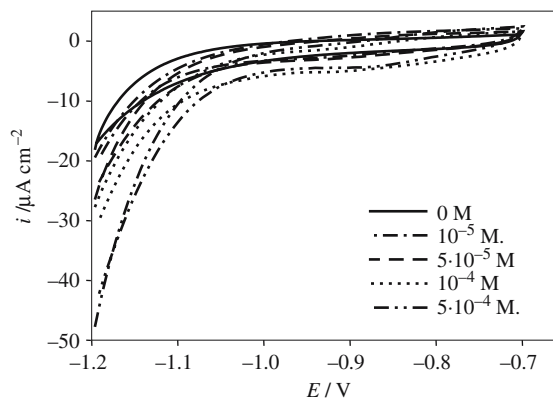

Fig. 1 The voltammetric curves of the copper electrode for different urea concentrations ν=100 mV/s

electrode in neutral solution. The similar effect was observed for the urea–silver system [4]. The acceleration of hydrogen ions discharge in neutral solution was also found for thiourea–silver electrode system [25, 26]. From surface-enhanced Raman spectroscopy data it follows that NH$_2$ group bonded to H$_2$O molecules can mediate in the proton discharge process [25]. It was suggested [26] that this effect is connected with the change of orientation of adsorbed molecules on the electrode surface. Hence, the resembling process can be responsible for the observed effect in the present study. However, it cannot be excluded that the part of adsorbed urea molecules can undergo reduction.

Differential capacity–potential curves were measured for different concentration of urea ranging from 10^{-6} to 5×10^{-4} M. Above this concentration, no changes in these curves was observed. It should be mentioned that the range of the bulk concentration of the adsorbate for the saturation of the copper electrode by urea molecules is similar as for the gold [2] and the silver electrodes [4] but quite different (much lower) to that for the mercury electrode [1].

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

The capacitance minimum in 0.01 M NaClO$_4$ solution corresponds to the potential of zero charge of copper electrode [19] and equals to −0.95 V. As can be seen in Fig. 2, the capacity curves corresponding to urea adsorption do not overlap the corresponding curve in the supporting electrolyte solution even at negative potentials. That is why the application of the back integration method for the surface-charge determination and further classical analysis for adsorption-parameters calculation was not possible. Therefore, a tentative analysis of the data had to be applied. The adsorption parameters can be achieved for electrode potential close to the potential of maximum adsorption, assuming Frumkin–Damaskin two parallel capacitors model [27]. Then, the maximum depression of the capacitance $(\Delta C = C_0 - C)$ corresponds to the maximum adsorption and potential at which this effect is observed is regarded as the potential of maximum adsorp-
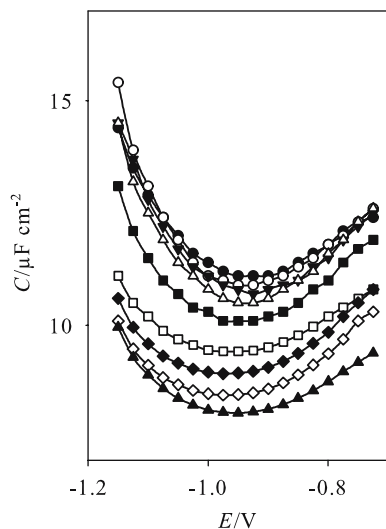
Fig. 2 Plots of capacity vs potential for the copper electrode in 0.01 M NaClO$_4$ and with the addition of urea to the solution: 0 M (•), 10^{-6} M (○), 5×10^{-6} M (▾), 10^{-5} M (△), 2×10^{-5} M (•), 5×10^{-5} M (□), 10^{-4} M (♦), 2×10^{-4} M (◊), 5×10^{-4} M (▴)

tion. In the case of urea adsorption on the copper electrode, the ΔC vs E plots were rather flat and no maximum was observed which means that the dependence of adsorption on electrode potential is weak. That is why, the maximum adsorption was assumed to be situated at E_{pzc} or near this potential.

According to the Frumkin–Damaskin model [27] the electrode coverage with organic molecules, θ, can be approximately expressed by Eq. (1):

$$\theta = \frac{C_{\theta=0} - C_\theta}{C_{\theta=0} - C_{\theta=1}} \tag{1}$$

where $C_{\theta=0}$, $C_{\theta=1}$, and C_θ are the capacities at $\theta = 0$, $\theta = 1$, and given θ.

The capacity $C_{\theta=1}$, corresponding to the full coverage $\theta=1$, was estimated by linear extrapolation of the data, using $1/C$ vs $1/c$ relationship at a constant potential, c being the concentration of urea. The similar procedure for $C_{\theta=1}$ estimation was applied earlier [28]. The value of $C_{\theta=1}$ was equal to 8.1 μF cm^{-2}.

The isotherm of urea adsorption on copper electrode at potential corresponding to E_{pzc} is shown in Fig. 3.

To ascertain whether the lateral interaction of adsorbed molecules plays any role in the adsorption process the Frumkin isotherm was firstly tested [2]:

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

where θ, X, β, and a are surface coverage, molar fraction, adsorption constant, and interaction coefficient, respectively. The plots of $\ln \theta /(1-\theta)X$ vs θ, at the potential corresponding to the E_{pzc} obtained from impedance measurements, are presented in Fig. 4.
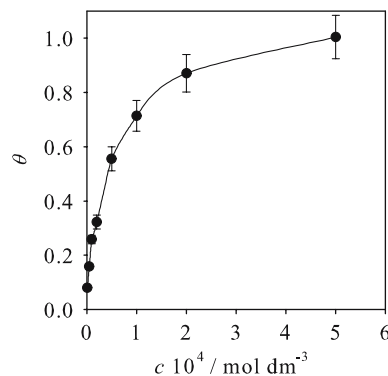

Fig. 3 The isotherms of urea adsorption on the copper electrode obtained by impedance measurements at E_{pzc}

The plots are practically parallel to the X-axis which means that interaction coefficient is near zero. The similar Langmuirian behavior of the urea adsorption was also observed on the mercury [1] and the silver electrodes [4]. The value of the Gibbs energy of adsorption: $\Delta G = -RT \ln \beta$ is equal to -34.7 ± 0.5 kJ/mol (standard state: $\theta=1$, $X=1$) and is only slightly lower than that obtained for urea adsorption on silver electrode (-36.0 ± 0.5 kJ/mol [4]).

Radiometric measurements

To inspect the reversibility of urea adsorption, potentiostatically controlled surface-to-bulk exchange experiments were carried out. After the adsorption was completed, a large excess of unlabeled urea was added to the cell (Fig. 5). The exchange process is slow and leads to displacement as much as 90% of labeled surface species in 20 min. Therefore, the urea adsorption processes can be considered as almost reversible with respect to the bulk concentration. Some experiments (not shown here) carried out for more negative potentials indicate that the exchange of labeled by unlabeled urea molecules is almost complete and is probably facilitated by the hydrogen deposition on
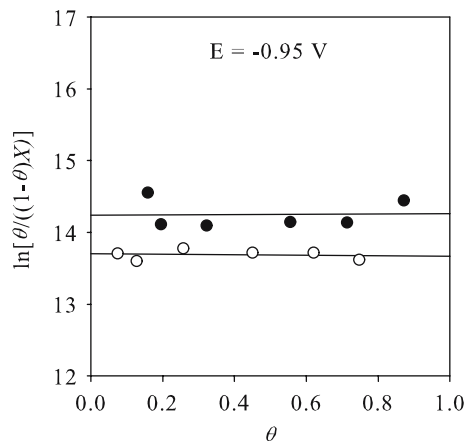

Fig. 4 Test of Frumkin isotherms of urea adsorption on the copper electrodes at $E=-0.95$ V obtained from impedance (•) and radiometric (○) measurements

the electrode. Similar results were observed for the silver electrode [4].

The kinetics of adsorption and desorption of urea on and from the copper electrode, respectively, expressed as the counting rate which is proportional to the surface coverage, is presented in Fig. 5.

As it can be seen, both processes are rather slow. The counting rate coming from the surface of the electrode attains constant value after 300 s and does not change for a long time. Similarly, the desorption process is also slow and the counting rate drop to the background counting rate after 25–30 min. As the Langmuir isotherm describes the adsorption process, the kinetics should follow the relation: $\nu_{ads.} = d\theta/dt = k(1-\theta)$. Hence, the linear plot of $-\ln(1-\theta) = -\ln(1 - N_t/N_{t=\infty})$ (N_t and $N_{t=\infty}$ are the counting rates at given t and when the counting rate does not change with time, respectively) vs time should be observed that is the case (see insert in Fig. 5). It confirms the Langmuir condition of adsorption kinetics.

The plots of the surface concentration of adsorbed urea vs potential for two urea bulk concentrations are presented in Fig. 6.

As it can be seen, the adsorption process takes place in the entire range of studied potential and is practically reversible with respect to the potential. The surface concentration of urea slightly increases with the change of potential towards the anodic direction.

The adsorption isotherm of urea on copper electrode, i.e., the dependence of Γ vs the bulk concentration, c at E_{pzc}, determined from radiometric measurements, is given in Fig. 7.

The limiting surface concentration of urea Γ_{lim} was determined from $1/\Gamma$ vs $1/c$ plot and extrapolation to $1/c \rightarrow 0$. It equals to $\Gamma_{lim} = (0.95 \pm 0.15) \times 10^{14}$, molecules $\times cm^{-2}$. The obtained Γ_{lim} for urea adsorption is smaller than that

Fig. 6 Potential dependence of urea adsorption in the presence of 10^{-5} M (•), 5×10^{-5} M (○) urea in 0.01 M NaClO$_4$

obtained for the silver ($1.10\pm0.15\times10^{14}$) [4], the gold (2.3×10^{14}) [3], and the mercury (4.2×10^{14}) [1] electrodes. The limiting surface concentration of urea for closed-packed monolayer can be estimated from the cross-section area of the urea molecule obtained from crystallographic data [29]. Assuming the rigid structure of the molecule and perpendicular orientation of the adsorbate on the Cu electrode, Γ_{lim} was estimated as 4.8×10^{14} molecules $\times cm^{-2}$. The comparison of this value with the experimentally obtained data of Γ_{lim} at E_{pzc} shows that the urea molecules occupy only ca 20% of the area of electrode surface which suggests that rather parallel or tilted than perpendicular orientation of urea molecules is preferred. No shift of E_{pzc} with increasing concentration of urea in the solution would confirm this conclusion. However, the small increase in the surface concentration with the change of potential in anodic direction suggests that some of urea molecules can
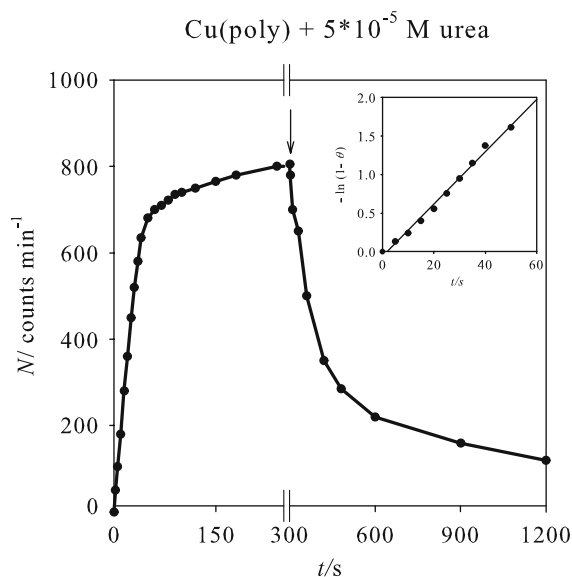

Fig. 5 Surface/bulk exchange of urea on the copper electrode at large excess of unlabeled urea molecules. Electrode potential $E_{pzc} = -0.95$ V. Starting point is marked with an *arrow*. The insert: the plot of the ln $(1-\theta)$ vs t
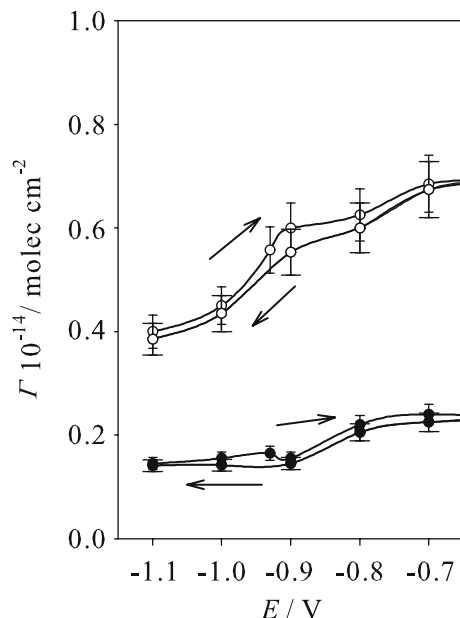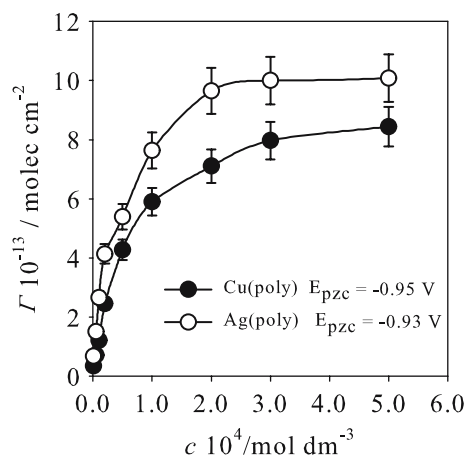

Fig. 7 The isotherms of urea adsorption on the copper and silver [4] electrodes determined by radiometric methods at E_{pzc}

be tilted with their CO groups directed towards the electrode surface. The small values of the surface concentration of adsorbed species imply very weak lateral interaction, which was confirmed by the Langmuirian type of the isotherm. If the surface atom density of the copper electrode ($n_{Cu}=1.46\times10^{15}$ atoms per square centimeter), considered as a mean value of the three low Miller index planes of copper single crystals [30], is taken into account, only 7% of the adsorption sites is occupied by urea molecules. It is much smaller in comparison with other studied metals: Ag 10% [4], Au 20% [3], Pt (100) 25% [7], and Pt (111) 43% [8]. It is an evidence of the influence of the kind of the metal as well as its surface structure on the urea adsorption.

The surface coverage of the Cu electrode by urea molecules can be determined, more directly than from impedance measurements, using the simple relation: $\theta=N_c/N_{sat}=\Gamma/\Gamma_{lim}$ where N_c and N_{sat} are counting rates at given urea concentration and under the saturation condition, respectively. The isotherm θ vs c, obtained from radiometric measurements, is shown in Fig. 8. The isotherm obtained from impedance measurements is given for comparison.

The test of Frumkin isotherm, based on radiometric data at the potential of zero charge (see Fig. 4), shows that the interaction coefficient of adsorbed urea molecules, $a\approx0$, like as it was obtained from impedance measurements. The value of the Gibbs energy of adsorption obtained from radiometric measurements is equal to -33.6 ± 0.5 kJ/mol and is slightly smaller than that from impedance measurements.

The values of Gibbs energy of adsorption obtained by electrochemical and radiometric methods do not differ significantly but some differences in the plots of the isotherms (see Fig. 8) can be observed. They are probably due to the slowness of the adsorption process. Also, the reversibility of the adsorption process is limited.

Because the surface concentration of urea was directly determined by radiometric method, the test of virial
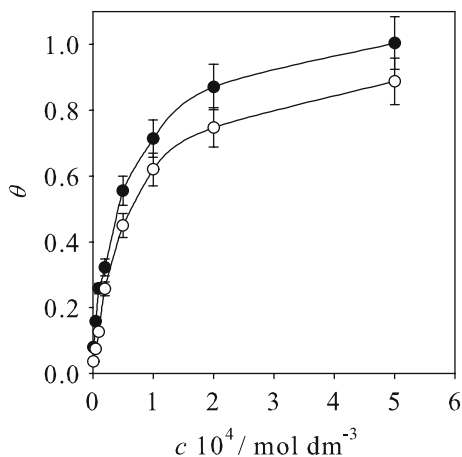
isotherm was also possible. The experimental data were fitted to the equation:

$$\ln \Gamma + 1B\Gamma = \ln \beta c \tag{3}$$

where B is the second virial coefficient. The results of the test are shown in Fig. 9.

The calculated value of the Gibbs energy of adsorption $\Delta G=-RT \ln\beta=-102.3$ kJ/mol refers to the other standard states ($\Gamma^\circ=1$ molecule $\times cm^{-2}$ and $c^\circ=1$ M) different than that used for calculation of Gibbs energy from the Frumkin isotherm ($\theta=1$, $X=1$). The Gibbs energy of adsorption derived from the virial isotherm can be recalculated for the same standard state as for the Frumkin one assuming $\Gamma_{lim}=0.95\times10^{14}$ molecules $\times cm^{-2}$ and $X=c/55.5$. The value of $\Delta G=-33.7\pm0.5$ kJ/mol is in good agreement with the value obtained from direct radiometric measurements. The data in this work indicate that the free energy of adsorption of urea on the copper electrode is almost the same as it was obtained for the silver electrode [4]. The pertinent data of the Gibbs energy of urea adsorption recalculated for the same standard state for the gold electrode equals to -24.0 ± 0.2 kJ$\times$mol^{-1} [2] and for the mercury electrode, evaluated from the work [1], it is equal to -10.6 kJ$\times$mol^{-1}. So, the adsorption ability of urea increases in the sequence Hg [1] < Au [2] < Cu (this work) ≤ Ag [4] and indicates that adsorption of urea depends on the nature of the metal. It is worth to note that the order of the adsorption energies of different metals in the studied systems follow the order of the ionization energies of these metals (Hg 10.4 eV, Au 9.2 eV, Cu 7.7 eV, and Ag 7.6 eV [31]).

The Gibbs energy of adsorption determined experimentally is the sum of the true energy of adsorption (A–M), energy of water molecules–metal adsorption (W–M), and adsorbate molecules–water interaction in the bulk (A–W). Because the value of the energy (A–W) is the same for all studied systems and the saturation coverage of the surface of the electrodes by urea molecules is relatively low, it seems that the energy of water molecules–electrode interaction plays an essential role in the experimentally obtained Gibbs energy of adsorption. According to Trasatti [32], the
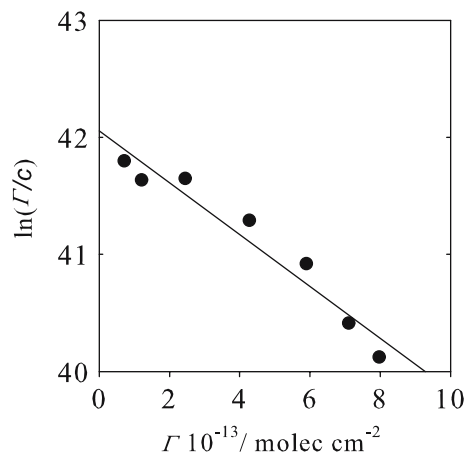

Fig. 8 A comparison of the adsorption isotherms of urea on Cu electrode obtained radiometrically (○) and from impedance measurements (•) at $E_{pzc}=-0.95$ V. The *points* represent the experimental values; *solid lines* were calculated using the values of β determined from the Frumkin isotherms

Fig. 9 Test of the virial isotherm of urea adsorption at E_{pzc} on the copper electrode obtained from radiometry

hydrophilicity of different metals follow the order Hg < Au < Ag < Cu. The data of the Gibbs energy of urea adsorption on these metals follow the hydrophilicity scale except the position of Cu and Ag. However, in the estimation of the scale the value of E_{pzc} for Cu electrode was assumed quite different than that found experimentally [19].

Conclusions

1. In neutral solution, the adsorption of urea catalyzes the process of hydrogen ion discharge on the polycrystalline copper electrode.
2. The adsorption of urea in neutral solution is practically a reversible process in respect to the bulk concentration of the adsorbate and the electrode potential.
3. The kinetics of the urea adsorption on the copper electrode follows the simple Langmuir condition of adsorption process.
4. The process of urea adsorption on Cu electrode determined by impedance and radiometric methods can be described by the Langmuir and virial isotherms.
5. The surface coverage of copper electrode by urea molecules is lower than that on other metals like mercury, gold, and silver.
6. The Gibbs energies of adsorption of urea on different electrodes follow the hydrophilicity scale proposed by Trasatti [32].

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