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ADSORPTION OF AZITHROMYCIN DIHYDRATE AT STATIONARY MERCURY AND SOLID ELECTRODE

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Adsorptive component in oxidation and renewal processes at different types of electrodes for antibiotic-macrolide azithromycin dihydrate has been studied. Adsorption parameters for azithromycin oxidation processes at glass-carbon electrode and for renewal processes at mercury-film electrode were calculated.

Introduction

Voltamperometric behavior of antibiotic of macrolide series of azithromycin dihydrate (azithromycin) should be studied for developing new more ultimate techniques of quantitative chemical analysis. The importance of developing such techniques is stipulated by the fact that the given antibiotic refers to the second generation of semisynthetic antibiotic of macrolide series. Presence of nitrogen atom in its structural formula defines azithromycin into a separate class of azalides. Antibiotic possesses high microbiological and clinical efficiency in treating a number of serious infections of breathing passages, skin and soft tissues, some urogenital infections. In connection of their high therapeutic efficiency preparations having azithromycin dihydrate as a reactant are the most adulterated ones on the market of pharmaceuticals.

It is shown in the paper [1] that azithromycin oxidation process at glass-carbon (GC) electrode and renewal process at mercury-film (MF) electrode seem to be complex processes with more than one electron complicated not only by additional intermediates but probably adsorption processes.

Earlier other authors have not carried out investigations on studying azithromycin adsorption. However, the results of such investigation are required for improving metrological performances of the technique of quantitative chemical analysis. It should be mentioned that there are not many methods for studying adsorption process of organic compounds and for its quantitative assessment. All these methods have considerable restrictions in electrode selection; many of them are implemented exclusively at «liquid» (MF) electrodes.

Experimental part

Experimental technique

To choose operating conditions of determining azithromycin the modern voltamperometric analyzer STA was used.

Quartz cup with base electrolyte 0,02 M Na₂HPO₄ with volume of 10,0 ml was placed into electrochemical cell of voltamperometric analyzer and indicator glass-carbon electrode, chloride silver reference electrode and one more glass-carbon electrode as an indicator one set into proper connectors of electrochemical cell were put into solution.

With the help of the programs STA and VAM [2] the survey regime of voltamperogram was selected and anode voltamperogram of background was recorded. Aliquot of process solution of azithromycin dihydrate was added and voltamperogram was recorded again at the same conditions.

The character of dependence of current magnitude of azithromycin electro-oxidation at GC electrode on electrode cure time in solution indicates the presence of adsorption processes (Fig. 1). If electrode after curing during some time (15...30 min) in azithromycin solution without overlapping polarizing voltage was transferred into electrolyzer with background solution and sediment electro-oxidation was carried out then the peak of this sediment electro-oxidation was observed; the current magnitude in this case was equal about 1/3 of current magnitude recorded before at the electrode in solution containing azithromycin that is confirmed by literary data [3].

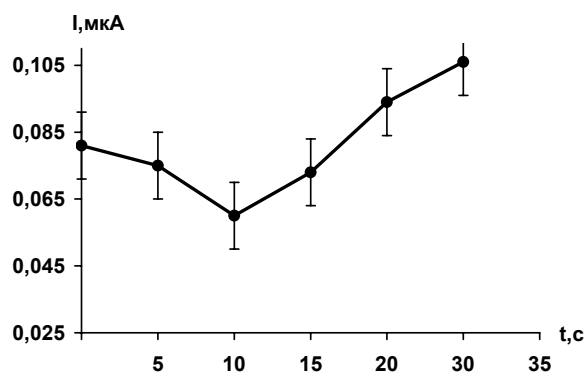


Fig. 1. Dependence of oxidation current magnitude (I_{ox}) of azithromycin on electrode curing time in solution (t) Na_2HPO_4 with 0,1 % ethanol, pH 8,2; potential change rate 30 mV/s, azithromycin concentration in solution $C_{az}=10^{-8}$ mole/l

In this case the influence of organic solvent of ethyl alcohol adsorbed at particle electrode was completely excluded [4, 5]. Unfortunately, the given dependence does not permit to estimate quantitative parameters of absorption process as well as adsorption constituent contribution into total part of electrochemical reaction.

The following methods were applied for such estimation: the method based on double back integration [6], the method suggested by S.G. Mayranovskiy [7]; and also the method of inverse voltamperometry (IVA) was used for the first time for these purposes.

To study adsorption processes at mercury-film electrode the polarograph PU-1 was used.

To calculate electrode surface charge, potential of zero-charge and surface tension on the metal-solution boundary the method of back integration of capacitive currents was used; it is applicable for stationary mercury electrodes (in this case the mercury-film electrode is used) and organic substance solution in the case when adsorption equilibrium is established rather rapidly [6].

The matter of this method consists in assumption that in the area of coincidence of capacitive current magnitude-potential curves the correspondent curves of dependence of charge density and surface tension on electrode potential coincide as well. Coincidence area is determined by potential value E_{cp} .

The investigations were carried out with the help of alternate-current voltamperometry with sinusoidal form of polarizing voltage with amplitude about 10 mV at backgrounds 0,1 M: Na_2SO_4 , NH_4Cl , NaOH . At all background electrolytes the capacitive currents were obtained, however, the most reproducible and satisfactory by all demands currents were obtained at the background 0,1 M NaOH (at the given background rather readable signals of azithromycin at the selected working conditions are recorded).

Dependences of azithromycin dihydrate capacitive current on electrode potential were recorded in potential range from 0,2 to $-1,8$ V for antibiotic concentrations in the range of $(0,01...0,5) \cdot 10^{-6}$ mole/l.

Dependence of charge density and surface tension change on MF electrode potential at different azithromycin concentration (Fig. 2) was determined by the equations:

$$q_i = A_k \int_{E_{cp}}^{E_i} I_{C_i} dE,$$

$$\Delta\sigma_i = - \int_{E_{cp}}^{E_i} q_i dE,$$

where q_i is the charge density in double electric layer (DEL) at azithromycin concentration C_i , C/cm^2 ; I_{C_i} is the value of capacitive current, A; E_i and E_{cp} are the specified electrode potential and comparison potential, V; A_k is the coefficient of proportionality which is determined by measuring capacitive current at the condenser of known capacitor, F/A ; $\Delta\sigma_i$ is the change of surface tension, J/cm^2 .

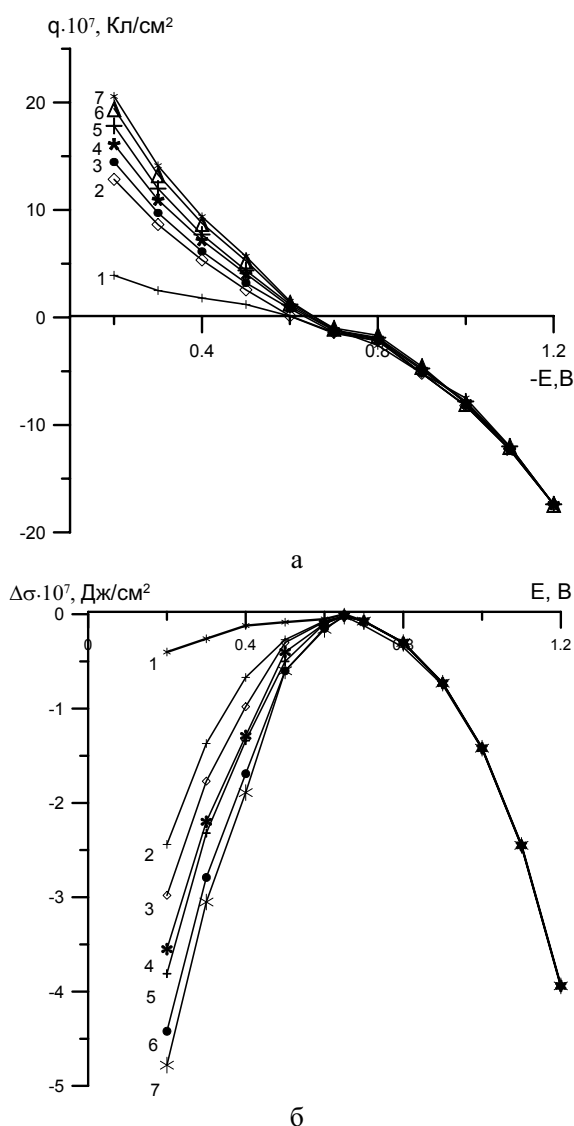


Fig. 2. Dependence of: a) charge density and b) changes of surface tension magnitude on mercury-film electrode potential at different concentrations of azithromycin dihydrate at the background 0,1 M NaOH : 1) 0; 2) $0,1 \cdot 10^{-7}$; 3) $0,3 \cdot 10^{-7}$; 4) $0,5 \cdot 10^{-7}$; 5) $0,8 \cdot 10^{-7}$; 6) $1,0 \cdot 10^{-7}$; 7) $5,0 \cdot 10^{-7}$ mole/l

Substituting value $\frac{\partial\sigma}{\partial C_i}$, obtained from the diagram (Fig. 2, b) into Gibbs equation the graph takes place in

coordinates $\frac{C_i}{\Gamma_i} = f(C_i)$ for calculating the value of maximal adsorption (Γ_∞ , mole/m²) and constant of adsorption equilibrium (k , dm³/mole)

$$\Gamma = -\frac{C_i}{RT} \left(\frac{\partial \sigma}{\partial C_i} \right)_E.$$

It was shown that adsorption process is described by Langmuir isotherm on the basis of antibiotic low concentrations that allows ignoring electrostatic interaction between the particles of surface-active organic substance (SAOS).

The value of adsorption free energy ($\Delta \bar{G}_A$, kJ/mole) was estimated from the equation $k = \frac{1}{55,5} e^{\frac{-\Delta \bar{G}_A}{RT}}$.

The data of quantitative estimation of adsorption value for azithromycin dihydrate at MF electrode are given in the Table.

Table. Parameters of adsorption process of azithromycin dihydrate at MF electrode (the method of double back integration)

Background	Potential, B	k , dm ³ /mole	Γ_∞ , mole/m ²	$\Delta \bar{G}_A$, kJ/mole
0,1 M NaOH	-0,3	$2,39 \cdot 10^7$	$1,10 \cdot 10^{-6}$	12,0
0,1 M Na ₂ SO ₄	-0,2	$0,20 \cdot 10^7$	$6,25 \cdot 10^{-6}$	46,0
0,1 M NH ₄ Cl	-0,3	$6,53 \cdot 10^{11}$	$3,93 \cdot 10^{-8}$	60,2

To study the absorption process of azithromycin at MF electrode at rather high values of antibiotic concentration the method suggested by S.G. Mayranovskiy was applied [7]. Azithromycin content in solution amounted to $(0,5...2,0) \cdot 10^{-3}$ mole/l.

It was shown that at high concentrations of azithromycin as surface-active organic substance the process is described by Frumkin isotherm. This circumstance conforms to theoretical data about the presence of specific adsorption at high concentrations of SAOS.

The above mentioned methods of quantitative determining adsorption parameters are rather informative and accurate but at the same time there is one significant disadvantage – they practically can not be used at solid electrodes.

To study the adsorption processes occurring at GC electrode the method of IVA the theoretical justification of which is stated in the paper was suggested [8].

The matter of suggested method for voltamperometric investigation of SAOS adsorption (by the example of azithromycin dihydrate) comes to solution of boundary value problem for the rate of adsorption layer formation when SAOS diffusion into electrode surface layer is the limiting stage of formation process (5):

$$\frac{\partial C_A(x,t)}{\partial t} = D_A \frac{\partial^2 C_A(x,t)}{\partial x^2}, \quad 0 \leq x \leq \infty. \quad (5)$$

$$\text{At } t=0; C_{A,i}(x,0) = C_{A,i}^0, \quad t>0, \quad x \rightarrow \infty, \quad C_{A,i}(\infty,t) \rightarrow C_{A,i}^0.$$

Besides,

$$D_A \frac{\partial C_{A,i}(x,t)}{\partial x} \Big|_{x=l} = k^* C_{A,i}^S \Gamma_\tau, \quad (6)$$

where $x=l$ is the electrode surface; $C_{A,i}^0$ is the specified concentration of adsorbable substance, mole/cm³; $C_{A,i}^S$ is the concentration of the compound by the time t , mole/cm³; t is the electrolyses time, s; D_A is the diffusion coefficient, cm²/s; k^* is the coefficient of proportionality between diffusion flow and equilibrium concentration of adsorbed substance.

The obtained data by quantitative estimation of adsorption parameters of IVA methods at glass-carbon electrode: $k = 4,79 \cdot 10^6$ dm³/mole; $\Gamma_\infty = 6,47 \cdot 10^{-8}$ mole/cm²; $\Delta \bar{G}_A = 2,4$ kJ/mole.

Results discussion

The following methods were considered for estimating adsorption activity of azithromycin at MF electrode: the method of double back integration of capacitive currents and the method suggested by S.G. Mayranovskiy. Application of these two methods allows estimating azithromycin adsorption capacity in wide range of antibiotic concentration in solution. So for large content of SAOS $(0,5...2,0) \cdot 10^{-3}$ mole/l the method suggested by S.G. Mayranovskiy was applied; by its results the conclusion was made that azithromycin renewal process is described by Frumkin isotherm.

The parameters of adsorption process were calculated by the method of double back integration for different background electrolytes in the wide range of defined azithromycin contents: the value of maximal adsorption, adsorption equilibrium constant and free energy value. Solid – glass-carbon electrodes are used, as a rule, for analytical purposes in the method of IVA for defining organic substances including azithromycin. The method of IVA for quantitative estimation of adsorption process parameters was firstly suggested.

The results obtained while using the method of inversion voltamperometry show the possibility of application to a first approximation the given method for quantitative estimation of adsorption processes coursing not only at mercury-film but also at glass-carbon electrodes. Such conclusion may be made comparing values by the main adsorption categories obtained by classical method of double back integration and method of inversion voltamperometry which can characterize the occurring process rather accurately. The obtained data allowed improving to a large degree signal reproducibility due to removal of substance adsorption influence on Faraday currents which appear in typical change of voltamperogram form.

Conclusions

1. Adsorption at stationary mercury and solid electrodes were studied by the method of double back integration and the method of S.G. Mayranovskiy for antibiotic of macrolide series. The method of inversion voltamperometry was firstly used for these purposes.
2. The main parameters of azithromycin adsorption process were firstly estimated: maximal adsorption value, adsorption equilibrium constant and free energy value in wide range of concentration of surface-active organic substances.

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DETERMINING RHENIUM IN CRUDE ORE BY THE METHOD OF X-RAY FLUORESCENCE ANALYSIS

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Optimal conditions of sorption concentration of perrhenate-ions with activated carbon have been considered. The possibility of rhenium determination with accompanying element is shown.

The analysis of geological rhenium samples is not an easy task owing to its low industrial contents as well as the presence of tungsten and molybdenum accompanying to it in ores. Rather complete review by the methods of rhenium determination in mineral raw materials is given in papers [1–3]. As rhenium is distributed nonuniformly over the analyzed sample then its determination is not possible without preconcentration. Sorption concentration of perrhenate-ions (ReO_4^-) with activated carbon (AC) is one of the most efficient methods of extracting ReO_4^- from solutions with high content of nonferrous and other metals salts. Increase of determination sensitivity is not the only and often not the main reason of concentration use. Concerning the method of X-ray fluorescence analysis (XFA) the concentration allows solving and decreasing acuity of the problem of obtaining calibration characteristics at single-type matrices [4].

The aim of the given work was to determine optimal conditions of perrhenate-ions sorption concentration at activated carbon and develop the technique of X-ray fluorescence rhenium determination in crude ore.

Experimental part

To study sorption characteristics the standard nitric acid solution Re(VII) in 3M HNO_3 with concentration of 100 mg/dm³ was used. After metal rhenium dissolution it is in solution in the form of perrhenate-ion (ReO_4^-).

Model mixtures containing different quantities of ReO_4^- ions were prepared by 3M HNO_3 dilution on the day of analysis. ReO_4^- sorption was carried out at activated carbon of BAU-A type with total pore water volume not less than 1,6 cm³/g and iodine adsorption activity not less than 60 %. For more uniform concentration sorbent granules were ground to powder in agathic mortar to the size of 50 mkm.

Influence of time contact of sorbent with solution on completeness of sorption of BAU-A ions was studied under the affect of ultra-violet radiation (UVR) of solutions and without it. Mercury lamp of high pressure DRT-220 without filter was used as a source of UVR. Distance from radiation source to the samples is 20 cm. Sorption of perrhenate-ions was carried out in static conditions. For this purpose 0,3 g of BAU-A was put into solution with volume of 10 ml. After concentration sorbent with sorbtive were filtered, the remainder was dried. Quantity of sorbed perrhenate-ions was determined by the method of XFA [5] using spectrometer «Spectroscan» (SPA «Spectron», Saint-Petersburg). The parameters of X-ray tube operation with molybdenum anode were as follows: voltage 40 kV, current 100 mA, crystallizer LiF. Time of one measurement was 200 s. $L_{\alpha 1}$, $L_{\beta 2}$ served as analytic lines at rhenium determination. Fluorescence radiation intensity at the stated lines was defined by subtracting the magnitude of background intensity.