

The use of ellipsometry for studying adsorption of organic corrosion inhibitors from aqueous solutions on metals. Review.

Part 1. Methods for obtaining adsorption isotherms¹

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Abstract

The review is devoted to the application of the ellipsometry method to study the adsorption of organic corrosion inhibitors (CIs) from solutions on the surfaces of metals and alloys. Part 1 of the review focuses on the basics of the method and discusses the necessary simplifications that should be taken into account in the study of real reflective systems. A rationale for using the ellipsometric method to determine small thicknesses of surface layers around 1 nm is given, since the basic equation of ellipsometry is derived for bulk phases. Various methods for obtaining adsorption isotherms from solutions are discussed and a brief analysis of theoretical adsorption isotherms is given. Particular attention is paid to the logarithmic Temkin isotherm. This isotherm is valid in the region of medium coverages ($0.2 < \Theta < 0.8$) and at sufficiently large heterogeneous factors f (> 4). The modified Temkin isotherm proposed by S.F. Timashev is valid in the entire range $0 < \Theta < 1$ and for $f > 0$. Articles are cited in which ellipsometry is used to determine the thicknesses of CI surface layers. Other methods of obtaining isotherms of CI adsorption from aqueous solutions are considered: analysis of anodic polarization curves, the concentration dependence of the degree of metal protection from the results of corrosion tests, electrochemical impedance spectroscopy, and quartz crystal microbalance. Part 1 presents a methodology for obtaining adsorption isotherms by the ellipsometric method and discusses as an example the adsorption of sodium *N*-phenylanthranilate on the surface of iron from a neutral solution. The adsorption isotherm thus obtained is also confirmed by another independent method, electrochemical impedance spectroscopy.

Received: November 12, 2022. Published: November 29, 2022 doi: [10.17675/2305-6894-2022-11-4-20](https://doi.org/10.17675/2305-6894-2022-11-4-20)

Keywords: *ellipsometry, adsorption isotherms, Temkin isotherm, XPS, electrochemical impedance spectroscopy, F-test, sodium N-phenylanthranilate.*

¹ The study received financial support from the Ministry of Science and Higher Education of the Russian Federation within the framework of State Contract with universities regarding scientific research in 2022–2024, project No. FZGU-2022-0003.

Introduction

The term “ellipsometry” refers to a branch of optics whose subject matter is the change in the polarization state of a light beam when reflected from any reflecting surface [1–10]. Ellipsometric method belongs to *in situ* methods. It allows monitoring the processes occurring on metal surfaces in liquid and gas–vapor phases. An important advantage of using ellipsometry in aqueous or water–organic solutions is the possibility of combining it with electrochemical measurements. This determines the use of ellipsometry to assess the surface properties of metals, including copper, in various corrosion processes and processes of applying metal films by chemical and electrochemical methods.

If a plane wave falls on the boundary of two homogeneous media with different optical properties, it splits into two waves: the wave passing into the second medium and the reflected wave. A light wave is characterized by amplitude, phase, frequency (wavelength) and polarization. Linearly polarized light, reflecting from the sample surface, becomes elliptically polarized. The task of ellipsometry is to determine parameters of this polarization ellipse. The reflection ellipsometry method allows to determine the ratio of complex Fresnel reflection coefficients for the light wave vector lying in the incidence plane (R_p) and in the orthogonal plane (R_s):

$$\rho = \frac{R_p}{R_s}$$

Usually this expression is given in the form $\rho = \tan\Psi e^{i\Delta}$. The experimentally determined quantities are the phase shift Δ and the amplitude ratio upon reflection Ψ . These angles characterize the relative changes in amplitude and phase experienced by the reflection of p and s components of the electric vector of the light wave.

On the surface of the sample (substrate) there is a plane-parallel film of thickness d_1 and complex refractive index $N_1 = n_1 - ik_1$, where n is the real part and k is the absorption coefficient. For a medium in which light with wavelength λ is incident at an angle φ to the surface, usually $N = n_0$. For a sample (substrate), the complex refractive index is $N_2 = n_2 - ik_2$. In this case, the equation for Δ and Ψ is written as:

$$\tan\Psi e^{i\Delta} = \rho(n_0, N_1, N_2, d_1, \varphi, \lambda) \quad (1)$$

In the general case, the function ρ depends on 8 quantities, and two parameters Δ and Ψ are determined experimentally. The problem of determining the thickness of the film, the optical parameters of it and the surface has no explicit solution. The most universal and reliable way is a numerical solution of the basic equation of ellipsometry for a number of models of reflecting systems and a set of parameters for these models. The inverse problem of ellipsometry is solved as follows: the values N_1, N_2, d are given and the theoretical Δ and Ψ are calculated [9–11]. Software for this can also be found in [12–14]. One can visually represent such a solution on the plane Δ – Ψ , where the parameter of each point is the thickness d . We obtain a set of nomograms on the plane Δ – Ψ , each characterized by N_1, N_2

and a change in thickness d . The experimentally determined and theoretically calculated values of Δ and Ψ are compared. As an example, let us consider the oxidation of copper in borate buffer solution with pH 7.4. At “pure” copper surface potential $E = -0.6$ V we obtained Δ and Ψ , through these angles determined the complex refractive index of copper $N_{\text{Cu}} = 0.6 - 3.2i$. During oxidation at $E = 0$ V, the angles Δ and Ψ were measured. Figure 1 shows a nomogram for calculating the thickness of copper oxides on the surface of the copper electrode in the coordinates $\delta\Delta - \delta\Psi$ where $\delta\Delta = \Delta - \Delta_0$ and $\delta\Psi = \Psi - \Psi_0$. The solid lines (1,2,3) in the nomogram are theoretical lines referring to film growth with different complex refractive indices: (1) for Cu_2O oxide – $N_{\text{ref}} = 2.75 - 0.05i$, (2) for CuO – $N_{\text{ref}} = 2.75 - 0.2i$, and (3) for CuO – $N_{\text{ref}} = 2.75 - 0.4i$. Nomograms are connected by lines of equal thickness. In this case they are drawn through 1.8 nm. The experimental angles are plotted on this plane and it is determined which oxide they belong to. This method is used when it is possible to trace film growth ellipsometrically. One of the first programs, the Mac Krakin program [9], is usually used for processing such results of the experiment.

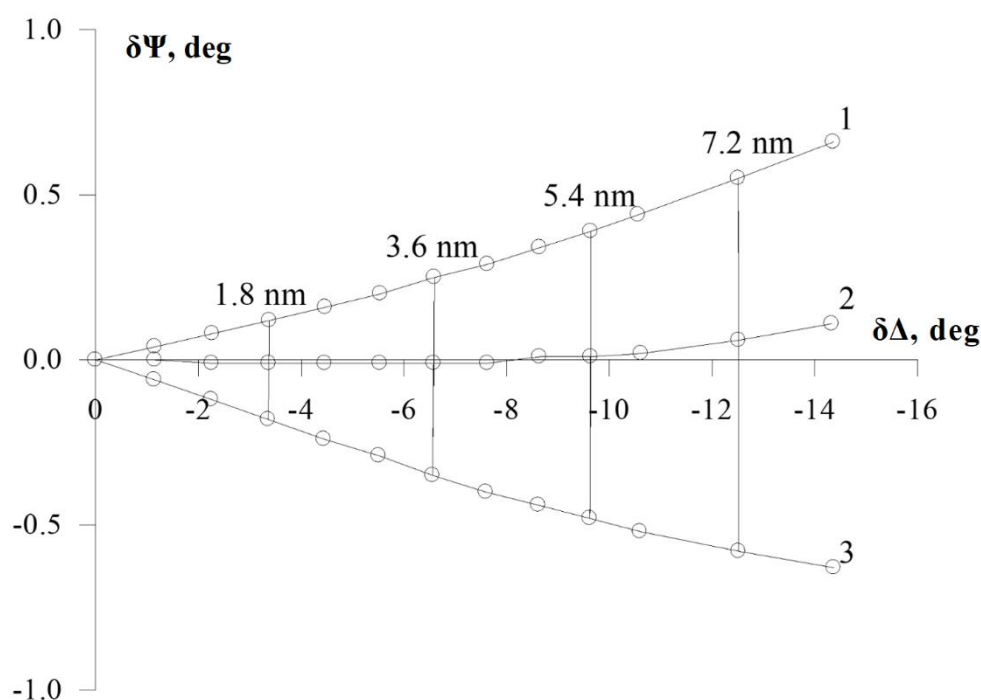


Figure 1. Nomogram for calculating the thickness of copper oxides on the surface of the copper electrode in borate buffer solution pH 7.4.

A completely new approach was developed in the creation of devices intended for complex research of parameters of micro objects in reflected light. Lateral spatial resolution of the device reaches 10–15 nm, the expected accuracy of determining the refractive index is about 0.5% [15]. Microscopy using the principles of ellipsometry makes it possible to obtain a positive image of the object under study, its negative image, as well as all intermediate states, selecting at which of them the object contrast will be maximal.

As a rule, ellipsometers have a horizontally arranged sample surface. Polarizing goniometers can be adapted for ellipsometry of vertically arranged surfaces. An ellipsometer for studying vertical surfaces can be constructed based on a conventional spectrometer-goniometer by equipping it with optical prisms and a compensator with reporting devices, a light source, and a photodetector with recording system. An example of such an ellipsometer is an ellipsometer for electrochemical studies designed in the 1980s at the Institute of Electrochemistry of the Russian Academy of Sciences [16].

High efficiency of ellipsometric nanometry has been noted for determining the composition of layers, crystal perfection of materials and, first of all, for determining their geometric characteristics with high accuracy. The theoretical basis of the method and its application in various fields of science and technology were reflected in the conference proceedings [17–19].

The IPC RAS laboratory of Physical and Chemical Bases of Metal Corrosion Inhibition has two ellipsometers with a vertically positioned sample surface and manual control. This is an upgraded standard Gaertner L119X ellipsometer, which uses a single-frequency low-noise LSM-S-111 solid-state laser of 540 nm wavelength as a light source, with an improved system of light flux modulation and registration. The second ellipsometer was modified from an automatic ellipsometer by Rudolf Research with a 640 nm HeNe laser, light flux modulation and a photomultiplier tube as a recorder of light reflected from the surface. An electrochemical cell, which is controlled by a potentiostat, is installed on the axis of the device.

The following simplifications are taken in the study of real reflecting systems:

1. All interfaces are geometric surfaces. The basic equation of ellipsometry is obtained for the case of a perfectly sharp surface interface.
2. Light passes through optical elements (compensator, lenses) without reflection losses.
3. The real light beam is replaced by a flat monochromatic electromagnetic wave. Such idealization allows the simplest analysis of ellipsometer measurement schemes and simplifies the interpretation of experimental results.

Back in 1983, at the 2nd All-Union Conference “Ellipsometry – a method for studying physicochemical processes on the surface of solids”, V.A. Shepelin gave a brief historical overview of the development of the ellipsometric method as applied to electrochemical studies [20]. He fairly noted that in electrochemical studies, ellipsometry is qualitative in nature, and to interpret the experimental data, it is necessary to compare them with the electrochemical parameters of the system: potential, current, capacitance, *etc.* This method provides valuable information about the composition and thicknesses of surface layers. This is necessary to control metal corrosion and to identify the mechanism of action of one of the effective means of corrosion protection of metals and alloys – corrosion inhibitors (CIs). CIs modify the protected metal (alloy) surface due to adsorption or formation of hard-soluble compounds with metal cations, usually reducing its active area.

2. Using ellipsometry to determine film thicknesses

In the vast majority of articles the CI on the metal surface is fixed by the change of Δ and Ψ angles, in some cases its layer thickness and possible orientation on the surface are determined. In [21], *in situ* ellipsometry and *ex situ* X-ray photoelectron spectroscopy (XPS) were used to investigate the nature of the copper surface during 1,2,3-benzotriazole (BTA) adsorption and to determine the stoichiometry, thickness and chemical composition of Cu-BTA top layer films. Films formed from Cu_2O and CuO under oxidizing conditions are typically 5–40 Å thick and are best described as Cu^+BTA . The thickness of the top CI layer is calculated from XPS data at the $\text{N}1\text{s}/\text{Cu}3\text{p}$ core level and agrees well with the thickness determination by ellipsometric measurements on similar samples. A study of zinc behavior with BTA solutions in alcohol medium was described in [22]. The authors note a good agreement in the thickness of the upper layer between the results of ellipsometry and the intensities of XPS peaks calculated using the Seah model. Formation and dissolution of oxide on copper under transpassive conditions in alkaline electrolyte was investigated by a combination of electrochemical techniques and *in situ* and Operando Raman spectroscopy and photoluminescence spectroscopy, as well as ny spectroscopic ellipsometry in [23]. In [24] the interaction of an organic corrosion inhibitor 2-mercaptobenzothiazole (MBT) with copper in alkaline solution was investigated by *in situ* infrared (IR) and Raman spectroscopy, and *in situ* spectroscopic ellipsometry coupled with cyclic voltammetry (CV).

Usually, when examining the surface by the ellipsometric method, adsorption is taken to mean “sticking to the surface”. Determination of CI film thicknesses and adsorption kinetics are described in detail in [25]. In this paper, the adsorption and desorption kinetics of organophosphorus CIs on the surface of OL37 steel are investigated. They are organophosphoric corrosion inhibitors: amino trimethylene phosphonic acid and 1-hydroxy ethylidene-1,1-diphosphonic acid. The concentrations of the inhibitor solutions were 1%. The steel plate was placed for 40 min in the CI solution. The parameters of the plate were measured before and after immersion. From these data, the thickness of the CI film was calculated. During CI desorption, the value of Δ increases, while the value of Ψ decreases as its film thickness decreases. The measured refractive index of the CI film is $n_{\text{ref}} = 1.63$. The CI desorption from the plates was determined in air. In [26] ellipsometry has been used to determine the thickness and growth rate of protective copper-benzotriazole (Cu-BTA) and copper-benzimidazole (Cu-BIMDA) surface films formed on CuO/Cu substrates by immersion in warm (60°C) aqueous (0.017 M) solutions of BTA and BIMDA. The growth rate of Cu-BTA films is found to be significantly less than that of CuBIMDA films. For 3 min immersions the Cu-BTA and Cu-BIMDA films grow to thicknesses of about 100 Å and about 475 h respectively. A possible explanation of the generally greater protective properties of Cu-BTA compared with Cu-BIMDA is discussed. Similar studies are given in [27]. In this work, the anti-corrosion layer of MBT on the surface of copper obtained in its solutions was analyzed by spectral ellipsometry. The results showed that the MBT anti-corrosion layer was formed on the Cu_2O layer in its solution at temperatures above 50°C.

In [28], the protein adsorption on plates made of tantalum, niobium, zirconium and titanium oxides (Ta_2O_5 , Nb_2O_5 , TiO_2 , ZrO_2) from solutions with different concentrations was studied using “dynamic” ellipsometry. The adsorption rate depended on the solution concentration and immersion time. The thickness and growth kinetics of CI films of adenine and purine on copper were determined in [29]. The obtained thicknesses correspond to at least monolayers (0.5 nm) formed from passivate solutions. The horizontal orientation of adenine on the copper surface was established.

The authors [30] use imaging internal reflection ellipsometry (IRE) in combination with a microfluidic device to study the adsorption of inorganic salt ions to silica–water interfaces. Due to the high resolution of our technique, we are able to quantify the adsorption of Na^+ and Ca^{2+} ions from aqueous solutions of their chloride salt as a function of their bulk concentrations at pH 3 and 10. Changes of ellipsometric parameters were recorded for each concentration (C), but without plotting the adsorption isotherm. The adsorption of benzotriazole (BTA), tolyltriazole (TTA) and two different N -methylamino substituted triazoles on copper surfaces in hydrocarbon media has been examined by *in situ* ellipsometry and time-of-flight secondary ion mass spectroscopy in [31]. All four triazoles were shown to form films, and the ellipsometric study estimated the film thickness to be in the range of 0.5–2 nm after a 1000-minute exposure. The layers formed from BTA and TTA were thicker (up to 2 nm) than those formed from N -aminomethyl substituted triazoles (0.5 nm). Desorption was studied qualitatively, but it was found that no more than 20% of the adsorbed material was desorbed. The time-of-flight secondary ion mass spectroscopy study showed that while BTA and TTA adsorbed intact did the N -aminomethyl substituted triazoles appear to lose their aminomethyl tails on binding since only signals corresponding to triazole moieties of the compounds were detected. The authors [32] established the adsorption of poly(acrylic acid) films in the form of sodium poly(acrylate) on polished calcite crystals in aqueous electrolytes at pH 9 by ellipsometric method. Ellipsometric angles were converted to adsorbed mass using an optical layer model. This model accounts for surface roughness by introducing an additional surface layer. It is found that the adsorbed mass saturates about 4 mg/m^2 .

The basic equations of adsorption isotherms

The study of CI adsorption on the surface of technically important metals *in situ* in aqueous solutions is a complex physicochemical task. Researchers of CI adsorption face the problem of selecting an adsorption isotherm equation that can adequately describe the experimental data and obtain the free energy of adsorption. The logarithmic Temkin isotherm was most often used to describe it:

$$\Theta = \frac{1}{f} \ln[B_{\max} C] \quad (2)$$

This equation is derived from the complete Temkin isotherm [33].

$$\Theta = \frac{1}{f} \ln \frac{1 + B_{\max} C}{1 - B_{\min} C} \quad (3)$$

where B_{\max} and B_{\min} are adsorption equilibrium constants corresponding to the highest and lowest values of adsorption energy (in 1/mol); C is the concentration of the substance in solution (in mol/L); f is the surface heterogeneity factor characterizing the change in the enthalpy of adsorption with coverage.

The logarithmic Temkin isotherm is valid in the region of medium coverage ($0.2 < \Theta < 0.8$) at sufficiently large f (> 4).

When selecting an equation to describe an experimentally obtained isotherm, the following criteria are used. If the isotherm is S-shaped and Θ proportional to $\lg C$ in the region of medium coverage, the Frumkin, Hill-de Boer, Parsons, Freundlich, Temkin or Bockris isotherms can be used to describe the experimental data in the region of medium coverage, the form of which is given in [34–36]. Comparison between experimental and theoretical curves is made by Fisher's F -criterion. In order to choose an equation for the adsorption isotherm, a statistical evaluation of the degree of adequacy of the proposed equations to the experimental results was carried out. At a statistical evaluation of the degree of adequacy of the model to the experimental results, the R^2 criterion is used.

The Frumkin isotherm equation is:

$$BC = \frac{\Theta}{1 - \Theta} e^{-2a\Theta} \quad (4)$$

where a is the attraction constant characterizing the interaction between adsorbate particles, B is the adsorption constant related to the standard free energy of adsorption ΔG_a^0 by the relationship:

$$B = \frac{1}{55.5} \exp\left(\frac{-\Delta G_a^0}{RT}\right) \quad (5)$$

Let's represent this equation as a linear relationship in the coordinates $X = \Theta$, $Y = \ln \frac{\Theta}{1 - \Theta} C$:

$$Y = d + bX, \quad (5a)$$

where d and b are regression coefficients.

For the same purpose, let us present the logarithmic Temkin equation (2) in the coordinates $X = \ln C$, $Y = \Theta$; and the Langmuir equation:

$$BC = \frac{\Theta}{1 - \Theta} \quad (6)$$

in the coordinates $X = \ln C$, $Y = \ln \frac{\Theta}{1 - \Theta} C$.

Often the adsorption of organic compounds on solid metals is adequately described by the logarithmic equation of the Temkin isotherm (2). Relatively recently [37], S.F. Timashev suggested to introduce into the expression for the full Temkin isotherm the difference values of dimensionless molar concentrations, so that $\Theta = 0$ at $C = C_0$:

$$\Theta = \frac{1}{f} \ln \frac{1 + n^{-1} B_{\max} (C - C_0)}{1 + n^{-1} B_{\min} (C - C_0)} \quad (7)$$

In this equation, the concentration C is an independent variable, C_0 is a known value of the minimum concentration, n is 55.5. The values f , B_{\max} , B_{\min} are unknown parameters. The algorithm for determining these values is given in the same place [37]. This isotherm, unlike the Temkin logarithmic isotherm, is valid for the whole range $0 < \Theta < 1$ and for $f > 0.0$.

4. Methods for obtaining adsorption isotherms from aqueous solutions

Often CI adsorption isotherms are obtained from the analysis of anodic polarization curves, from the concentration dependence of the degree of metal protection according to the results of corrosion tests. The inhibition efficiency was calculated from the assumption of the blocking effect of the adsorbed particles on the electrode. In [38] the protective effect of Furfuryl alcohol as CI of N80 steel in HCl can be explained by adsorption of its molecules on the active areas of the metal surface. The degree of surface coverage was determined by weight loss of the metal during corrosion tests. The inhibitory effect increases linearly with increasing inhibitor concentration C_{inh} , which, according to the authors, indicates a logarithmic Temkin isotherm with $-\Delta G_a^0 = 20.1$ kJ/mol. In [39] the synergistic effect of *N*-hexadecylpyridinium bromide (PyC₁₆Br) and different sodium halides (NaCl, NaBr, and NaI) on the corrosion of mild steel in 0.5 M H₂SO₄ solution has been investigated using electrochemical methods, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The degree of surface coverage was estimated by the current density in the presence and absence of CI. The experimental results in this study for the systems PyC₁₆Br and PyC₁₆Br/halide ions were found to agree with the Temkin isotherm. $-\Delta G_a^0$ varies from 43 (in the absence) to 50 kJ/mol (in the presence of halides). Protection efficiency obtained in the presence of PyC₁₆Br with the coexistence of halides increases in the order: I > Br > Cl, which seems to indicate that the radii and the electronegativity of the halide ions play a significant role in the adsorption process. Thus, both physical and chemical adsorption occurred. In [40] the adsorption and corrosion properties of 3 different organic molecules: 2-naphthalenesulfonic acid, 2,7-naphthalenedisulfonic acid and 2-naphthol-3,6-disulfonic acid were studied on Fe-Armco in H₂SO₄ solution. The degree of surface coverage by adsorbed CIs was calculated by comparing current densities in the absence and presence of CIs. The experimental data were described by the Frumkin isotherm with an adsorption energy of 17–21 kJ/mol.

A more correct method for determining the parameters of adsorption isotherms is the calculation of electrochemical impedance spectroscopy (EIS) measurements [41–45]. In [45] a new corrosion inhibitor, namely (*NE*)-*N*-(furan-2-ylmethylidene)-4-({4-[*E*]- (furan-2-ylmethylidene)amino]phenyl}ethyl) aniline (SB) has been synthesized and its influence on corrosion inhibition of copper in 1 M hydrochloric acid solution has been studied by both electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements. The investigated inhibitor has shown good inhibition efficiency in 1 M HCl. The adsorption of SB on the copper surface follows the Langmuir isotherm. Copper surface characterization was performed using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Quantum chemical calculations show that SB has large negative charge in nitrogen and oxygen atoms, which facilitates the adsorption of SB on the copper surface. In [46], adsorption of the macrocyclic compartmental ligand: (*2E*)-3,6,10,13-tetramethyl-2,7,9,14-30-tetraaza-1,8(1,4)dibenzena cyclotetradecaphane-2,6,9,13-tetraene and its Ni(II) and Cu(II) complexes on the surface of Cr10Ni alloy in 3.5% NaCl solutions obtained by the EIS method is described by the Freundlich isotherm. The corresponding values $-\Delta G_a^0$ lie between 17.09 and 20.19 kJ/mol, which corresponds to physical adsorption. In [47], the synergism between rare earth cerium(IV) ion and vanillin on the corrosion of cold rolled steel in 1.0 M HCl solution was first investigated by weight loss, potentiodynamic polarization, ultraviolet and visible spectrophotometer (UV-vis), X-ray photoelectron spectroscopy (XPS) and atomic force microscope (AFM). The results revealed that vanillin had a moderate inhibitive effect, and the adsorption of vanillin obeyed the Temkin adsorption isotherm. In [48], three Schiff bases named 1,5-bis[2-(2-hydroxybenzylideneamino)phenoxy]-3-oxopentane (D1), 1,5-bis[2-(5-chloro-2-hydroxybenzylideneamino)phenoxy]-3-oxopentane (D2) and 1,5-bis[2-(5-bromo-2-hydroxybenzylideneamino)phenoxy]-3-oxopentane (D3) were synthesized and their inhibitive capabilities on the aluminium corrosion in 0.1 M HCl were investigated by means of electrochemical impedance spectroscopy, Tafel polarisation and scanning electron microscopy techniques. Results showed that, compounds under study exhibit inhibitor properties and adsorption of these compounds was found to accord with Temkin adsorption isotherm. The values of surface coverage calculated for different concentrations of Schiff bases were used to test graphically to various adsorption isotherms including Freundlich, Langmuir, Temkin and Frumkin isotherms. To choose the isotherm that best fit to experimental data, the correlation coefficient (R^2) was used and the best fit was obtained from the Temkin isotherm. The calculated values of $-\Delta G_a^0$ ranged from 49.38 to 57.49 kJ/mol for studied Schiff bases and these values point out the adsorption of compounds occur by chemisorption. In [49, 50], the adsorption of IFKhAN-92 CI on mild steel from H_2SO_4 and 2.0 M HCl was investigated by this method. The logarithmic Temkin isotherm was applied to describe the adsorption. Nevertheless, an important argument in favor of CI chemisorption is rightly considered the possibility of describing the adsorbate adsorption kinetics by the Roginsky–Zeldovich equation [51].

$$\Theta = \frac{1}{b} \ln \left[\frac{k}{b} \tau + 1 \right], \quad (8)$$

where τ is time; b and k are constants. The possibility of describing the adsorption kinetics of adsorbate by this equation indicates a slow, logarithmic growth of adsorption degree over time, which reflects the kinetic difficulties of adsorption of subsequent portions of it due to the growth of activation energy during energy heterogeneity of the surface, when it begins with filling the centers with the lowest activation energy.

In [52], the adsorption isotherm of benzyldimethyldodecylammonium chloride on the steel surface was obtained by another independent method, quartz crystal microbalance. Experimentally determined adsorption isotherms were described by the Langmuir model.

5. The ellipsometric method for obtaining adsorption isotherms

The main assumptions to be guided by when studying adsorption on metals of organic CI by the ellipsometric method are:

- homogeneity of the adsorption film by its thickness d ;
- its stability in time – the angle Δ_0 characterizing the state of the surface before adsorption is constant, so the change can be attributed to adsorption itself
- proportionality between d and changes in the angle Δ , *i.e.* the difference $\delta\Delta = -(\Delta - \Delta_0)$, where Δ is the current value of the angle;
- when the Δ angle stops changing with the increase in concentration of the adsorbate C , *i.e.*, it comes to a plateau on the $\delta\Delta = f(\lg C)$ curve, it can be regarded as evidence that the adsorbate coverage Θ approaches 1 and that the adsorbate forms a monolayer.

In order to interpret the experimental data on the magnitude of the Δ angle change more confidently, it is always necessary to estimate the thickness of the adsorption layer and compare these changes with the size of the CI molecule, determined through the bond lengths of its components. This makes it possible to assume monolayer coverage (when the isotherm reaches a plateau), the formation of complexes, or the formation of a second layer. Knowing the thickness of the adsorption layer and the size of the molecule allows us to judge the position of the adsorbed molecules on the adsorbent surface. Adsorption isotherms of organic compounds from solutions using the method described above can be described by the Frumkin, Langmuir, or Temkin equation. These isotherms straighten in the medium coverage region in logarithmic coordinates. However, if we use Fisher's criterion for statistical evaluation of the adequacy of the experimental results to the Frumkin and Temkin equations, we can show that, in terms of statistical hypotheses, the Frumkin and Temkin isotherms are reliable in the region of medium coverage [53]. In this regard, the choice of an isotherm often depends on the will of the researcher. The main condition is to choose such an adsorption isotherm that would most fully describe the experimental data.

To obtain the isotherm of CI adsorption on the metal by the ellipsometric method, the electrode potential must be kept constant. During the experiment, the angles Δ and Ψ ,

characterizing the electrode surface, are continuously measured at a fixed value of the electrode potential. When the angles stop changing (their changes lie within the measurement error range of 0.05°), it is considered that the surface is stable. The CI concentrate is added to the electrochemical cell and, if the Δ angle decreases, this decrease is attributed to CIs adsorption. It follows from the solution of the basic equation of ellipsometry (1) that the maximum value of angle Δ_0 refers to a “clean” surface. As the oxide film or CI adsorption film grows, the Δ angle decreases. For each C , concentration of CI, measurements are taken until the Δ angle stops changing. To construct an isotherm, *i.e.* function $\delta\Delta=f(\lg C)$ for each C , the corresponding value $\delta\Delta=-(\Delta-\Delta_0)$ is taken. From the solution of equation (1) in the region of small thicknesses, for $d<10$ nm a linear dependence between film thickness d and changes of Δ :

$$d=-\alpha\delta\Delta=-\alpha(\Delta-\Delta_0) \quad (9),$$

where α is the proportionality coefficient. The value of C at which the angle stops changing corresponds to monolayer coverage, *i.e.*, the surface coverage with the adsorbate $\Theta \rightarrow 1$. Assuming that Θ is proportional to $\delta\Delta$, equation (9) takes the form

$$\Theta=-\beta\delta\Delta, \quad (10)$$

where β is the proportionality coefficient. This makes it possible to construct the adsorption isotherm from the experimental data and estimate its standard free energy of adsorption.

6. Adsorption of organic corrosion inhibitors

The main requirement for the electrode is a flat “mirror” surface that reflects the light beam well. For electrochemical studies, the metal electrode is ground on optical glass with sandpaper, gradually reducing the degree of its granularity. It is polished on felt impregnated with aluminum oxide suspension. The electrode surface is considered degreased if a drop of moisture is retained on it when washed with distilled water. The electrode with the moisture drop is placed in an electrochemical cell with a background solution. To perform electrochemical and ellipsometric measurements simultaneously, a cylindrical Teflon cell with quartz windows for light entrance and exit is designed. The electrode is placed vertically on the optical axis of the ellipsometer.

In the 1980s, many works appeared on the application of this *in situ* method for the analysis of surface layers on iron in neutral solutions. In our Institute the object of ellipsometric studies of such surface layers was also Fe, including those in borate buffer. The refractive indices of “pure” Fe surface $N=n-ik$, *i.e.* surface without oxide film at $E=-0.65$ V potential, N and thickness of oxide layers and kinetics of electrode oxidation at different potentials were determined [54]. The data obtained agreed with the literature data [55–60].

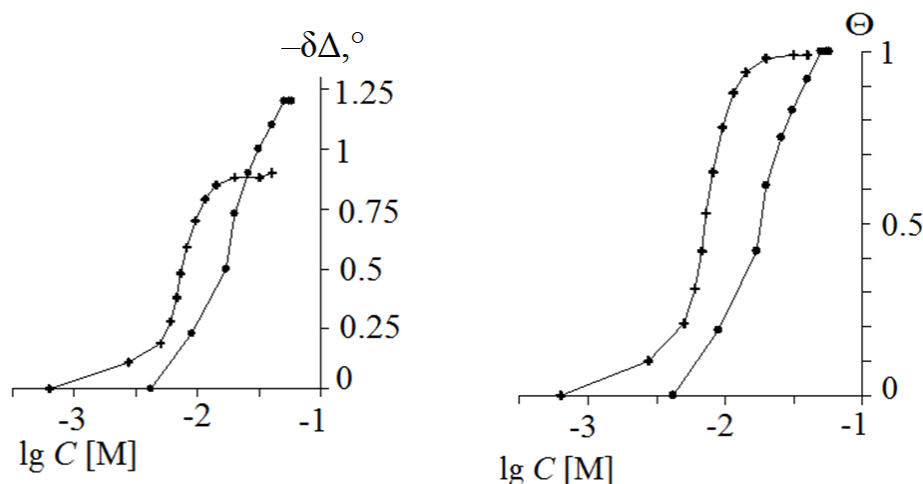


Figure 2. Variation of the ellipsometric angle Δ (a) and the degree of surface coverage Θ (b), as a function of SPhA concentration in borate buffer with pH 7.4 at adsorption on the iron surface. $E = -0.65 \text{ V}$ (●) and $E = 0.2 \text{ V}$ (+).

Among such ellipsometric studies we should especially mention the study of the possibility of adsorptive oxide-free passivation of Fe by organic CI in a neutral solution. It was first demonstrated by one of the authors of this review with collaborators on the example of sodium *N*-phenylanthranilate (SPhA) $\text{C}_6\text{H}_5\text{NHC}_6\text{H}_4\text{COONa}$ using coulometric *in situ* analysis [61]. SPhA suppresses the dissolution of iron in borate buffer with pH 7.4, transferring it to the passive state without formation of an oxide film. Its absence on the surface of a passive iron electrode is shown by coulometric analysis. Although studies of such “oxide-free” passivation of Fe conducted by various methods (electron diffraction, secondary ion mass spectrometry, ellipsometry, XRD and IR spectroscopy) and summarized in the monograph [61] suggested that the oxide film, if formed, is very thin and after a considerable time interval. Meanwhile, the Fe passivation itself occurs rather quickly (several minutes), so the listed physical methods of *extra situ* surface studies could only indirectly show the ability of SPhA to slow down the oxide formation, but the thin oxide layer they found could be formed when transferring the electrode from the solution to the device chamber. Therefore, another *in situ* method, more sensitive than coulometry, was required. It seemed reasonable to use the ellipsometric method in these studies.

At $E = -0.65 \text{ V}$, there is no oxide film on an iron surface in neutral borate buffer solution according to the Pourbaix diagram [62]. Applying the ellipsometric method, it was found [63] that in the SPhA solution on “pure” Fe at $E = -0.65 \text{ V}$, a film begins to grow, which they explained by CI adsorption. Varying the concentration of SPhA it was possible to obtain isotherms of SPhA adsorption on reduced ($E = -0.65 \text{ V}$) and oxidized ($E = 0.2 \text{ V}$) Fe surfaces in this solution. These isotherms are shown in Figure 2. The isotherms were S-shaped and Frumkin isotherms were applied to describe them. In the cathodic region, $E = -0.65$, $-\Delta G_a^0 = 15.6 \text{ kJ/mol}$, and at $E = 0.2 \text{ V}$, $-\Delta G_a^0 = 16.8 \text{ kJ/mol}$.

When discussing the results of adsorption measurements by the ellipsometric method, questions arise that require additional explanations. Changes of $\delta\Delta \sim 0.1^\circ$ in the area of low concentrations are usually associated with the beginning of film growth. Is it valid to use the ellipsometric method for such small values since the basic equation of ellipsometry is derived for bulk phases? Can such changes be attributed to film growth rather than to changes in the surface layer electron concentration? However, in [64] for a three-layer system on the Fe surface (outer layer of adsorbed molecules of an organic compound is a thin oxide layer, electron-rich or electron-poor – phase oxide) it is shown that changes in the phase angle $\delta\Delta$ due to a twofold increase or decrease in the electron concentration are small ($\ll 0.1^\circ$). Since in measurements of adsorption of organic compounds, as a rule, the values $\delta\Delta$ are many times (sometimes by orders of magnitude) higher, in our works they were associated only with changes in the amount of adsorbed compound or ion. How are changes in solution concentration related to the refractive index of the adsorption layer? How is the refractive index of the adsorption layer determined? As for the refractive indices of adsorption layers, they have previously been determined through the refractions of their constituent elements. SPhA solutions are colored and absorb in the region of 200 to 300 nm. There is no absorption in the working region of the spectrum ($\lambda = 640$ nm). We measured the refractive index of the solution n_p on an IRF-23 refractometer with a hydrogen Heissler tube ($\lambda = 653.5$ nm). The dependence of n_p on C was determined to be linear with an angular coefficient of 0.06. If $n_p = f(C)$ is linear, the adsorption of Γ can be determined by the formula [64, 65]:

$$\Gamma = d(N_{\text{ref}} - n_p) \frac{dN}{dC}, \quad (11)$$

where d is the thickness of the adsorbed layer and N_{ref} is its refractive index determined by ellipsometric method. In the same works, we observe a symbate relationship between the amount of adsorbed substance (Γ) and the thickness of the adsorption layer (d). Obtaining the thickness of the adsorption layer, we also determined the degree of surface coverage. When the dependence $\delta\Delta - f(\lg C_{\text{inh}})$ goes into a plateau, we can assume the formation of a monolayer. The monolayer thickness at $\Theta \rightarrow 1$, for the SPhA molecule is 1.3 nm. This thickness corresponds to the size of the phenylanthranilic acid molecule as determined by the bond lengths of its constituent elements.

To confirm the correctness of the interpretation of ellipsometric adsorption measurements, we also used other independent methods for measuring SPhA adsorption. For example, in [66] an isotherm of SPhA adsorption on an iron electrode was obtained by another *in situ* method – EIS, which proved to be adequate to the isotherm observed earlier when measuring the adsorption of this CI by the ellipsometric method in the same borate buffer.

Later in [53] comparison of SPhA adsorption isotherms obtained on a gold electrode in neutral borate buffer using two independent *in situ* methods: ellipsometry and piezoelectric quartz crystal microbalance. Fisher's F -criterion analysis showed that these SPhA isotherms

were statistically indistinguishable with 95%. In addition, repeated comparison of the results of ellipsometric studies of adsorption with its *ex situ* measurements (XRD, infrared spectroscopy) also indicated the absence of at least serious contradictions [67].

In the review [68] special attention is paid to three fundamental aspects: the adsorption of CI on the metal surface, its relationship with the passivity of the protected metal (alloy) and the dependence of CI efficiency on its chemical structure. In the next part of the review we will present examples of studies of adsorption on metal surfaces by the ellipsometric method of known CI: salts of carboxylic and phosphonic acids, acidic dialkyl phosphates, as well as azoles.

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