

DETERMINATION OF THE DEGREE OF ADSORPTION ON COPPER AND BRASS TINS BY CHANGING THE TEMPERATURE ON THE SURFACE BEFORE INHIBITION, BY FOLLOWING THE CORROSION PARAMETERS

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Abstract

The protection degree of gelatin as the adsorption inhibitor is in direct dependence with the way of forming of adsorption layer and its structure, which has been used for following the very process of adsorption by measuring corrosion. In this study, the temperature of copper and brass plates was varied (293, 15-353, 15 K) before submerging into a solution of inhibitor, after which, under the same conditions (electrolytes and the treatment time), the samples were exposed to the corrosion effect. Observing corrosion parameters and comparing them to the assumed adsorption degree of gelatin, codependences of corrosion and adsorption were established. This led to determining the activation energy of gelatin adsorption on the surface of copper and brass.

Key words. *Inhibitor, corrosion, copper and brass tins, gelatin, adsorption*

Introduction

Metal corrosion is a destruction of metal under the influence of physical-chemical factors, and it occurs on the surface of metal from where it spreads, slower or faster, into the depth of metal. By mechanism of formation there are two types: chemical and electro-chemical corrosion. The chemical type of corrosion manifests in a formation of different layers on the metal surface in forms of oxides- carbonates, sulfides and sulfates. Chemical corrosion occurs by immediate action of different substances on metals in the atmosphere of dry gases and in some liquid mediums, like non-electrolytes and liquid metals[1].

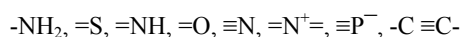
Electro-chemical corrosion happens in electrolytes by the laws of electro-chemical kinetics. In most cases it manifests by corrosion of metal constructions in atmosphere (air), by destruction of pipes in the ground, by ruination of machines as a result of exposure to acidic, basic and salt solutions and by corroding in melted salts.

Copper has a satisfying corrosion resistance towards the effect of water and atmosphere, and it is considered as relatively noble metal. In moist air and in water it wraps (envelops) itself with thin layer of carbonates, so called *patina*. It is soluble in sulfuric and nitric acid, which are strong oxidation agents. Brass, under certain conditions, exhibits less resistance to corrosion than pure copper, because of the presence of zinc in the alloy [2].

Inhibition in general sense includes changing the rate of chemical reaction under the influence of different agents, which adsorb on the metal surface and form a protection layer on the phase border metal-corrosion layer [3,4]. Thin film, which forms, is in most cases mononuclear layer and it efficiently stops corrosion.

From the reaction kinetics point of view, inhibitors stop anode process, cathode process or both in heterogenic system metal-electrolyte. Effects of inhibitor can be such, so that inhibitor does not undergo chemical changes at the end of the process, or it can be an active product of a chemical reaction if it undergoes chemical changes on the surface of the metal [5]. It is important to know if an inhibitor affects anode or a cathode process, because one inhibitor can inhibit cathode with simultaneously inhibiting anode process. For a compound to have good inhibiting characteristics, it has to have atoms with one or more free electron pairs. Efficiency of inhibitors depends on the character and spatial arrangement of these centers. In order for inhibitor to have better efficiency, it is convenient to have the inhibition centers in one short branch close to the middle of the molecule, while the rest of the molecule should "fan-like" cover the surface of the metal.

Next to the specific structure of a molecule, his size plays an important role. Efficiency of linear compounds is the highest when the longitude of the chain is optimal. If chain-like compounds include only one active centre, than the rule of inhibitor efficiency depends on the quality of the active centre. These centers can have the following comparison:



Efficiency of the above-mentioned centers decreases from left to right.

The action mechanism of inhibitors is explained by different theories, but as the most acceptable there are: the theory of electrical resistance, the theory of layers and the theory of adsorption exchange.

Gelatin represents the main protein of intercellular substance in animal tissue, and it is made by partial hydrolysis of collagen. After the first base treatment and extraction with warm water, the material rich with collagen produces the gelatin type B, which exhibits isoelectric value (point) of 5. After the first acid treatment, gelatin type A is produced, which exhibits isoelectric value between 7 and 9. Gelatin is relatively insoluble in cold water but easily hydrates in lukewarm water. Mixed with cold water, granules of gelatin swell a little absorbing water 5 to 10 times, comparing to their weight. On 313 K swelled particles of gelatin dissolve and form solution, which cools down and reaches the point of gelatification. The degree of swelling of the gelatin granules depends of pH and the greatest effect is achieved when pH of the solution is the most different from isoelectric value of the gelatin. The degree of solubility can be changed by changing different factors like temperature, concentration and the size of

particles. In aqueous solutions, depending of pH value, gelatin behaves differently and exhibits ionic character[6,7].

Gelatin produces thermo-changeable gels, which when heated to 303-308 K change into a solution. When it reaches the point of gelification, gelatin solution forms a gel of a different structure. That process of gel changing into a solution is variable and can be performed more times.

Primary structure of protein gives us the sequence of amino acid remains in polypeptides. The first remainder in the sequence has a free α -amino group, and the last remainder has α -carboxylic group.

The secondary structure of protein represents conformation of polypeptide chain. On the sequence of amino acids depends the orientation of the polypeptide chain in space.

Collagen appears in forms of long treads, which by heating change to amorphous balls called gelatin. They have high percent of glicyn (up to 30%), also 10 to 12% of hidroxiprolin and hidroxisilizin. The basic structure of collagen comprises of three polypeptide chains, which are not spiraled but wrapped around each other (as a rope that has a few treads) into a so-called super-spiral (tropocollagen), which is represented in Figure 1[6].

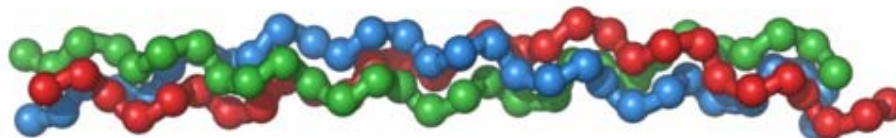


Figure 1. Secondary structure of gelatin (tropocollagen)

Appearance of adsorption on a solid surface relates to a fact that on a solid surface, molecules, atoms and ions don't have saturated force field, so with adsorption of particles from a solution the surface energy decreases, so the process occurs spontaneously. Molecules attach to a surface in two ways, depending on the nature of the bond between adsorbent and adsorbate.

With physical adsorption there is an appearance of Van der Waals forces, which have a long range, but weak intensity. The energy that releases has a value of the order of condensation enthalpy.

In a case of physical adsorption, adsorbed molecules vibrate in their shallow potential well and since the energy of the bond is small, they are removable from the surface. It could be assumed that molecules are tied to the surface for a short period of time, so abandoning of the surface is related to an equation of Arrhenius type, and the rate coefficient of desorption k_{des} is given by the following equation (1):

$$k_{des} = A \exp(-U_{ad}/RT) \quad (1)$$

In the previous equation, in case of physical adsorption, U_{ad} is about 25 kJ/mole, A corresponds to a value of vibration frequency of a weak bond between molecules of adsorbate and surface, and R is a universal gas constant.

In case of chemical adsorption or chemisorptions, molecules attach to the surface by forming chemical, covalent bonds and overtake places that will increase the value of their coordination number with substrate. The bonding energy is much greater than for physical adsorption, and typical values are about 200 kJ/mol [8].

Experimental

The experiment plan was made in such a way that it follows the corrosion process on 24 samples of copper and brass tins with dimensions 50x50x1 mm (12 pieces of Cu and 12 pieces of KCuZn35). Surfaces of the samples were previously cleaned first with rough, than with more fine sand paper. After the cleaning, surfaces were polished and degreased with the solution of methanol and ether. Prepared samples were marked and weighed on the analytical scale (m1). Samples were than thermally treated in the dryer for intervals of 15 minutes, at the temperatures of 293, 303, 313, 333, 343 and 353 K. Samples than underwent the process of inhibition with a 2% solution of gelatin, previously heated to the temperature of 303-308 K. The process of inhibition lasted for 5 minutes, after which the samples were dried and put away in the dessicator[3].

Protected samples were submerged into the solutions of 10% and 20% of citric acid and were treated for 48h under the same conditions. After the electrolyte treatment samples were dried and returned to the dessicator. After this followed individual removing of the corrosion products by mechanically removing scale, after which the samples were treated with a 5% solution of sulfuric acid at the temperature of 298 K, washed with distilled water a dried again. After such treatment the samples were measured again on the analytical scale (m1'). On the basis of the measured difference in mass, precisely the loss of mass because of the corrosion, Δm was determined. The rest of the corrosion parameters were calculated on the basis of Δm .

Results and discussion

In the next tables the results of the experiments are represented. The most important of them is Δm and the rate of the corrosion a . Rate of the corrosion a is the measurement of the moving force of the corrosion. The value of a could be calculated from the following equation:

$$a = \Delta m / S \cdot \tau \text{ (g/ m}^2 \text{ day)} \quad (2)$$

In this equation S is the size of the surface of the investigated sample, t is time.

Table 1. The results of the measurements of corrosion on the copper and brass tins with the 2% solution of gelatin as inhibitor in 10% citric acid as electrolyte.

sample	T(K)	$1/T \cdot 10^3 (K^{-1})$	$\Delta m(g)$	$1/\Delta m (g^{-1})$	$a(g/m^2h)$	D(%)
Cu	293	3.40	0.0197	50.76	6.57	100.00
Cu	303	3.30	0.0257	38.91	8.57	76.65
Cu	313	3.19	0.0308	32.47	10.27	63.96
Cu	333	3.00	0.0435	22.99	14.50	45.29
Cu	343	2.90	0.0502	19.92	16.73	39.24
Cu	353	2.83	0.0561	17.83	18.70	35.12
CuZn37	293	3.40	0.0330	30.30	11.00	100.00
CuZn37	303	3.30	0.0582	17.18	19.40	56.70
CuZn37	313	3.19	0.0848	11.79	28.27	38.91
CuZn37	333	3.00	0.1229	8.14	40.90	26.85
CuZn37	343	2.90	0.1533	6.52	51.10	21.53
CuZn37	353	2.83	0.1856	5.39	61.87	17.78

Table 2. The results of the measurements of corrosion on the copper and brass tins with the 2% solution of gelatin as inhibitor in 20% citric acid as electrolyte.

sample	T(K)	$1/T \cdot 10^3 (K^{-1})$	$\Delta m(g)$	$1/\Delta m (g^{-1})$	$a(g/m^2h)$	D(%)
Cu	293	3.40	0.0064	156.25	2.13	100.00
Cu	303	3.30	0.0110	90.90	3.67	58.08
Cu	313	3.19	0.0152	65.80	5.07	42.10
Cu	333	3.00	0.0288	34.72	9.60	22.22
Cu	343	2.90	0.0359	27.85	11.97	17.82
Cu	353	2.83	0.0391	25.58	13.03	16.37
CuZn37	293	3.40	0.0569	17.57	18.97	100.00
CuZn37	303	3.30	0.0864	11.57	28.80	65.87
CuZn37	313	3.19	0.1142	8.76	38.07	49.80
CuZn37	333	3.00	0.1621	6.17	54.03	35.11
CuZn37	343	2.90	0.1883	5.31	62.77	30.22
CuZn37	353	2.83	0.2160	4.63	72.00	26.35

The connection between the degree of inhibitor adsorption on the surface and the loss of mass by corrosion is obviously in reverse dependence and it means that a great loss of mass is followed by a decrease in adsorption of inhibitor on the surface of the metal. In the state of equilibrium the adsorption process is equal to the desorption process. In this experiment we did not have the possibility of measuring the absolute degree of adsorption; therefore we determined the relative degree of adsorption, starting with the assumption that the greatest adsorption is when the loss of mass is minimal. In this case that was at the temperature of 293K.

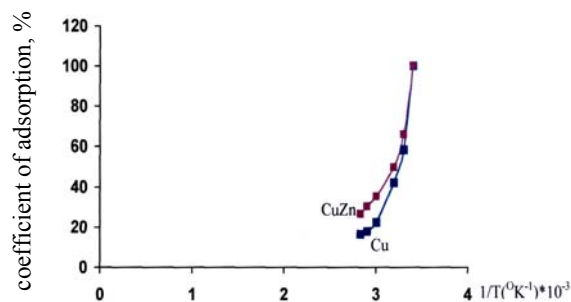


Figure 2. Graphic representation of the dependence of adsorption coefficient to the reverse value of temperature with 10% citric acid-2% gelatin.

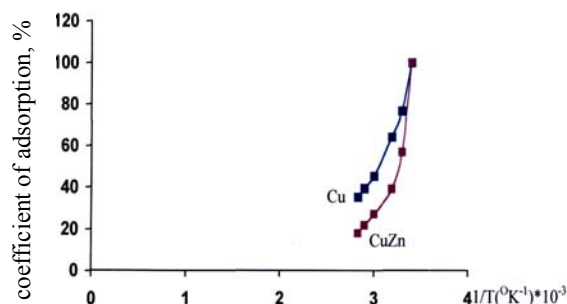


Figure 3. Graphic representation of the dependence of adsorption coefficient to the reverse value of temperature with 20% citric acid-2% gelatin.

Let us assume that on the temperature of 293K the adsorption coefficient is 100% and a maximum value of reverse value for the loss of mass ($1/\Delta m$). By relating the reverse value of the loss of mass to all of the rest temperatures we determine the value of relative degree of adsorption expressed in percents (D).

In the Figures 2 and 3 we can see the approximate exponential dependence between reverse value of temperature and the relative degree of adsorption, which enables us to conclude that in the stated case the following equation is applicable (3):

$$D = A \exp(-U_{ad} / RT) \quad (3)$$

If the previous equation corresponds to the experimental results, it could be used for determination of activation energy of gelatin adsorption on the copper and brass tins.

The last equation could be written in the logarithm form, which would give a linear equation ($y=kx+b$) and in this case it would be (4) [4]:

$$\ln D = -U_{ad} / R \cdot 1/T + \ln A \quad (4)$$

To determine the activation energy of adsorption, diagram for $\ln D - 1/T$ should be drawn, in which coefficient of direction and segment on the y-axis would determine the appropriate parameters given in the equation (4).

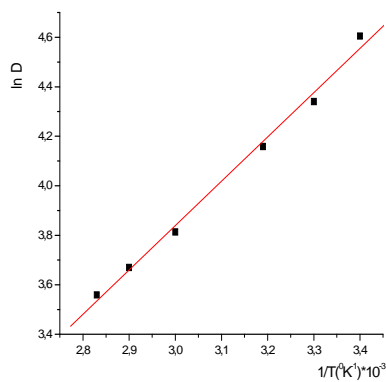
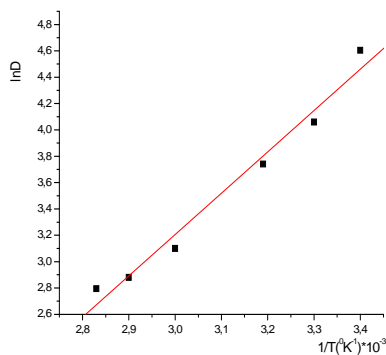


Figure 4. Dependence $\ln D - 1/T$ for copper with 10% citric acid (a) and with 20% citric acid (b)

The dependence shown in the Figure 4. (a and b) could be approximated with the equation:

$$Y = -6.20875 + 3.13816 X$$

$$Y = -1.53004 + 1.78975 X$$

On basis of this equation, coefficient A (coefficient of vibration) and the activation energy of adsorption could be determined so that for the gelatin adsorption on copper we can produce the equation:

$$D = 0.002011 \exp(-26.09 / RT)$$

$$D = 0.21653 \exp(-14.88 / RT)$$

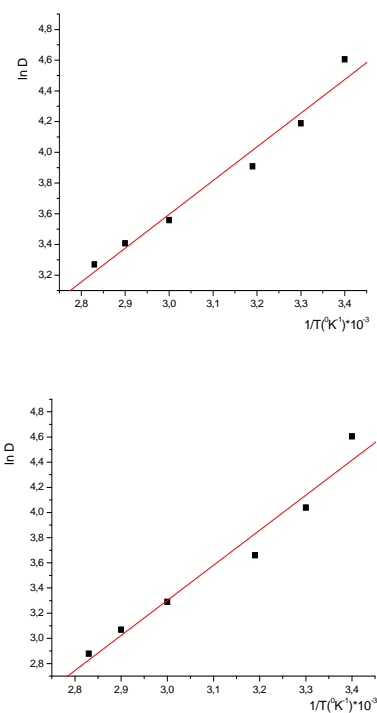


Figure 5. Dependence $\ln D - 1/T$ for brass with 10% citric acid (a) and with 20 % citric acid (b)

The dependence shown in the Figure 5. (a and b) could be approximated with the equation:

$$Y = -3.00462 + 2.20004X$$

$$Y = -5.00545 + 2.78554X$$

On basis of this equation, coefficient A (coefficient of vibration) and the activation energy of adsorption could be determined so that for the gelatin adsorption on brass we can produce the equation:

$$D = 0.04956 \exp(-18.29 / RT)$$

$$D = 0.00670 \exp(-23.16 / RT)$$

Conclusion

1. With the increase in temperature on the surface of copper and brass plates, corrosion process increases, which is explained by an increase of desorption process of inhibitor (gelatin) and that weakens the protection role of adsorption layer.
2. At the temperatures of overheating (70-80°C), the desorption process underwent in such degree so that parts of the surface are left unprotected, and with that the remaining quantities of the gelatin on the surface increase the corrosion, comparing to the uninhibited samples.
3. On the basis of the calculated values for activation energy of adsorption of gelatin on copper and brass it could be concluded that the inhibitor in question adsorbs on the surface of the metal mostly by physical adsorption.
4. On the surface of copper the energy of adsorption decreases with the increase in acidity of electrolytes, because it comes to the faster dissolving of the adsorption layer. With brass, the same regularity in decrease of activation energy of the adsorption with the increase in concentration of electrolyte wasn't discovered. This directs the conclusion to the existence of secondary reactions, which are induced by the presence of zinc.

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