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ADDUCTS OF LEVOPIMARIC ACID WITH ACRYLIC ACID AND ETHANEDITHIOL AS ACID CORROSION INHIBITORS OF METALS

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Abstract: *The adducts were synthesized by means of diene condensation reaction of levopimaric acid with acrylic acid, and through carrying out the free radical addition of ethandithiol to levopimaric acid. The composition and structure of these adducts were identified through data of the elemental analysis, IR and PMR spectroscopy. The efficiency of the synthesized diacids as corrosion inhibitors was determined by means of the gravimetric method (on mass losses of a sample of steel plate of mark C-3) in an acidic medium (solutions of 1H and 5H of sulfuric acid). The influence of the medium temperature and concentration of the used compounds on the degree of protection and corrosion inhibition coefficient was analyzed. It found that rise in temperature results in the increase of protective effect of the inhibitor. Note that the increase of the inhibitor concentration, raising the degree of protection though, is not so noticeable.*
Keywords: *synthesis, free radical addition, adducts, acid corrosion of metals, corrosion rate, inhibitor*
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Introduction

In recent years, the problem of metal corrosion prevention has been of particular importance. This is largely due to the fact that the scientific-technological progress inevitably results in economic losses caused by corrosion. All chemical, oil-refining and gas industry, space technology and other industries with their high temperatures, pressures and aggressive mediums call for highly effective metal corrosion inhibitors [1]. In this vein, the development of new inhibitors on the basis of cheap and accessible raw materials is undoubtedly one of the basic methods of metals' protection from corrosion.

As everyday experience shows, all processes occurring in nature have a certain direction. In this connection, any process behavior where the metal passes into an oxidized or ionic state with the formation of appropriate compounds is specified as the corrosion process.

There are qualitative and quantitative methods of corrosion estimation [2].

One of the most effective methods of metal corrosion prevention is the inhibition that deserves special attention. Suffice it to say that the metal protection with coatings, along with the use of inhibitors is one of the main and most widespread methods [3].

The corrosion inhibitors can be both inorganic and organic compounds [4,5]. The most effective metal corrosion inhibitors in acidic media are organic compounds containing nitrogen, sulfur, phosphorus, oxygen, unsaturated bonds, amide and other groups in their molecules as functional groups. The effect of inhibitors is due to changes on the metal surface caused by the inhibitor adsorption or the formation of soluble compounds with metal cations [6].

The inhibitors must meet the following requirements: have a high efficiency of protective action, be technological and cheap, meet sanitary-hygienic standards, do not create a threat of environmental pollution.

The paper presents results of research into diacid adduct synthesized by us as metal corrosion inhibitors.

Experimental part

1. Materials

1.1. Preparation of adduct of levopimaric acid with acrylic acid (compound **1**).

10 g of levopimaric acid and 2.4 g of acrylic acid containing 0.5% of hydroquinonea, (ratio levopimaric acid and acrylic acid 1.05:1.0) was heated in nitrogen atmosphere at 140°C for 2 h, at 160°C – 2 h and, finally, at 175°C – 1 h. The solid mass was then cooled and washed with water to remove unreacted acrylic acid. The obtained adduct was purified by recrystallization with petroleum ether from solution of diethyl ether.

1.2. Preparation of bis-adduct of levopimaric acid with ethanedithiol (compound **2**).

The reaction of levopimaric acid **1** with ethanedithiol was carried out in the presence of AIBN at temperature 70°C for 60-120 min. The quantity of the initiator was taken 0.5% of mass of levopimaric acid. The ratio of levopimaric acid to ethanedithiol was taken 2:1. Bis-adduct **2** was obtained with nearly quantitative yield (yield 87%).

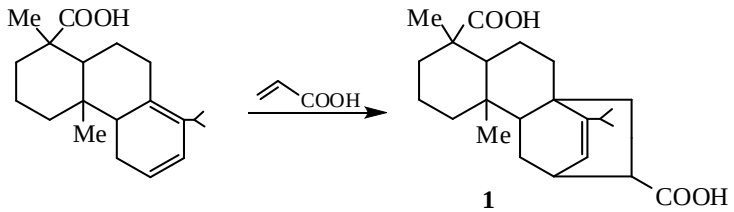
2. Methods

2.1. Testing of adducts as steel corrosion inhibitors in sulfuric acid.

The inhibitory properties of the synthesized adducts **1** and **2** were studied by the gravimetric method on the mass loss of a steel sample subjected to the corrosion for the same time in the solutions of pure and inhibited acids, respectively [7]. The testing was carried out with plates from low-carbon steel ST-3 with a size of 30x30x2 mm. Before each experiment, the samples were purified and ground on a grinding machine until preparation of a shiny homogeneous surface, then degreased with acetone. The solution with sulfuric acid (c.p.) and concentration 1H and 5H of H_2SO_4 served as a corrosive medium. The tests were carried out at 20, 40, 60 and 80ºC. The experiment duration was 2 hours at 20°C and 1 h at other temperatures. The inhibited acid solutions were prepared immediately before the experiment. All experiments were repeated three times. The quantitative estimation of the inhibiting efficiency of the investigated adducts was carried out by means of the gravimetric method (on the mass loss of a steel sample subjected to the corrosion for the same time in solutions of pure and inhibited acids, respectively). The corrosion resistance was determined based on the values of the most reproducible results.

Results and discussion

Numerous studies made it possible to establish that the compounds used as corrosion inhibitors contain heteroatoms (sulfur, phosphorous, nitrogen, etc) and functionally-active groups (amine, carboxyl, double or triple bonds, etc) in their molecules [8,9,10]. It could be assumed that the compound 1 and 2 synthesized by us (see the scheme), obtained as a result of the condensation reaction of levopimaric acid with acrylic acid, and also by the free-radical addition of ethanedithiol to levopimaric acid will be also show the inhibiting activity. As follows from the reaction scheme, the synthesized adducts contain acid groups, double bonds, and also sulfur atoms in their molecules [9]:



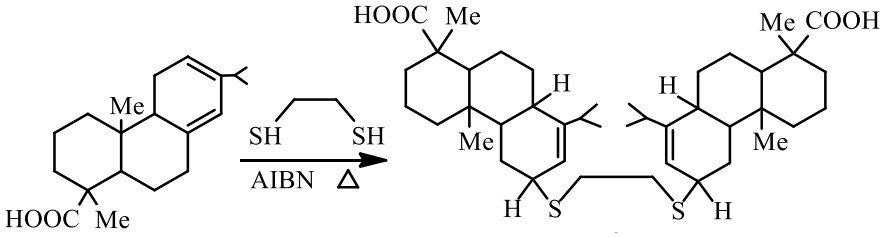
1

As a result of the reaction behavior between levopimaric acid (diene) and acrylic acid (dienophile) on Diels-Alder, the adduct **1** – diacid was obtained, the composition and structure of which has been confirmed by data of the elemental analysis, IR and PMR

spectroscopy [11]. The adduct is a white solid product soluble in many organic solvents, but not soluble in alkanes, cycloalkanes and carbon tetrachloride.

The adduct **1** had the following indices: yield – 70-72%, MW=374, content: C – 72.5% (73.8% – calculated.), H – 8.9% (9.1% – calculated), solubility – methanol, ethyl acetate, benzene, toluene, diethyl ether, THF, dioxane, acetone, methyl ethyl ketone, cyclohexanone, chloroform, 1,2-dichlorobenzene, DMF, DMAA, DMSO, *m*-cresol, acetic acid.

As a result of the free radical addition reaction of ethanedithiol to levopimaric acid, the sulfur-containing bis-adduct – diacid (compound **2**) was obtained:



The sulfur-containing bis-adduct had the following indices: yield – 85%, MW=698, A.N.=159.48 (160.47 – calculated), sulfur content – 8.96% (9.17% – calculated), solubility – acetone, DMF, DMSO, esters.

The addition reaction was carried out in the presence of AIBN in a quantity of 0.5 mass % from rosin mass at 70°C at various duration (to 120 min.). The composition and structure of the obtained bis-adduct was also confirmed by data of the elemental and spectral analyses [11].

The efficiency of the synthesized compounds was established by the gravimetric method (on the mass loss of a sample of a steel plate (mark C-3) with sizes of 30×30×2 mm, subjected to the corrosion for the same time, in the solution of sulfuric acid (solutions 1H and 5H of H_2SO_4 served as a corrosive medium) and pure water, respectively (Table 1) [7]. The obtained results showed that the compounds **1** and **2** had the high inhibiting ability. The degree of protection in this case exceeds >99.5 at inhibitor concentration 0.5÷1.0 g/l. The increase in the inhibition coefficient of corrosion is simultaneously observed. Also, it revealed that temperature rise contributes to increase of the protective effect of the inhibitor. Possibly, this has been connected with the fact that at higher temperatures, the physical adsorption occurs on the metal surface, and at low temperatures, the chemical adsorption is predominant.

The high protective efficiency shown by the proposed compounds was undoubtedly due to their structural peculiarity, namely, to availability of polar carboxyl groups, double bond and sulfur heteroatom in their molecules. The availability of these substituent influences on the change of the electron density in the adsorption center.

Table 1. Inhibiting properties of levopimaric acid adducts with acrylic acid and ethanedithiol.

Compound code	Compound concentration, g/l	T,°C	1H H_2SO_4			5H H_2SO_4		
			Corrosion rate, g/m^2·h	Degree of protection, %	Inhibition coefficient	Corrosion rate, g/m^2·h	Degree of protection, %	Inhibition coefficient
1	0.5	20	0.14	96.5	20.8	0.11	97.1	35.0
		40	0.17	97.0	40.7	0.14	97.9	47.9
		60	0.21	97.6	42.3	0.14	98.6	68.2
		80	0.36	97.5	40.0	0.25	98.5	67.2
	1.0	20	0.14	96.9	32.5	0.11	98.0	50.9
		40	0.16	97.3	35.6	0.15	98.2	44.7
		60	0.20	97.7	44.5	0.22	97.7	44.1
		80	0.21	98.8	32.7	0.52	91.9	32.2

2	0.5	20	0.18	96.0	25.6	0.16	97.2	35.0
		40	0.21	96.2	41.4	0.20	96.6	30.4
		60	0.20	95.6	44.5	0.25	97.0	30.8
		80	0.30	96.3	40.0	0.39	97.7	43.1
	1.0	20	0.17	96.8	27.1	0.16	97.2	35.0
		40	0.20	97.2	28.5	0.21	98.0	31.9
		60	0.18	97.0	49.4	0.16	98.4	60.6
		80	0.22	98.1	65.5	0.29	98.3	57.9

As follows from the results shown in Table 1, the analyzed compounds – adduct of levopimaric acid with acrylic acid (compound **1**) and the sulfur-containing derivative of levopimaric acid (compound **2**) show a high ability of steel protection against corrosion in the acidic medium, even at comparatively low temperatures. As the temperature of the medium grows, the protective effect rises as well. This is possibly due to the fact that as the temperature rises, the process of chemisorption of adduct-inhibitor molecules on the metal surface is enhanced. An increase of the inhibitor concentration from 0.5 g/l to 1.0 g/l, i.e. by 2 times, although increases a degree of protection, but this effect is not so noticeable. The used inhibitor forms the films on the metal surface at concentration of already 0.5 g/l. The subsequent increase of the inhibitor concentration does not so much influence on the film formation and, thereby, on its protective effect.

It follows from Table 1 that at the inhibitor concentrations 0.5 g/l and 1.0 g/l, the protective effect in 1H solution of sulfuric acid is changed in the range of 95.6÷97.6 and 96.8÷98.8, respectively. At the same time, these values in 5H solution of sulfuric acid correspond to the intervals of 96.6÷98.6 (at the inhibitor concentration 0.5 g/l) and 97.2÷98.4 (at the inhibitor concentration 1.0 g/l). In this case, the inhibition coefficient in 1H solution of sulfuric acid is changed in the range from 21 to 45 (at the inhibitor concentration 0.5 g/l) and from 27 to 27 (at the inhibitor concentration 1.0 g/l). Nearly same results of inhibition coefficients were obtained in 5H solution of sulfuric acid. These sufficiently high values of the protective effect and inhibition coefficient indicate that the used adducts can be used as metal corrosion inhibitors. The high values of the protective effect of the adducts used as metal corrosion inhibitors in an acidic media have been probably connected with the structural peculiarities of the used compounds, namely, by availability of carboxyl group, tricyclic fragment, and also sulfur atom in their molecules. It is also possible that the corresponding configuration structure and conformation of the adduct molecules and also availability of its substituents influence on this effect. In addition, an increase of the adsorption centers also influences positively on the inhibitory properties.

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АДДУКТЫ ЛЕВОПИМАРОВОЙ КИСЛОТЫ С АКРИЛОВОЙ КИСЛОТОЙ И ЭТАНДИТИОЛОМ В КАЧЕСТВЕ ИНГИБИТОРОВ КИСЛОТНОЙ КОРРОЗИИ МЕТАЛЛОВ

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Реакцией диеновой конденсации левопимаровой кислоты с акриловой кислотой, а также осуществлением свободнорадикального присоединения этандитиола к левопимаровой кислоте синтезированы аддукты, состав и структура которых установлены данными элементного анализа, ИК и ПМР спектроскопией. Гравиметрическим методом (по потерям массы образца стальной пластинки марки С-3) в кислой среде (растворах 1Н и 5Н серной кислоты) определена эффективность синтезированных дикислот в качестве ингибиторов коррозии. Изучено влияние температуры среды и концентрации используемых соединений на степень защиты и коэффициент торможения коррозии. Показано, что повышение температуры способствует возрастанию защитного эффекта ингибитора. Повышение же концентрации ингибитора, хоть и увеличивает степень защиты, но не столь ощутимо.

Ключевые слова: *синтез, свободнорадикальное присоединение, аддукт, кислотная коррозия металлов, скорость коррозии, ингибитор.*

LEVOPİMAR TURŞUSUNUN AKRİL TURŞUSU VƏ ETANDİTİOLLA ALINAN ADDUKTLARININ KORROZİYA İNHİBİTORLARI KİMİ TƏDQİQİ

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Levopimar turşusunun akril turşusu ilə dien kondensasiyası və həmçinin levopimar turşusuna etanditiolun sərbəst radikal birləşməsi nəticəsində adduktlar alınmışdır. Alınan adduktların tərkib və quruluşları element analizi, İQ və PMR spektroskopiya üsulu ilə müəyyən olunmuşdur. Sintez olunmuş diturşuların qravimetrik metodla (C-3 tipli polad lövhənin kütlə itkisinə əsaslanaraq) turşu mühitdə (1H və 5N sulfat turşusunun məhlulunda) korroziya inhibitorları kimi səmərəliliyi müəyyən edilmişdir. Mühafizə dərəcəsinə və korroziyanın qarşısının alınmasının əmsalına mühitin temperaturu və istifadə olunan birləşmələrin qatılılığının təsiri öyrənilmişdir. Temperaturun artması inhibitorun qoruyuculuq effektinin artmasına təsir göstərmişdir. İnhibitorun qatılılığının artması isə onun qorunma dərəcəsini nəzərə çarpacaq dərəcədə artırmır.

Açar sözlər: *sintez, sərbəst radikal birləşmə, addukt, metalların turşu mühutində korroziyası, korroziya sürəti, inhibitor.*