Polarization Resistance parametrs of cucurbit[n]urils based corrosion inhibitors with gossypol for №3 mild steel in 10% sulfhydric acid media

E.Berdimurodov[1,a], A.Kholikov[2,b], Kh.Akbarov[3,c]

[1]Teacher, Department of Natural Sciences, Karshi State University, Karshi, 730003, Uzbekistan

[2]Doctor of chemical sciences, Department of Natural Sciences, Samarkand State University, 703004, Uzbekistan

[3]Professor, Doctor of chemical sciences, Department of Chemistry, National University of Uzbekistan, 700174, Uzbekistan

[a]elyor_170690@inbox.ru, [b]habduvali@rambler.ru, [c]akbarov_Kh@rambler.ru

Abstract. The adsorption and inhibition effects of new mixed type of efficient inhibitor of cucurbit[n]urils based corrosion inhibitors with gossypol at 50:50 proportion for mild steel were tested by using weight loss and electrochemical methods in 10% H_2S media at 300-360 K. These inhibitors are easy to synthesize, readily available, nontoxic and biodegradable, efficient and cheapest. The polarization resistance showed that the cucurbit[n]urils based corrosion inhibitors with gossypol catalyze the oxide film dissolution. These results were confirmed by surface examination via scanning electron microscope.

Keywords: Cucurbit[n]urils, gossypol, mild steel, polarization resistance.

1. Introduction:

Mild steel is widely used in oil and gas industries as a result it corroded at several processes such as transportation systems of acid pickling, industrial cleaning, acid de-scaling and oxidization of oil wells, addition in some regions of world here oil and gas resours were saturated with hydrogen sulfide (H_2S) which impacts to growth internal corrosion process into mild steel pipelines and wells. Mild steel is more cost-effetive for oil and gas recycling and refining facilities as a good material option. Damaged mild steel construction by corroded with hydroged sulfide is enormous problem at economy, environmental pollution and ecological disasters in some areas. Using inhibitors can solve theses problems through inhibitors are added to oil and gas into pipelines to minimize acid attack on metal [1-2].

At the high temperature and concentration of hydrogen sulfide mild steel corrosion progression can increase. In H_2S environment, the reaction of iron with hydrogen sulfide provides many types of iron sulfide chemical compounds: amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigte, pyrrhotite, troilite and pyrite [3].

The selection of cucurbit[n]urils as corrosion inhibitor is based on the presence of nitrogen and oxygen in macrocyclic molecules system, which facilitates electrophilic attack. They are important N-heterocyclic compounds which are easy to synthesize, readily available, nontoxic and biodegradable corrosion inhibitors for mild steel. This makes the investigation of their inhibiting properties significant in the context of the current priority to produce eco-friendly and cheap inhibitors. The cucurbit[n]urils (fig. 1) have strong chemisorption (donation) on metal surface, this condition is major role for adsorption properties. However they have not re-donation properties because re-donation is connected with π-electrons, cucurbit[n]urils have not π-electrons thus their donor adsorption properties of π-electrons is very low but donation as p-electron donor-acceptor process reached huge peak at adsorption on metal surface [3-4].

The gossypol (fig. 2) contain centers for π-electrons and donor oxygens, which this condition has biggest role in growth its adsorption properties on metal surface in alkaline media containing chloride ions. Its re-donation properties is very high with delocalization aromatic π-electrons. The adsorption of gossypol on the mild steel surface reduces the surface area that is available for the attack of the aggressive ion from the sulfhydric acid media containing chloride ions. As a result its θ reach a peak effects on reduced corrosion ratio [5-7].

The main aim of this research work is to study the inhibition of corrosion of mild steel by Cucurbit[n]urils (CB[n]) based corrosion inhibitors with Gossypol (GPL) at 50:50 proportion was investigated using electrochemical measurements, hydrogen evolution techniques with the aim of determining its inhibition potentials in 10% sulfhydric acid medium, investigate the effect of temperature on the corrosion of mild steel, study the effect of different concentrations of

Cucurbit[n]urils (CB[n]) based corrosion inhibitors with gossypol (GPL) at different temperatures, calculate polarization parameters and propose the mechanism of corrosion inhibition of mild steel in 10% sulfhydric acid medium.

2. Materials and methods.

2.1. Materials.

2.1.1. Mild steel sample

Experiments were performed on №3 mild steel sample having composition, % (mas.): Fe – 98,36; C – 0,2; Mn – 0,5; Si – 0,15; P – 0,04; S – 0,05; Cr – 0,3; Ni – 0,2; Cu – 0,2.

Mild steel samples used in the weight loss experiment were mechanically cut into 2.5 cm × 2.5 cm × 0.1 cm dimensions, abraded with SiC abrasive papers of grade 300, 450 and 550 respectively. For the electrochemical studies on, mild steel samples having dimension 1.0 cm×1.0 cm×0.1cm were mechanically cut and abraded similarly to a previous procedure, with an exposed area of 1 cm^2 (the rest covered with araldite resin) with 3 cm long stem. Before starting the experiment, mild steel samples were washed with distilled water, and next with alcohol, degreased in acetone, dried and stored in vacuum desiccator.

2.1.2. Test solution

The test solutions (10% H_2S solution) were prepared by H_2S dissolved in distilled water. The concentration range of inhibitors was 100–250 ppm and the volumes of test solution used for weight loss measurement and electrochemical studies were 250 mL and 150mL, respectively.

2.2. Inhibitor synthesis

2.2.1. Synthesis of glycoluril

Urea (60 g, 1 mol) was dissolved in 100 mL water, then 36% HCl (5 mL) was added. The solution was stirred at room temperature and 30% glyoxal (60 mL) was added in this mixture. The solution was stirred at room temperature for 12 h. The precipitate was filtered, washed with water for three times and twice with acetone, dried in the air to give a white powder weighing 26.15 g, on the overall yield was 67.1% . (fig.3)

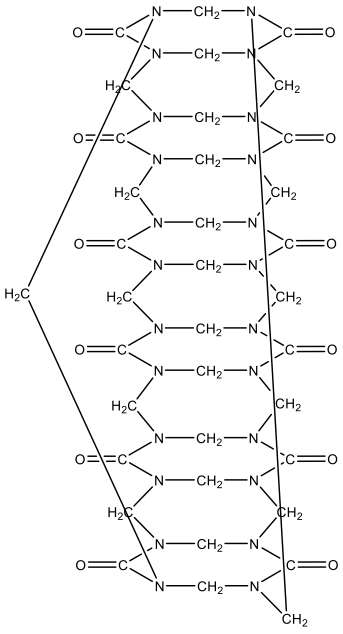

Figure 2. The structure of Cucurbit[6]urils.

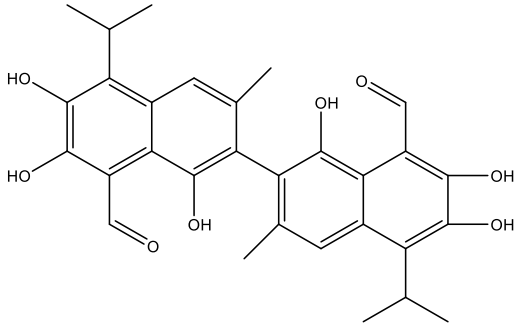

Figure 1. The structure of Gossypol.

2.2.2. Synthesis of cucurbiturils

250 mL 36% HCl was added to a mixture of glycoluril (15.7 g, 0.1 mol) and formaldehyde (7.5.0 g, 0.25 mol), and the mixture was stirred at room temperature until solid had been dissolved. The solution was heated at 90 ^{0}C for 4 h to give a brown solution. The solution was allowed to cool to room temperature and evaporated in vacuum to give a puce solid weighing 17.5 g. The brown solid was dissolved in 70 mL water and added slowly into 500 mL acetone with strong stirring. A yellow precipitate was collected by filtration and dried in

air to give a yellow-red mixed of cucurbit[n]urils' weighting 15 g at the yield of 75-82% . (fig.4)

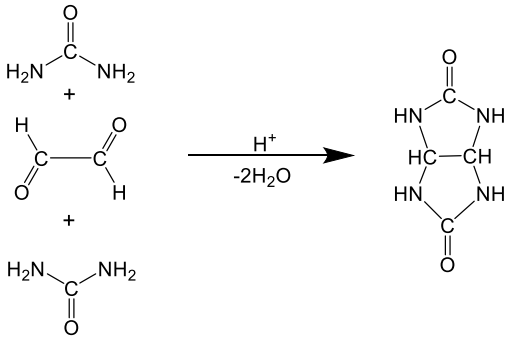

Figure 3. Synthesis of glycoluril

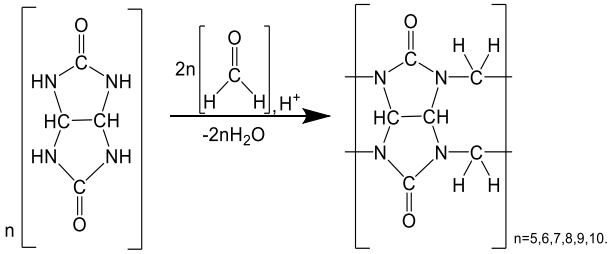

Figure 4. Synthesis of cucurbit[n]urils

2.3. Electrochemical measurements

We used the Gamry Potentiostat/Galvanostat (Model G-300) containing EIS software Gamry Instruments Inc., the USA containing Echem Analyst 6.22 software package in order to calculate electrochemical paremetres. The instrument consists of a three-electrode glass assembly, in which pure platinum foil acts as the counter electrode, the saturated calomel acts as the reference electrode and rectangular №3 mild steel specimen of the working electrode. The working electrode's immersed time is 30 min because during this time the state potential reached nochangeable position before performing the electrochemical experiments.

2.3.1. Polarization Resistance

The polarization resistance measurements were performed with polarization resistance parameters, which from -0.02 to 0.02 V E (v) vs Eoc, Scan Rate (mV/s) is 0.125, sample area is 1 cm^2, density g/cm^3 is 7.87, equiv.Wt. is 27.92 and 0.12 (V/Dec).

2.4. Scanning electron microscopic and analysis

For surface morphological study of the uninhibited and inhibited mild steel samples, SEM images were recorded using the instrument HITACHI TM3000.

3. Results and discussion

3.1. Polarization Resistance

In the presence of hydrogen sulfide, inhibitor reduced corrosion speed as the cathode and the anode the partial cial electrochemical processes, as the inhibitors thus mixed action slightly shifting the corrosion potential in the positive tional side. In a survey of the effectiveness of inhibitors of metal corrosion in the conditions necessary to study not only their influence on general corrosion and partial electrochemical processes, but also on hydrogenation. The process of hydrogen embrittlement complex and depends on many parameters important. It plays a role in the character of the state of stress metal, which affects the structure of the inhibitor [4-5].

The mechanism of iron dissolution containing H_2S based on following reaction equations:

I. $$Fe + H_2S = Fe + H_2S_{adsorbed}$$

II. $$Fe + H_2S_{adsorbed} = Fe + HS^-_{adsorbed} + H^+_{adsorbed}$$

III. $$Fe + HS^-_{adsorbed} + H^+_{adsorbed} = Fe + S^-_{adsorbed} + 2H^+_{adsorbed}$$

IV. $$Fe + S^-_{adsorbed} + 2H^+_{adsorbed} = FeS_{adsorbed} + 2H_{adsorbed}$$

At the first this processes H_2S can adsorbed on metal surface after there anodic and catodic corrosion starts. The adsorbed speed of S^{-2} ions depend on temperature and concentration also press [6]. If we inter inhibitors into this medium the electrodonor groups of ($= N^+$) gives its localization electrons to (S^{-2}). The 5 picture indicates that this electrostatic interaction processes as a known physisorption increase re-passivation process and occure thicker film (passivate film) of inhibitors, according to the following sequence:

$$S^-_{adsorbed} + (= N^+) \rightarrow (= NS)_{adsorbed}$$

Secondly, there is next anodic anticorrosion sequence by electrodonor oxygen groups (=O) share its free electrons into iron's free d-orbitals thus electrodonor complex of inhibitor with irons adsorbed on metal surface [7]. The 5 picture shows the delocalization electrons of aromatic cyclies of gossypol can increase up this chemical donation processes vie these delocalization free electron pairs are absorbed on iron free d-orbitals, according to the following sequence:

$$Fe^{2+} + (= O:) \rightarrow (= OFe^+)$$

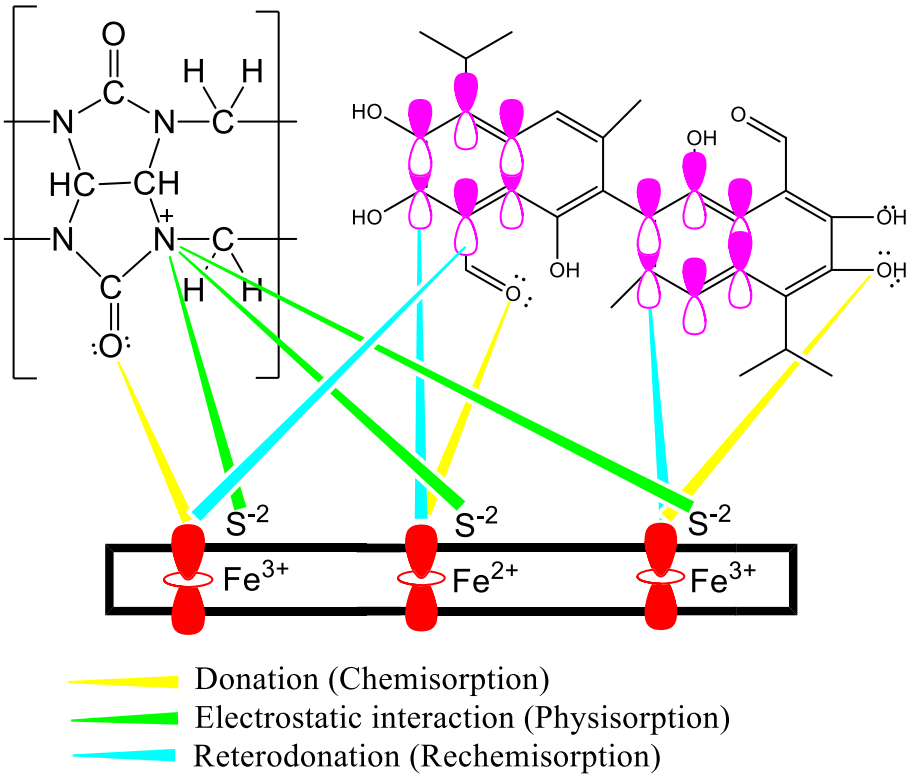

Figure 5. The mechanism of electrochemical adsorption of cucurbit[n]urils based corrosion inhibitors with gossypol at steel surface in 10% H_2S medium of solution.

The total resistances are compared with the values of R_p, determined by the direct current polarization resistance method. Typical polarization resistance curves are presented in (Fig. 10.) at 300 K. It is seen that on concentration increase the slope and thus the polarization resistance decreases as well. The results are in table 4 represents cucurbit[n]urils based corrosion inhibitors with gossypol account for maximum protection degree is 94.47, corrosion rate is 0.350 (mmy-1), the values of R_p is 20.174 (kohms) and -240.8 E_{corr} (mV) at 250 (ppm) concentration by 300 K. This suggests that the cucurbit[n]urils based corrosion inhibitors with gossypol catalyze the oxide film dissolution [8-10].

From the values of R_p the inhibitor efficiency g was determined according to:

$$\eta\% = \frac{R_{p,i} - R_{p,0}}{R_{p,i}} \times 100\%$$

In this equation $R_{p,0}$ and $R_{p,i}$ are the polarization resistance in absence and in presence of inhibitor.

Table 1. The inhibitors' polarization resistance parameters with deferent concentration at 300 K in 10% H_2S solution.

Concentration (ppm)	E_{corr} (mV)	R_p (kohms)	Corrosion Rate(mmy^{-1})	η%
Blank	-290.5	1.115	28.456	-
100	-115. 5	13.567	1.845	91.78
150	-225.1	15.452	1.120	92.78
200	-229.4	17.127	0.712	93.48
250	-240.8	20.174	0.350	94.47

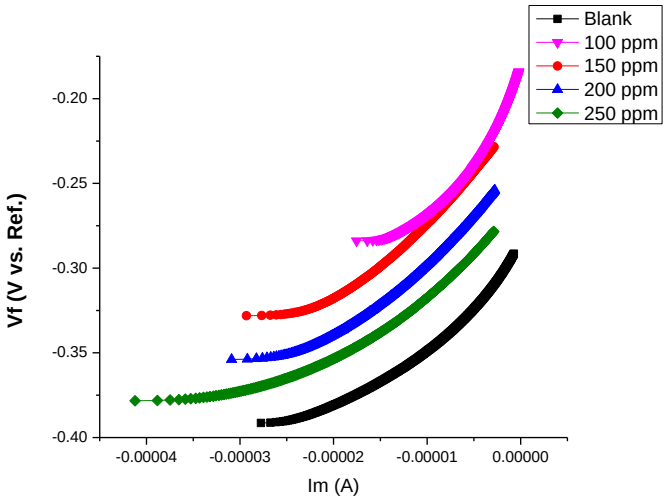

Figure 6. The relationship of Im (A) with Vf (V vs. Ref.) in 10% H_2S solution for (CU[n]) + (GPL) at 300 K.

3.2. Scanning electron microscopy

It is clear from (Fig. 7) the surface roughness of №3 mild steel in 10% H_2S medium is very high vie deeper pores in contrast with in the presence of inhibitor of the cucurbit[n]urils based corrosion inhibitors with gossypol at 250 ppm concentration, the surface morphologies (Fig. 8.) are remarkably improved because of the inhibitor's molucules adsorbed on metal surface and informed a protective surface film [11-12]. All SEM expremente provided at room temperatore.

ACKNOWLEDGEMENT

Authors gratefully acknowledged state key laboratory of chemical engineering and technology, Tianjin University, Tianjin, P.R. China, for support.

4. Conclusions

The results showed that cucurbit[n]urils based corrosion inhibitors with gossypol at the proportion of 50:50, is mixed type inhibitors and is excellent inhibition efficiency for mild steel in in alkaline media containing chloride ions. The results obtained from electrochemical and surface calculations were in good agreement. The Polarization Resistance results suggest that the presence

of cucurbit[n]urils based corrosion inhibitors with gossypol at the proportion of 50:50, decreases the rate of anodic mild steel dissolution as well as cathodic hydrogen evolution and act as mixed type inhibitors. Increased value of activation energy suggested that inhibitors adsorb physically during the first step of the adsorption process. The results of the SEM studied showed that the surface smoothness increases in the presence of Cucurbit[n]urils based corrosion inhibitors with gossypol due to the formation of the protective surface film. Lastly, it was concluded that inhibition efficiency increases on increasing electron releasing – oxygen and nitrogen groups.

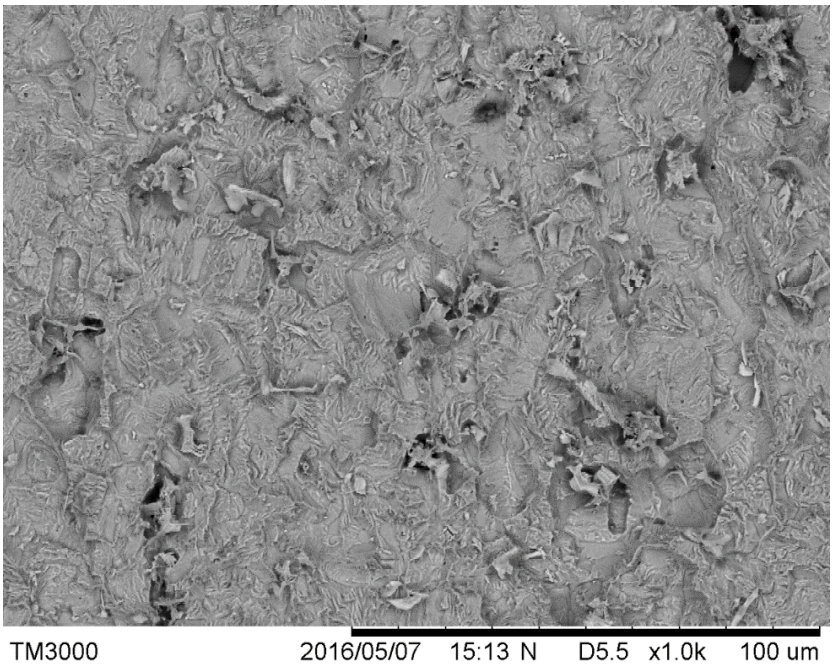

Figure 75. The SEM images of mild steel: in 10% H_2S solution.

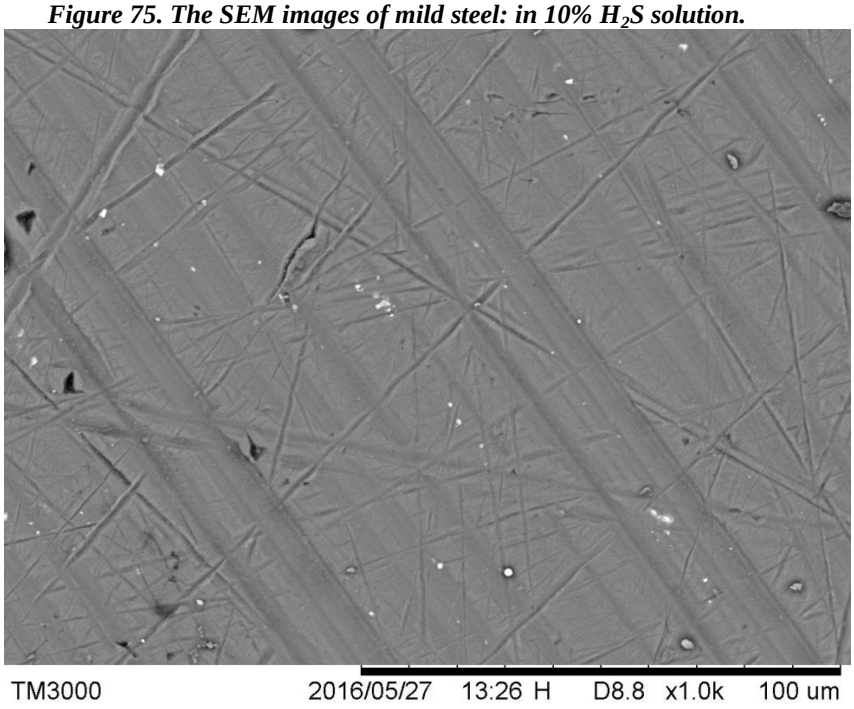

Figure 8. The SEM images of mild steel: in the presence of this inhibitors at 250 (ppm) in 10% H_2S solution.

5. References

1. *Плотникова М.Д., Шеин А.Б.* Ингибирование коррозии малоугле-родистой стали в кислых и нейтральных средах // Известия вузов. Химия и химическая технология. 2013. Т. 56. № 3. С. 35-40.
2. *Вигдорович В.И., Стрельникова К.О.* Критерии оценки защитной эффективности ингибиторов коррозии // Конденсированные среды и межфазные границы. 2011. Т. 13. № 1. С. 24-28.
3. *Ким Я.Р., Цыганкова Л.Е., Кичигин В.И.* Ингибирование коррозии и наводороживания стали в модельных пластовых водах // Корро-зия: материалы, защита. 2005. № 8. С. 30-37.
4. *Вигдорович, В.И., Н.В. Сафронова, Н.В. Шель,* Эффективность амидов высших карбоновых кислот в качестве загустителя масел и маслорастворимой антикоррозионной присадки // Защита металлов. – 1996. – Т. 32,№ 1. – С. 56–60.
5. *Моисеева Л.С.* Разработка научных принципов защиты металлов от углекислотной коррозии ингибиторными композициями. Дисс. на соиск. уч. степени докт. хим. наук. М., 1996.
6. *Цыганкова Л.Е., Ким Я.Р., Кичигин В.И., Вигдорович В.И.* // Прак-тика противокоррозионной зашиты. 2005. № 4 (38). С. 31-40.
7. *Цыганкова Л.Е., Иванищенков С.С., Кичигин В.И.* // Конденсиро-ванные среды и межфазные границы. 2006. Т. 8. № 2. С. 105.
8. *Ким Я.Р., Цыганкова Л.Е., Кичигин В.И.* // Коррозия, материалы, защита. 2005. № 8. С. 30-36.
9. *Лигносульфонаты* как основа водорастворимых смазочно-охлаждающих жидкостей / Е. В. Лебедев, Л. П. Морозова, Е. А. Клявлина, А. К. Маскаев //Нефтепереработка и нефтехимия. – 1984. – Вып. 27. – С. 21–23.
10. *Тупикин Е. И.*, *Рудомино М. В.*, *Крутикова Н. И*. Коррозия стали в водных растворах хлорида натрия с добавками фосфорсодержащих комплексов // Химические реактивы и особо чистые вещества // Науч. труды. Вып. 51. – М.:ИРЕА; 1989. – С. 72–76.
11. *Гройсман А. Ш.*, *Попова З. А.*, *Хомутов Н. Е.* Исследование ингибиторов для защиты от коррозии трубопроводов и резервуаров со сточными водами неф-тебаз // Транспорт и хранение нефтепродуктов и углеводородного сырья. –1983. – № 2. – С. 19–21.
12. *Хомутов Н. Е.*, *Скорнякова Т. Н.* Сравнение стандартных электродных потен-циалов, вычисленных различными термодинамическими методами // Журнал физической химии. – 1965. – Т. 39, № 2. – С. 195.