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THE INHIBITORY EFFECT OF IMIDAZO [1,2-A] AZEPINIUM BROMIDES ON CORROSION OF CARBON STEEL IN HYDROCHLORIC ACID MEDIUM

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The mechanism of corrosion protection of mild steel by imidazo [1,2-a] azepinium bromides was considered in this work. These compounds are effective inhibitors of carbon steel corrosion in acid chloride medium. Their high protective action manifests itself within the temperature range of 293 to 333 K. The inhibition efficiency measured by means of gravimetric method at 293 K is 93.0−96.8%, it changes insignificantly with the temperature. The inhibition properties of the compounds are caused by the formation of a protective film of up to 4 nm thickness on the carbon steel surface, which is demonstrated by Auger electron spectroscopy. The chemisorption of the inhibitors molecules also ensures considerable protective aftereffect. The correlation between the inhibition efficiency and molecules energy characteristics, in particular the difference in energy values of lower vacant and higher occupied molecular orbitals, was determined. The possible realization of macrocycle effect was shown under the chemisorption of the inhibitors, molecules of which have four negatively charged adsorption-reaction centres and present a formed chelate bond.

Keywords: imidazo [1,2-a] azepinium bromides, inhibitor, acid corrosion, carbon steel, mechanism.

Introduction

The capacity of chemical compounds to adsorb on the metal surface is important for defining their anticorrosion properties. That is why the problem of the adsorption is of particular importance when studying the inhibitors [1−3].

In works [4,5] we have shown that imidazo[1,2-a]azepinium bromides are effective for the inhibition of acid corrosion of carbon steel. At the same time, the adsorption properties of the inhibitors still require additional research and the mechanism of their action has not been fully established yet. These issues are important for both developing the theory of the inhibition of carbon steel acid corrosion by compounds which have the condensed imidazoazepinium cycle and purposeful synthesizing new effective inhibitors.
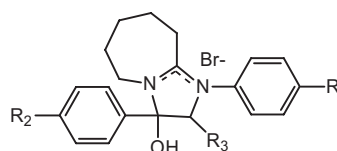
The aim of this study is to determine the mechanism of imidazo[1,2-a]azepinium bromides action during the inhibition of acid corrosion of carbon steel in chloride medium.

Experimental

Imidazo[1,2-a]azepinium bromides have been studied (Table 1), the synthesis method of which is presented elsewhere [4].

Table 1

Imidazo[1,2-a]azepinium bromides under study

No.	R_1	R_2	R_3
I	–H	–H	–H
II	–H	–Cl	–H
III	–Br	–OCH$_3$	–H
IV	–Br	–OC$_2$H$_5$	–CH$_3$
V	–OCH$_3$	–H	–H
VI	–OCH$_3$	–Cl	–H
VII	–OCH$_3$	–OCH$_3$	–H
VIII	–OCH$_3$	–OC$_2$H$_5$	–CH$_3$
IX	–OC$_2$H$_5$	–Br	–H
X	–OC$_2$H$_5$	–OC$_2$H$_5$	–CH$_3$
XI	–OC$_2$H$_5$	–C$_4$H$_6$O$_2$	–H

The corrosive tests were carried out by means of gravimetric method using steel 45 sample of cylinder form (diameter of $1.4 \cdot 10^{-4}$ m and height of $1.5 \cdot 10^{-4}$ m) polished to the 4−5 class of accuracy. Before being placed in the corrosive medium, the steel samples were cleaned with alcohol and weighed by analytical scales with the accuracy of $5 \cdot 10^{-5}$ g. Corrosion rate in the presence and in the absence of inhibitors was calculated with by the following formula: $k=\Delta m/(S \cdot \tau)$, where Δm is the weight loss of sample (in g); S is the exposed surface area (in m^2); τ − exposure time (in hours). Corrosion inhibition coefficient was calculated by the formula: $\gamma=k/k'$, where k and k' are the corrosion rates in the presence and in the absence of the inhibitor, respectively. The inhibition efficiency (IE, %) was calculated using the following equation: $IE=(1-1/\gamma) \cdot 100\%$.

0.1 M, 1 M and 2.8 M solutions of HCl were used as corrosive environments. The duration of corrosion tests was was 24 hours at 293 K, and 1 hour at 303 K and 333 K. Inhibitor concentration was in the range of $0.5 \cdot 10^{-3}-2 \cdot 10^{-3}$ mol/L.

The existence of the aftereffect was established while testing steel samples, previously exposed to the action of the inhibited solutions (24 hours at 293 K or 1 hour at 303 K), in uninhibited solutions. The inhibition efficiency was evaluated by the aftereffect (denominated in $IE_{a.f.}$, %).

The chemical elements distribution in the near-surface layers of the steel 45 samples was determined by means of Auger spectrometer AES-2000 of combine-laboratory LAS-2000 apparatus, produced by «Riber» (France), from the surface of 300r300 μm. The energy of the beam of electrons was 3 keV, the current was 0.5 μA. While profiling, the sample surface was bombarded with argon ions with the energy 4 keV. The rate of etching was 30 Å/m. Before testing, the steel 45 samples were immersed in the inhibited and the uninhibited corrosive medium (0.1 M HCl) in the vertical position. The inhibitor concentration was $3 \cdot 10^{-3}$ mol/L. After the exposure the samples were thoroughly washed with the distilled water and dried out.

Electrochemical tests were performed by using potentiostat П-5848. A cylindrical steel 45 electrode, which had been molded into Teflon casing, was used. The preparation of the electrode surface included polishing, washing with distilled water and with the studied solution. A three-electrode cell with the separated cathode and anode departments was used. A saturated chloride silver electrode was used as a reference electrode. The electrode potential measurements were conducted with the help of electrolytic bridge and Luggin capillary. An auxiliary electrode was made of platinum. The chronograms of the cathode current under the potential of 0.6 V, that is lower than the stationary one, were recorded under electrolyte stirring by magnetic stirrer when the inhibitor was added to the 0.1 M HCl solution.

All experiments were replicated three times. Statistical analysis of experimental data (i.e. the values of the corrosion rate) was conducted by Microsoft Excel (confidence probability of 95%).

The calculations of the molecule atomic charges and their energetic characteristics were carried out using the computer software Chem3D 9.0 (Cambridge Soft).

Results and discussion

The inhibition properties of imidazo[1,2-a]-azepinium bromides towards the corrosion of steel 45 in 2.8 M hydrochloric acid solutions are presented in Table 2.

The characteristic peculiarity of the studied inhibitors is their high inhibition efficiency; it is higher than 88.5% within the temperature range of 293−333K. The existence of considerable protective aftereffect should be noted too.

Table 2

Inhibition efficiency and protective aftereffect of imidazo[1,2-a]azepinium bromides derivatives ($1 \cdot 10^{-3}$ mol/L) towards the corrosion of steel 45 in 2.8 M HCl solution

No.	Inhibition efficiency			
	293 K		313 K	333 K
	IE, %	$IE_{a.f.}$, %	IE, %	IE, %
I	94.1±0.3	94.1±0.3	89,0±0,6	89.9±0.6
II	96.6±0.4	91.0±0.4	90.0±0.6	94.3±1.0
III	96.8±0.4	90.8±0.5	93.2±0.6	93.4±0.6
IV	95.0±0.5	90.0±0.6	96.3±0.5	98.4±0.3
V	93.0±0.1	88.5±0.4	93.4±1.0	90.4±0.3
VI	95.0±1.0	90.3±0.9	95.3±0.3	95.5±0.1
VII	96.1±0.5	90.3±0.7	95.7±0.4	95.1±0.6
VIII	94.6±0.5	88.8±0.4	93.8±0.6	93.0±0.3
IX	93.4±0.1	89.7±0.3	96.6±0.5	98.1±0.4
X	95.6±0.3	90.1±0.6	97.2±0.5	98.3±0.1
XI	97.3±0.4	90.2±0.8	97.4±0.4	98.2±0.7

The inhibition efficiency of imidazo[1,2-a]-azepinium bromides depends to a small degree on their concentration. For example, with an increase in the concentration of compound with No. III from $0.5 \cdot 10^{-3}$ mol/L to $2.0 \cdot 10^{-3}$ mol/L, the inhibition efficiency increases only from 95.9% to 97.1%. With a decrease in medium acidity the inhibition efficiency

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of the compounds reduces a little, but remains still high: the inhibition efficiency of compounds with No. II, III and IV in 0.1 M HCl is equal to 89.2, 90.8 and 92.1%, respectively. This can indicate the chemisorption of inhibitors on the steel.

The results of Auger electron spectroscopy (Fig. 1), obtained while testing the steel samples surface, exposed to uninhibited and inhibited solutions (by compounds No. IV), demonstrate the formation of the surface compounds.

The iron depth distribution indicates that Fe concentration after the depth of 15 nm is the highest for the sample etched in the inhibited solution (Fig. 1,a). This is explained by the existence of the corrosion products, oxygen-containing compounds, on the surface of the sample immersed in the uninhibited solution. The content of carbon for the sample etched in the inhibited solution is also high since the molecules of the inhibitors contain this element (Fig. 1,b). For the sample etched in the inhibited solution, nitrogen can be observed in a small amount up to the depth of 3.6 nm (Fig. 1,c), which definitely shows the formation of the polymolecular protective film. The concentration of oxygen in the film of the steel 45 sample immersed

in the inhibited solution is considerably low as compared with the uninhibited one (Fig. 1,d). The mass fraction of oxygen in molecule of compounds with the number IV is 0.061%; hence, one can conclude that the inhibitor adsorption occurs on the thin layer of the oxygen-containing corrosion products.

The molecules of the imidazo[1,2-a]azepinium bromides compounds can be characterized by higher electron density at practically all possible adsorption-reaction centres (nitrogen and oxygen atoms); in addition, there are either negative or low positive charges at nitrogen atom of heterocyclic system. This causes bond formation by transferring electrons from adsorption-reaction centres to the iron d-orbital.

It should be mentioned that we failed to observe any correlation between the charges at certain adsorption-reaction centres and the protection degree of imidazo[1,2-a]azepinium bromides compounds. This is illustrated in Fig. 2 using nitrogen atom N^2 as an example.

A high ability of the molecules of compounds No. I−XI to transfer electrons to metal and create the bonds with its surface and surface compounds is also confirmed by quantum-chemical calculations
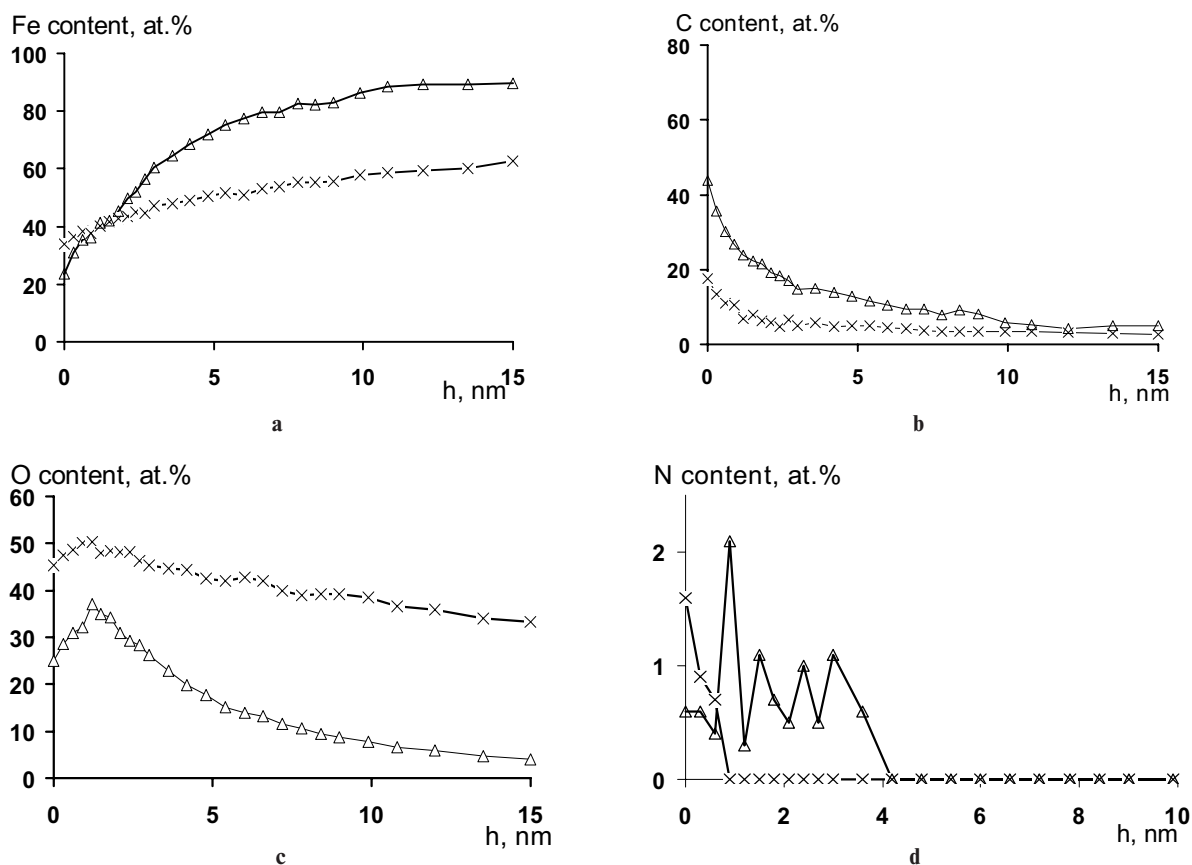

Fig. 1. The elements depth distribution for steel 45 samples etched in 0.1 M HCl inhibited and uninhibited solutions: a − iron; b − carbon; c − oxygen; and d − nitrogen; −×− 0.1 M HCl; −т− 0.1 M HCl In IV

The inhibitory effect of imidazo [1,2-a] azepinium bromides on corrosion of carbon steel in hydrochloric acid medium

(Table 3): imidazo[1,2-a]azepinium bromides are characterized by high energies of higher occupied molecular orbital (E_{HOMO}).
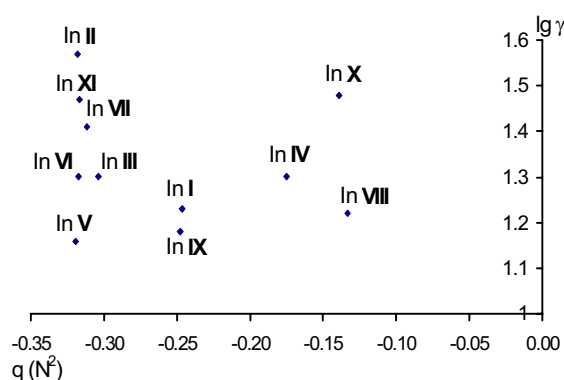

Fig. 2. Charges at N^2 atoms of imidazo[1,2-a]azepinium bromides compounds with the inhibition efficiency of 93.0%−97.3% (steel 45 in 2.8 M HCl)

According to the molecular orbital theory developed by Fukui [6], molecular reactivity is defined by the energy difference of the lower unoccupied (E_{LUMO}) and higher occupied molecular orbitals. The use of such approach allows establishing the correlation between the inhibition efficiency and the difference ($E_{LUMO}-E_{HOMO}$) (Fig. 3). This is consistent with the studies of the correlation «inhibition activity − quantum-chemical indices» carried out by Lukovits [7] and Khalil [8].

According to the hard and soft acids and bases concept (HSAB), the bond "soft-soft" or "hard-hard" reagent are preferred. The value of energy gap ($E_{LUMO}-E_{HOMO}$) indicates the «hardness» of the studied molecules of the compounds [6]. Due to the appearance of the corrosion products layer, the steel surface also acquires the properties of the hard reagent [9], which facilitates the creation of strong bonds between the molecules of imidazo[1,2-a]azepinium bromides and metal surface.
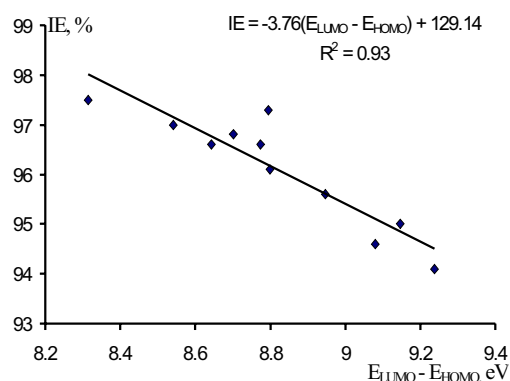

Fig. 3. Correlation between the inhibition efficiency (IE) of imidazo[1,2-a]azepinium bromides in 2.8 M HCl and ($E_{LUMO}-E_{HOMO}$)

The inspection of cathodic chronoammograms recorded on steel samples in the prescience of the addition of imidazo[1,2-a]azepinium bromides to 0.1 M HCl solution (Fig. 4) revealed the group of compounds (No. III, V, VI and VII), the equilibrium time of which reaches 300 s which is typical characteristic of chemisorption [10], and the group of compounds (No. IV, VIII and X), for which the equilibrium time is much shorter (up to 60 s). This indicates that the macrocycle effect is realized during the chemisorption of the compounds of the second

Table 3

The charge distribution at the main adsorption-reaction centres (N^1 as the nitrogen atom mutual for the heterocyclic system; N^2 is the nitrogen atom of imidazo cycle; O^1 is in OH− group; O^2 is in R_1; and O^3 is in R_2) and energy characteristics of imidazo [1,2-a] azepinium bromides molecules

No.	Charges on the atoms					Molecule energy characteristics		
	N^1	N^2	O^1	O^2	O^3	E_{LUMO}, eV	E_{HOMO}, eV	($E_{LUMO}-E_{HOMO}$), eV
I	0.1396	−0.4724	−0.3684	−	−	0.1666	−9.0703	9.2369
II	0.0344	−0.3169	−0.3369	−	−	−0.3095	−8.9530	8.6435
III	0.0371	−0.1751	−0.3365	−	−0.2032	−0.0045	−8.7061	8.7016
IV	−0.1078	−0.3037	−0.3512	−	−0.2026	0.0227	−9.1241	9.1468
V	0.0324	−0.3114	−0.3375	−0.2035	−	−0.0154	−8.7894	8.7740
VI	0.0340	−0.3180	−0.3371	−0.2031	−	−0.3010	−8.8415	8.5405
VII	0.0371	−0.3192	−0.3379	−0.2064	−0.2057	0.0431	−8.7569	8.7999
VIII	−0.1172	−0.1393	−0.3729	−0.2014	−0.2005	0.1594	−8.9200	9.0794
IX	0.1886	−0.5278	−0.4044	−0.2003	−	−0.5366	−8.8510	8.3144
X	−0.1166	−0.1332	−0.3716	−0.2039	−0.2006	0.0092	−8.9366	8.9457
XI	0.0320	−0.3178	−0.3364	−0.2039	−0.1902 −0.1586	−0.0779	−8.8732	8.7953

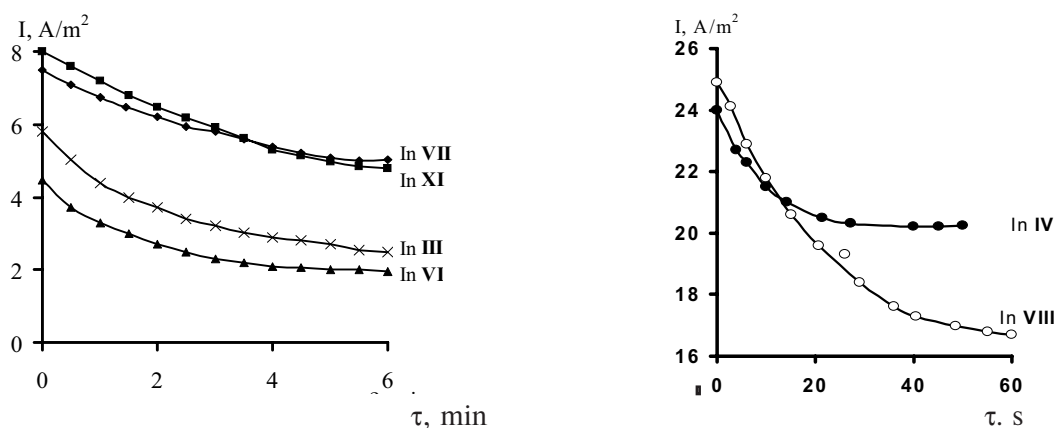*I.M. Kurmakova, O.S. Bondar, V.I. Vorobyova, O.E. Chygyrynets*

Fig. 4. Cathode chronoammograms measured on steel 45 samples immersed in 0.1 M HCl after adding $1\cdot10^{-3}$ mol/L of inhibitors: a − In VII, In IX, In III, and In VI; b − In VIII and In IV. The electrode potential is 0.6 V

group. The molecules of inhibitors No. IV, VIII and X form a chelate bond (four negatively charged adsorption-reaction centres), and the formation of chelate occurs much faster.

Conclusions

High inhibition efficiency (93.0%−98.4%) of imidazo[1,2-a]azepinium bromides in acid chloride environment is explained by their adsorption properties. The mechanism of inhibition efficiency implies the formation of surface compounds and a thin (4 nm) polymolecular protective film. As molecules of imidazo[1,2-a]azepinium bromides contain four negatively charged adsorption-reaction centres, the macrocycle effect occurs, substantially reducing the time of chemisorption.

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ІНГІБУВАЛЬНА ДІЯ БРОМІДІВ ІМІДАЗО [1,2-A] АЗЕПІНІЮ ПРИ КОРОЗІЇ ВУГЛЕЦЕВОЇ СТАЛІ У КИСЛОМУ ХЛОРИДНОМУ СЕРЕДОВИЩІ

І.М. Курмакова, О.С. Бондар, В.І. Воробйова, О.Е. Чигиринець

У статті запропоновано механізм захисної дії бромідів імідазо [1,2-a] азепінію. Ці сполуки є ефективними інгібіторами корозії вуглецевої сталі в кислих хлоридних середовищах в інтервалі температур 293—333 К. Ступінь захисту, визначений гравіметричним методом, при 293 К становить 93,0—96,8%, із підвищенням температури він змінюється незначно. Захисні властивості сполук зумовлені утворенням на поверхні вуглецевої сталі захисних плівок товщиною до 4 нм, що доведено методом Оже-спектроскопії. Хемосорбція молекул також забезпечує значний ефект захисної післядії. Встановлено залежність ефективності інгібування від енергетичної характеристики молекул, а саме від різниці значень енергій нижчої вакантної та вищої зайнятої молекулярних орбіталей. Показана можливість реалізації макроциклічного ефекту при хемосорбції інгібіторів, молекули яких мають чотири негативно заряджених адсорбційно-реакційних центри та являють собою сформований хелатний вузол.

Ключові слова: броміди імідазо [1,2-a] азепінію, інгібітор, кислотна корозія, вуглецева сталь, механізм.

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