Electrochemical study of the adsorption and inhibiting properties of halogen derivatives of aniline on iron in sulfuric acid

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Abstract

The adsorption of halogen derivatives of aniline on an iron electrode in sulfuric acid medium has been studied in relation to their inhibiting properties using electrochemical a.c. impedance and d.c. polarization techniques, as well as quantum chemical calculations of chemical structure and distribution of electron charges in the organic molecules. It is established that the adsorption process is described by Frumkin's isotherm. The adsorption parameters characterizing the interaction forces between the molecules in the adsorbed layer, the free energy of adsorption, the maximum surface excess of adsorbed species, the area occupied by each molecule etc. have been calculated on the basis of this isotherm.

It is shown that the inhibition efficiency, as well as the free energy of adsorption, increases in the sequence: aniline < *p*-Cl-aniline < *p*-Br-aniline < *p*-I-aniline. It was found that the adsorption behaviour of the substances studied is characterized by two adsorption states: vertical and planar orientation of the molecules. Combining data from electrochemical measurements with data from quantum chemical calculations the correlation between the chemical structure of the aniline derivatives and their adsorption capability and inhibition efficiency has been ascertained.

1. Introduction

The inhibiting action of organic compounds on the corrosion of metals in acid media is usually related to their adsorption on the metal surface [1–6]. Adsorption results in an effective blocking of the active sites of metal dissolution and/or hydrogen evolution, thus diminishing the overall corrosion rate.

The relationship between the adsorption of organic inhibitors and their molecular structure has attracted the attention of many investigators [7–15]. The presence of functional groups and the electron density distribution in the molecules of the organic substances are factors that strongly influence their adsorption behaviour. Combining data from quantum chemical calculations with data from electrochemical measurements a correlation between the adsorption and the molecular structure of the inhibitors can be obtained [16–26]. Parameters like the degree of surface coverage, the attraction constant characterizing the interaction forces between the molecules in the adsorption layer, maximum surface excess of the adsorbed species, energy of adsorption as well as the variation of the adsorption energy with the electrode potential and the orientation of the adsorbed molecules are of great relevance to those attempts.

The aim of the present work is to study the adsorption behaviour of halogen derivatives of aniline on iron in sulfuric acid in relation to their inhibiting properties. These compounds have attracted attention mainly because they have two adsorption centres, which may result in a different mode of adsorption interaction as a function of electrode potential. The data obtained by electrochemical a.c. impedance and d.c. polarization measurements are analyzed taking into consideration the quantum chemical calculations of the chemical structure and the distribution of the electron charge in the organic molecules. The correlation between the chemical structure of aniline derivatives and their adsorption capability and inhibiting efficiency in respect to acidic corrosion of iron are discussed.

2. Experimental details

All electrochemical experiments were performed in a three-electrode conventional glass cell containing 250 cm^3 of solution. A cylindrical electrode (1 cm^2

exposed surface area) made of spectral purity grade iron (15 ppm impurity level) was used as working electrode. The counter electrode was a platinum cylindrical mesh, placed coaxially around the working electrode. The reference electrode was a saturated calomel electrode connected to the cell via a salt bridge. All potential values are referred to the normal hydrogen electrode.

To obtain a reproducible surface the iron electrode was polished mechanically and electrochemically. The electrode was immersed in the cell under current and subjected to cathodic polarization for 1 h at a potential of −0.6 V. This procedure results in a mean roughness factor of 1.66 [27]. Thus, all the capacitance values were evaluated with respect to the real electrode surface area.

The solutions of 0.1 M H_2SO_4, used as a model corrosion medium, were prepared from analytical grade H_2SO_4 (Merck) and doubly distilled water. The organic substances studied: aniline, Cl-, Br- and I-aniline (Merck) were introduced in the corrosive medium as ethanol solutions. The solutions were deaerated with pure hydrogen before and during each measurement. All measurements were carried out at 20 °C.

The differential capacitance of the iron electrode was recorded using an impedance bridge (AC P-568) at a frequency of 870 Hz. This frequency was determined from the investigation of the relationship between the capacitance and a.c. frequency, which show that the capacitance of iron does not practically depend on the perturbation frequency at frequencies above 800 Hz [27].

The capacitance measurements were carried out in a potential range between −0.55 and −0.25 V. The rather narrow potential range investigated is determined by the fact that at potentials more negative than −0.6 V hydrogen is evolved, while at potentials more positive than −0.25 V the passivation of iron starts. The potentiodynamic polarization curves were recorded (Solartron ECI 1286 potentiostat) at a sweep rate of 0.1 mV s^{-1} after the steady-state corrosion potential had been established.

Quantum-chemical calculations were carried out by the use of the AM1 method [28–30] to estimate the partial charges of the atoms in the molecule, energies E_{HOMO} and E_{LUMO}, as well as the length of valence bonds and dihedral torsion angles.

3. Results and discussion

3.1. Quantum chemical calculations

It is known [31] that aniline and its derivatives are protonated in acid medium (the nitrogen atom of the amino group accepts a proton). The distribution of the partial charges in the molecules of protonated aniline and its halogen derivatives are presented in Figure 1. From the data on the electron density of the organic substances studied it can be concluded that:
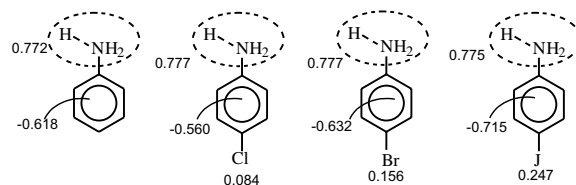

Fig. 1. Molecular structure and distribution of partial charges in the protonated form of the molecules of aniline and its halogen derivatives.

(i) A positive charge (δ^+) is localized in the amino groups which is the same for the all compounds.

(ii) A positive charge is also localized at chlorine, bromine and iodine atoms of the aniline derivatives which increase in the order: $\delta^+_{Cl} < \delta^+_{Br} < \delta^+_I$. This δ^+ charge is rather small than δ^+ localized at the amino group.

(iii) A partial negative charge (δ^-) is localized in the benzene ring. The value of the δ^- increases in the following sequence: p-chloro-aniline < aniline < p-bromo-aniline < p-iodo-aniline.

Using the same AM1 method the geometric area of the molecules studied was determined.

3.2. Double layer capacity measurements

The differential capacitance against potential dependencies for iron electrode in solution of 0.1 M H_2SO_4 without and with addition of aniline, p-chloro-aniline, p-bromo-aniline and p-iodo-aniline are plotted in Figure 2.

The change in shape of the capacitance curves C/E as well as the considerable decrease in capacitance with increasing concentration of the organic additives indicates adsorption of those compounds on the iron surface. The adsorption takes place on the negatively, as well as on the positively, charged electrode surface. The comparison of the C/E curves shows that the decrease in capacitance is commensurable for all derivatives of aniline, while in the presence of aniline a considerable decrease in capacitance of the iron electrode is obtained at much higher concentration.

Quantitative evaluation of the adsorption of the organic substances on the iron/sulfuric acid solution interface can be obtained from the adsorption isotherm which gives the correlation between the degree of surface coverage (θ) and the bulk concentrations of the organic substance (c_{or}) at the constant potential (E is const). The degree of surface coverage of the electrode was evaluated using the relation [32]:

$$\theta = \frac{(C_o - C)}{(C_o - C')} \tag{1}$$

where C_o is the capacitance at the minimum of C/E curve of iron electrode in the blank solution and C is the capacitance for a definite bulk concentration of the surfactant. The capacitance C′, corresponding to a full
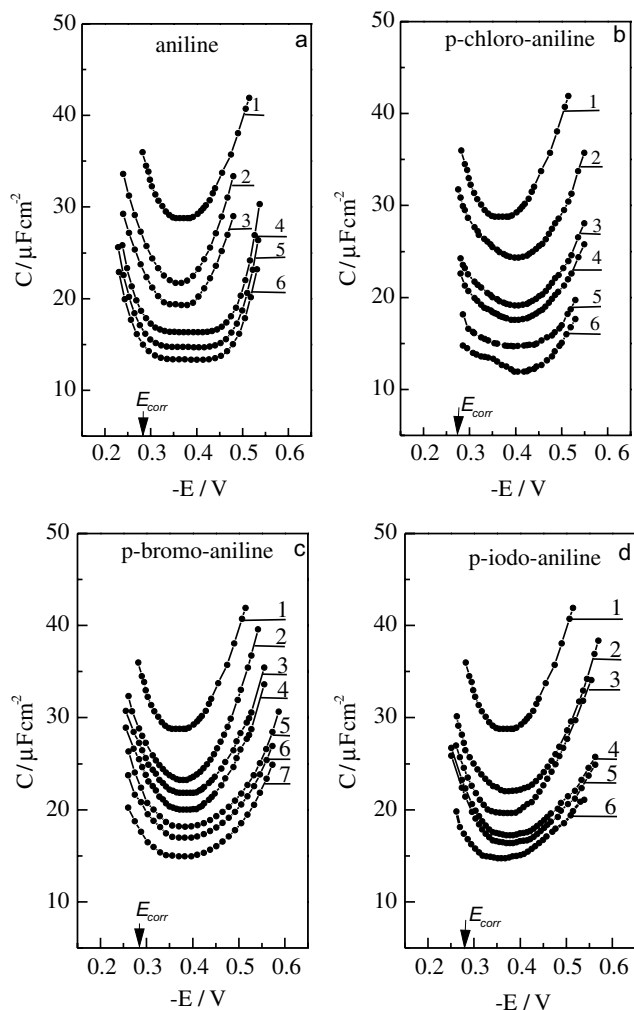
Fig. 2. Capacitance against potential curves of iron in 0.1 M H₂SO₄ +
2 vol % ethanol (curve 1) and in the presence of: (a) aniline: 2 5, 3 10, 4
20, 5 50 and 6 200 μM; (b) p-chloro-aniline: 2 0.1, 3 0.5, 4 1, 5 5 and 6
50 μM; (c) p-bromo-aniline: 2 0.05, 3 0.1, 4 0.2, 5 0.5 and 6 1 and 7:
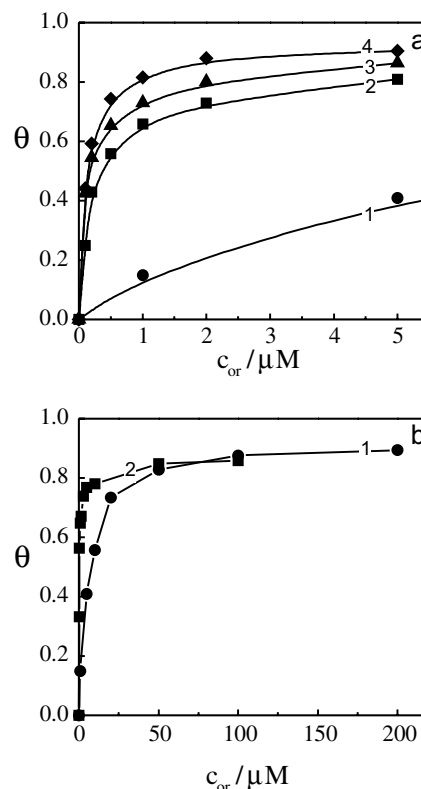5 μM; and (d) p-iodo-aniline: 2 0.1, 3 0.2, 4 0.5, 5 1 and 6 5 μM.

Fig. 3. Dependence of the surface coverage on additive concentration
for (1) aniline (2) p-chloro- aniline (3) p-bromo-aniline and (4) p-iodo-
aniline.

coverage of the surface with organic compound ($\theta = 1$)
is estimated from the plots of $1/C$ against $1/c_{or}$ [32].

The dependencies of the degree of surface coverage (θ)
on the concentration (c_{or}) of the substances studied at
the potential of the maximum adsorption are presented
in Figure 3. It can be concluded that:
(i) The values of θ for the aniline derivatives (curves 2,
3 and 4) are higher than this for aniline (curve 1) and
they increase in the order: p-chloro-aniline < p-
bromo-aniline < p-iodo-aniline (Figure 3(a)).
(ii) The maximum surface coverage (θ_{max}) for the p-
chloro-aniline is reached at concentrations of 50 μM
and for aniline at 200 μM (Figure 3(b)), while θ_{max}
for the p-bromo-aniline and p-iodo-aniline is ob-
tained at 5 μM.

Using a criterion proposed by Damaskin [32] it was
found that the adsorption process is described by
Frumkin's isotherm:

$$Bc_{or} = \left(\frac{\theta}{1-\theta}\right)\exp(-2a\theta) \tag{2}$$

where B is the equilibrium constant of the adsorption
process and a is the attraction constant characterizing
the forces of interaction between the molecules in the
adsorbed layer.

To obtain sufficiently accurate values of the attraction
constant (a), an algorithm of Damaskin [33] was
applied. As a first step in these calculations a relative
concentration $y = c/c_{\theta=0.5}$ was introduced [32, 33]. The
value of $c_{\theta=0.5}$ is determined from the plot θ against c_{or}
at different electrode potentials (E is const).

For $\theta = 0.5$ Frumkin's isotherm is simplified to

$$B = \frac{1}{c_{\theta=0.5}}\exp(-a) \tag{3}$$

The ratio of Equation 2 and Equation 3 gives the
following expression for y:

$$y = \left(\frac{\theta}{1-\theta}\right)\exp[a(1-2\theta)] \tag{4}$$

Equation 4 gives for a:

$$a = \left(\frac{1}{1-2\theta}\right)\ln\left[y\left(\frac{1-\theta}{\theta}\right)\right] \tag{5}$$

Using the method of iteration the values of attraction
constant and equilibrium constant were calculated at the
different potentials. The energy of adsorption ($-\Delta G_A$)

was also calculated at different potentials (E is const) using the equation:

$$B = \frac{1}{55.5} \exp\left(\frac{-\Delta G_A}{RT}\right) \tag{6}$$

The variation of the energy of adsorption ($-\Delta G_A$) with potential for all substances studied is presented in Figure 4. The adsorption process for aniline and its halogen derivatives is described by two parabolas, characterizing two adsorption states. The first adsorption state (curves 1–4) at the negatively charged electrode surface ($E < E_N$, where E_N is the potential of uncharged surface) is a result of a vertical orientation of the molecules. The second adsorption state (curves 1′–4′) at positively charged surface ($E > E_N$) is attributed to the planar orientation. The vertical orientation of the molecules of the aniline derivatives can be realized through the amino group or through the halogen atoms where the δ^+ charge is also localized (cf. Figure 1). The higher δ^+ localized at amino group supposes vertical adsorption of the molecules through the amino group. This presumption explains the similar character of the $\Delta G_A/E$ dependencies as well as the same potential of reorientation for all substances studied. The planar orientation of the molecules at $E > E_N$ is determined by the π-electron interaction of the benzene ring with the electrode surface. The values of ΔG_A obtained for the

Fig. 4. Variation of the energy of adsorption on potential of iron electrode in 0.1 M H_2SO_4 with (1) aniline (2) p-chloro-aniline (3) p-bromo-aniline and (4) p-iodo-aniline.

derivatives of aniline are greater than those for aniline. This difference can not be explained on the basis of the data for the electron density of the molecules.

The constants of the equations which describe the parabolic dependence ΔG_A against E:

$$-\Delta G_A = c_o + c_1 E + c_2 E^2 \tag{7}$$

were calculated. The potential of the maximum adsorption for the both adsorption states can be calculated from the ratio:

$$E_{\max i} = -c_{i1}/2c_{i2} \tag{8}$$

The identical potentials of maximum adsorption ($E_{\max 1}$ and $E_{\max 2}$) for all substances studied, in both adsorption states (Table 1), as well as the identical potentials of reorientation of the molecules (Figure 4), indicate that the adsorption of aniline and its halogen derivatives is realized by one and the same adsorption centres.

The calculated values of the attraction constant (a) in the case of planar orientation of the molecules at $E_{\max 2}$ are summarized in Table 1. The negative values of a obtained for all compounds investigated indicate lateral forces of repulsion between the molecules in the adsorbed layer. These forces of repulsion are greater in the case of the adsorption of aniline derivatives in comparison with the aniline. This fact can be explained by the presence of symmetrically situated functional groups with the same charges by sign [34]. The values of the attraction constant depend on the charge δ^+ at the halogen atom in the molecules (the forces of repulsion between the molecules in the adsorbed layer increase with increasing of the charge δ^+ at the halogen atoms of the aniline derivatives).

The adsorption parameters: the maximum surface excess ($\Gamma_{\max}$) and area (S) occupied by one adsorbed molecule were evaluated using the method already described in [25, 26]. For this purpose the dependence of the equilibrium constant B on the potential can be presented in form [32].

$$B = B_{\max} \exp[-b(E - E_{\max})^2] \tag{9}$$

where $B_{\max} = B$ at $E = E_{\max}$.

Equation 9 can be applied when the adsorption equilibrium is established at each potential and the electrode charge is a function of the potential and the
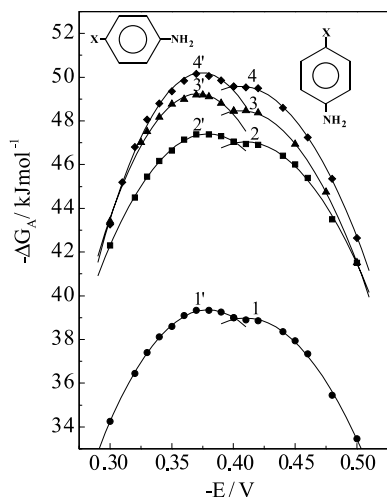
Table 1. Adsorption parameters for halogen derivatives of aniline

Compound	a	$-E_{\max 1}$ /V	$-E_{\max 2}$ /V	$10^{10} \Gamma_{\max 1}$ /mol cm^{-2}	$10^{10} \Gamma_{\max 2}$ /mol cm^{-2}	S_1 /nm^2	S_2 /nm^2
Aniline	−0.25	0.41	0.38	3.74	1.93	0.44	0.84
Cl-aniline	−0.45	0.41	0.38	3.85	1.83	0.43	0.91
Br-aniline	−0.52	0.41	0.37	3.90	1.79	0.42	0.92
I-aniline	−0.60	0.41	0.38	3.82	1.73	0.43	0.96

degree of surface coverage, that is, $q = q(E, \theta)$. The substitution of B in Equation 2 with B from Equation 9 gives for Frumkin's isotherm:

$$B_{max}c_{or} \exp[-b(E - E_{max})^2] = \left(\frac{\theta}{1 - \theta}\right) \exp(-2a\theta) \qquad (10)$$

The Equation 10 gives the relation between the degree of surface coverage (θ) and the electrode potential (E) at a definite concentration of the organic substance (c_{or}). For maximum concentration of the organic additive ($c_{or,max}$) which corresponds to a maximum value of θ, Equation 10 can be written as

$$B_{max}c_{or,max} \exp[-b(E - E_{max})^2] = \left(\frac{\theta}{1 - \theta}\right) \exp(-2a\theta) \qquad (11)$$

which logarithmic form is

$$\ln\left(\frac{\theta}{1 - \theta}\right) - 2a\theta = \ln(B_{max}c_{or,max}) - b(E - E_{max})^2 \qquad (12)$$

The dependencies $[\ln(\theta/(1 - \theta)) - 2a\theta]$ against $(E - E_{max})^2$ presented in Figure 5 indicate that the adsorption of the substances studied is characterized by two adsorption states. The straight lines (1–4) correspond to vertical orientation of the molecules and the lines (1'–4') to planar orientation. This confirms the result obtained from the dependencies $\Delta G_A/E$. The slope of these lines gives the values of the constant b_i in Equation 12. They were used for the calculation of the maximum surface excess (Γ_{max}) by applying the relationship:

$$\Gamma_{max,i} = \frac{(C_o - C')}{b_i RT} \times 10^{-6} \qquad (13)$$

The area (S_i) occupied by one adsorbed molecule for the different substances was calculated using the relation:

$$S_i = 1/\Gamma_{max,i}N_A \qquad (14)$$

From the calculated values of S_i (Table 1) it can be concluded that the area occupied by one vertically adsorbed molecule is the same for all compounds, while the area of one adsorbed molecule for planar orientation increases with increasing halogen atom radius.

3.3. Polarization measurements

The effect of aniline and its halogen derivatives on the partial corrosion reactions was studied by electrochemical polarization measurements. The potentiodynamic polarization curves of iron in 0.1 M H_2SO_4 solution without and with organic inhibitors (5 μM) are presented in Figure 6. The addition of aniline and its halogen derivatives predominantly affects the rate of hydrogen evolution, that is all additives can be considered as predominantly cathodic inhibitors.

The inhibition efficiency IE(%) was determined from the change in corrosion current density in the presence of inhibitor (Table 2). The inhibition efficiency of the aniline derivatives increases in the sequence: aniline < p-Cl-aniline < p-Br-aniline < p-I-aniline.

The correlation between the inhibition efficiency and the energy of adsorption for planar orientation of the molecules is shown in Figure 7. The linear dependence indicates that the inhibiting effect of the aniline and its halogen derivatives on acidic corrosion of iron is a result of surface adsorption. As already mentioned, the difference between the values of the energy of adsorption of the substances studied cannot be explained by the data from the quantum chemical calculations of the electron
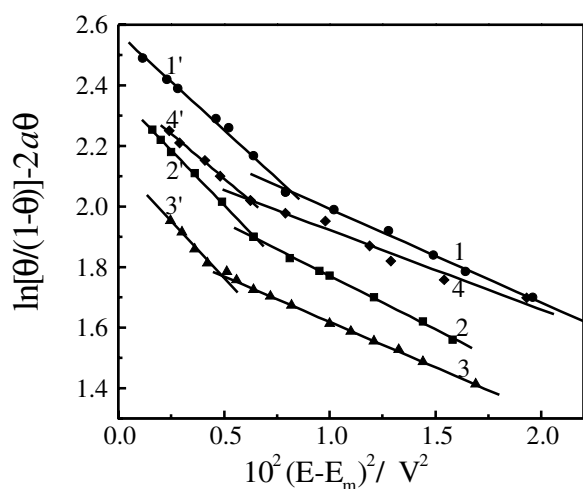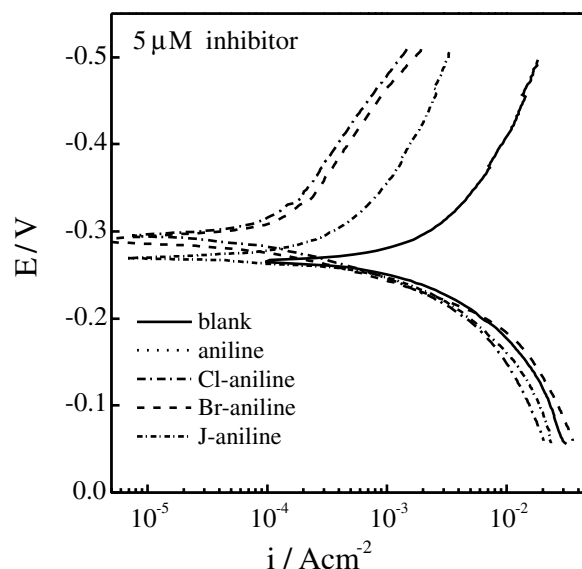

Fig. 5. Dependence of $[\ln(\theta/(1 - \theta)) - 2a\theta]$ on $(E - E_{max})^2$ obtained in 0.1 M H_2SO_4 with (1) aniline (2) p-chloro-aniline (3) p-bromo-aniline and (4) p-iodo-aniline.

Fig. 6. Polarization curves of iron in 0.1 M H_2SO_4 and in the presence of 5 μM inhibitor.

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Table 2. Data from polarization measurements

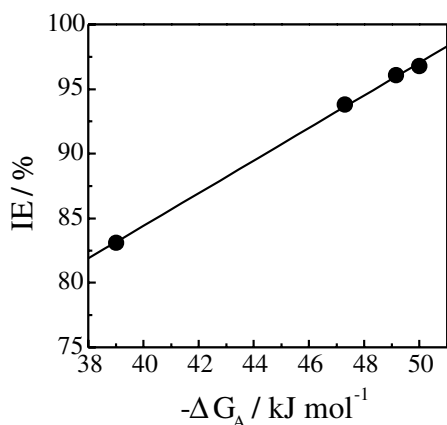| Compound	E_{corr} /V	I_{corr} /mA cm^{-2}	IE /%
Blank	−0.266	2.37	–
Aniline	−0.270	0.400	83.1
Cl-aniline	−0.290	0.145	93.8
Br-aniline	−0.291	0.092	96.1
I-aniline	−0.293	0.074	96.8

Fig. 7. Dependence of the inhibition efficiency, *IE* (%), on the energy of adsorption of aniline and its halogen derivatives.

density of the molecules, that is, with a simple electrostatic interaction between the molecules and the metal. A linear relationship between the energy of adsorption and the energy of the highest occupied molecular orbital (E_{HOMO}) of the substances was obtained. It can be seen from Figure 8 that the energy of adsorption and, consequently, the inhibiting effect increases with increasing E_{HOMO}. The obtained correlation indicates that charge transfer from the adsorbed inhibitors to the metal surface may take place during adsorption. This is possible because, at the corrosion potential, the electrode surface is charged positively ($E > E_N$) and electron
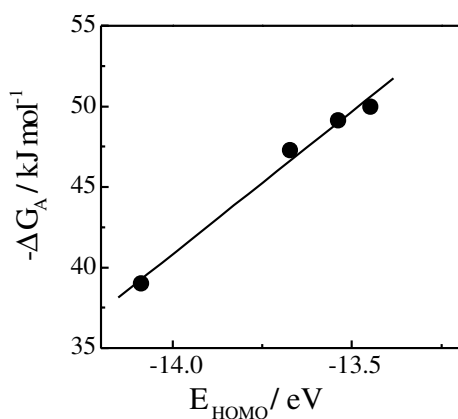
Fig. 8. Dependence of the energy of adsorption on E_{HOMO} of the aniline and its halogen derivatives.

transfer from the HOMO of the molecules of adsorbed inhibitors to the metal can occur. Iron has vacant d-orbitals, which favour the charge transfer process.

4. Conclusion

The adsorption capability, as well as the inhibition efficiency, increases in the sequence: aniline < *p*-chloro-aniline < *p*-bromo-aniline < *p*-iodo-aniline.

Adsorption of the organic substances is described by Frumkin's isotherm and this process is characterized by two adsorption states: vertical orientation of the adsorbed molecules through the amino group (at $E < E_N$) and planar orientation resulting from π-electron interaction of the benzene ring with the electrode surface (at $E > E_N$).

The inhibiting effect of aniline and its halogen derivatives on acidic corrosion of iron is a result of their adsorption on the metal surface. The energy of adsorption, as well as the inhibition efficiency, depends on the energy of the highest occupied molecular orbital (E_{HOMO}).

Thus, combining electrochemical a.c. impedance and d.c. polarization measurements with data from quantum chemical calculations the correlation between the chemical structure of the aniline derivatives and their adsorption capability and inhibition efficiency is ascertained.

Acknowledgement

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