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INFLUENCE OF FUNCTIONALIZED POLYHEXAMETHYLENEGUANIDINES ON THE ELECTROCHEMICAL CHARACTERISTICS OF METALS IN A METHANESULFONATE ELECTROLYTE

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ABSTRACT

In aqueous methanesulfonate electrolytes, the adsorption behavior of modified cationic polyelectrolytes on zinc and iron electrodes was investigated. A pronounced dependence of the adsorption free energy on the degree of incorporation of carboxyl and aromatic functional groups into the polymer chains was established. The individual contributions to the free energy of oligomer adsorption on metal surfaces were quantified. Increasing the degree of functionalization strengthens the interaction between the organic adsorbate and the metal interface. It simultaneously suppresses solvent-induced desorption of macromolecules, attributable to the enhanced hydrophilicity of the polymer chains. The adsorption equilibrium constants of the oligomers were significantly higher on zinc compared to Armco iron, a difference attributed to variations in surface charge and hydrophilicity at the applied potentials. The highest corrosion-inhibition efficiency in mildly acidic media was observed for polyelectrolytes modified with aromatic groups, predominantly due to a steric inhibition mechanism.

Keywords: methanesulfonate electrolyte, surface-active substances, adsorption isotherm, polyelectrolyte, activation factor.

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1. INTRODUCTION

Methanesulfonate electrolytes are recognized as a promising platform for electrochemical processes, including metal coating, deposition, and purification [1], [2]. Although the research and implementation of these systems are relatively new, they are advancing rapidly due to their environmental safety, high stability, and lack of volatile, toxic products compared with traditional acids [3], [4].

However, fundamental data on the physicochemical structure of the electric double layer, the kinetics of ion transport, and the mechanisms of electrode reactions in methanesulfonate media remain poorly understood.

The problem of protecting metallic materials from corrosion and controlling electrodeposition processes [5] remains relevant to the development of new technologies in the fields of energy [6], electronics [7], mechanical engineering, and materials science [8], [9], [4].

Among the various approaches to solving these problems, considerable attention has been paid to the use of polymeric inhibitors and surface modifiers. Synthetic water-soluble cationic polymers, in particular, are promising in this field due to their high efficiency, chemical and thermal stability, their compatibility with the aqueous medium, biodegradability, and relatively low toxicity [10], [11], [12].

Despite their positive properties, the high hydrophilicity of these polymers, due to the presence of polar and charged groups, often limits their ability to adsorb onto metal surfaces [13], [14]. This complicates the formation of a stable adsorption layer, which is necessary for effective inhibitory or modifying effects [15].

To overcome this limitation, studies [16], [17] have proposed an approach based on the formation of polyelectrolyte complexes in solution by associating polymers with low-molecular-weight surfactants. This kind of association allows the reduction of the hydrophilic-lipophilic balance (HLB) of macromolecules, activating their adsorption at the interface due to hydrophobic hydration [18], [19].

Another approach to increasing the adsorption capacity and inhibitory activity of cationic polymers is to modify the polymer chain structure by introducing functional groups that can interact specifically with metal surfaces. In particular, aromatic and carboxyl groups can form π–π or coordination interactions with metal atoms, thereby facilitating polymer fixation on the surface and contributing to the formation of a protective layer [20], [21], [22].

In this context, it is relevant to examine the influence of the nature and degree of functional substituents on the adsorption and corrosion-inhibitory properties of modified cationic polymers on metal surfaces, particularly zinc and iron, in a methanesulfonate medium. Considering the differences in the electrochemical characteristics of these metals, it is especially important to investigate the mechanisms of interaction of polymer systems with metal surfaces in mildly acidic media.

The purpose of this work is to establish the regularities of the influence of the chemical nature of functional groups and their attachment degree on the free

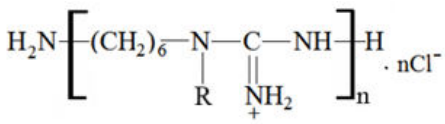
energy of adsorption, equilibrium constants, and inhibitory efficiency of polyelectrolytes in their interaction with zinc and iron surfaces in the methanesulfonate electrolyte.

2. EXPERIMENTAL SECTION

2.1 Preparation

The studies were performed in a methanesulfonate medium. A 1 M aqueous solution of sodium methanesulfonate ($NaCH_3SO_3$) was used as the supporting electrolyte to provide the required ionic conductivity. The solution pH was maintained at 5.5, a slightly acidic value considered optimal for stable electrochemical behavior without hydrolysis or side reactions. When necessary, the pH was adjusted using sodium hydroxide (NaOH) or methanesulfonic acid (CH_3SO_3H). All solutions were prepared using doubly distilled water.

The polyelectrolyte studied was polyhexamethyleneguanidine hydrochloride (PG) with an average molecular weight of 10,000 g/mol. Its functionalized derivatives were synthesized at the Department of Fuel, Polymer, and Polygraphic Materials Technologies of the Ukrainian State University of Chemical Technology. Chemical modification was performed using monochloroacetic acid (yielding a carboxylated polymer, PG-K) and phthalic anhydride (introducing aromatic groups into the macromolecule, PG-F). Such modification of polyhexamethyleneguanidine enables targeted adjustment of its structural and functional characteristics, including hydrophilic-lipophilic balance, complexation ability, and adsorption activity on metal surfaces. The selected samples were used as model systems to study the influence of functional group nature on the electrochemical behavior and inhibitory properties of cationic polymers (1):



(1)

where R: $-CH_2COOH$ or $-COC_6H_4COOH$.

Polyelectrolytes with different degrees of carboxyl group attachment were obtained by reacting polyhexamethyleneguanidine with monochloroacetic acid under a controlled ratio of the functional groups of the macromolecule and the modifier. The degree of attachment varied within the range α = 0.1, 0.3, 0.5, 0.7, and 0.9, which made it possible to modify the chemical structure of the polymer chain and to study the effect of functionalization on its adsorption properties. In the case of PG-F, modified with phthalic anhydride, the maximum degree of attachment was α = 0.5, which is attributed to steric and reactivity limitations associated with the size and structure of the aromatic group.

2.2 Characterization

The surface tension of the solutions (σ) was determined using the Wilhelmy plate method [23], which enables precise measurement of the force acting on a plate wetted by the liquid. The force was measured using Vibra HT-120 digital analytical balances (Shinko Denshi, Japan), which provided sufficient sensitivity and stable readings. A rectangular platinum Wilhelmy plate was used as the measuring element and was flame-annealed before each experiment to remove residual impurities and ensure complete wetting (contact angle ~0°).

Surface tension measurements were performed three to four times for each sample, and the average value was taken. The temperature was maintained at 298.00 ± 0.01 K using a Flüssigkeitsthermostate Baureihe U/UH8 thermostatic system (Germany), which ensured a stable solution temperature required for accurate determination of surface thermodynamic parameters.

To determine adsorption at the air/solution interface, the initial portions of the surface tension isotherms were graphically differentiated in accordance with the Gibbs equation:

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}, \quad (2)$$

where Γ is the adsorption (surface access), σ is the measured surface tension, c is the molar concentration of a surfactant in the solution, R is the universal gas constant, and T is the thermodynamic temperature.

The obtained isotherms were further treated using the linearized coordinates of the Langmuir equation:

$$\frac{c}{\Gamma} = \frac{1}{\Gamma_\infty \cdot B} + \frac{c}{\Gamma_\infty}, \quad (3)$$

where Γ_∞ is the adsorption corresponding to complete surface coverage, and B is the equilibrium constant of adsorption.

The adsorption of polyelectrolytes on metal surfaces was studied using the coulostatic method [24], [25], [26], which was used to evaluate the parameters of the electric double layer on zinc and iron electrodes (using technically pure iron of the Armco brand).

The coulostatic method is based on the analysis of the electrode potential relaxation following a short current impulse. A brief current impulse introduces charge into the electrical double layer and causes an instantaneous shift of the electrode potential from its stationary value. After the impulse is switched off, the potential returns to the stationary level due to the discharge of the double layer and the occurrence of the faradaic reaction.

Within the framework of the Ershler-Randles model, the relaxation of the potential is described by an exponential dependence [24]:

$$E_t = E_0 \cdot \exp\left(-t/C_d R_F\right) \quad (4)$$

where E_0 is the starting potential of the relaxation; C_d is the double layer capacitance; R_F is the faradaic resistance. The parameters C_d and R_F were determined by fitting the experimental E_t curves in semilogarithmic coordinates. The automated coulostatic system provided these values directly as final results.

Measurements were performed at the stationary potential, which was established spontaneously in the studied electrolyte in the absence of external current. Working at the stationary potential ensured a stable state of the metal surface and the formation of the polyelectrolyte adsorption layer. The equilibrium potential of the metal was not used, since the electrolytes employed for the adsorption studies did not contain Zn^{2+} or Fe^{2+} ions. Conducting measurements at the stationary potential eliminated potential drift and ensured the correct determination of the relaxation parameters, double-layer capacitance, and surface coverage.

The double-layer capacitance is sensitive to the adsorption of organic molecules, because the adsorbed layer alters the thickness and dielectric properties of the interfacial region. The obtained Cd(c) dependencies were analyzed using the model of two parallel capacitors, which allowed quantitative determination of the surface coverage by the organic adsorbate:

$$\theta = \frac{C_d^0 - C_d^\theta}{C_d^0 - C_d^1} \quad (5)$$

where C_d^0, C_d^θ and C_d^1 are the values of C_d at the coverage of 0, θ and 1, respectively.

The electrodes were renewed by cutting the electrode surface directly in the solution before each measurement [24].

The resulting θ(c) dependence was analyzed in Langmuir isotherm coordinates, which enabled the determination of the adsorption equilibrium constant (B) and characterization of the interaction between the organic molecules and the electrode surface:

$$\theta = \frac{Bc}{1+Bc}, \quad (6)$$

where (B) is the adsorption equilibrium constant.

Free energy of adsorption ($\Delta\overline{G}_0^0$) was calculated by the following equation:

$$\Delta\overline{G}_0^0 = -RTlnB \quad (7)$$

An increase in R_F in the presence of the polyelectrolyte reflects the blocking of active surface sites and a decrease in charge-transfer rate, which allows evaluation of the influence of the adsorbed layer on the kinetics of the electrode reaction.

Based on the values of the faradaic resistance, the inhibition coefficient (m) and the activation factor (γ) of the polyelectrolytes were calculated as:

$$\gamma = 1/m = R_0/R_i \quad (8)$$

where R_0 is the faradaic resistance in the pure electrolyte; R_i is the faradaic resistance in the presence of the polyelectrolyte at concentration c_i.

Experiments were carried out in a three-electrode glass cell. A solid working electrode was prepared by pressing the corresponding metal wire into a Teflon shell. In order to obtain a reproducible and homogeneous surface, the end of the electrode was cut off by a ruby knife before each measurement [27].

3. RESULTS AND DISCUSSIONS

In the general case, the free energy of adsorption of organic substances on a metal consists of the following components [28]:

$$\Delta\overline{G}_0^0 = \Delta\overline{G}_{Me/A}^0 + \Delta\overline{G}_{A/sol}^0 - \Delta\overline{G}_{sol/Me}^0 \quad (9)$$

where $\Delta\overline{G}_{A/sol}^0$ is the energy of interaction between adsorbate and solvent, which roughly corresponds to the free energy of adsorption of the adsorbate at the $NaCH_3SO_3$/air phase boundary ($\Delta\overline{G}_{A/air}^0$) [28]; $\Delta\overline{G}_{Me/A}^0$, $\Delta\overline{G}_{sol/Me}^0$ are the energies of interaction of the adsorbate and solvent with the metal, respectively.

3.1 Polyelectrolyte Adsorption at the $NaCH_3SO_3$/Air Interface

The values of the free energy of adsorption of polyelectrolytes $\Delta\overline{G}_0^0$ at the $NaCH_3SO_3$/air interface were determined experimentally using the Wilhelmy method (Table-1). Differentiation of these data allowed the calculation of surface excess values, the determination of degrees of coverage, and the construction of adsorption isotherms, which were adequately described by the Langmuir isotherm. The data presented in Figure-1 show that the most significant decrease in surface tension was observed in the presence of the base polyelectrolyte, and the attachment of additional functional groups to it led to a decrease in the surface activity of macromolecules; the decrease was greater in the presence of carboxyl groups in the macromolecules.

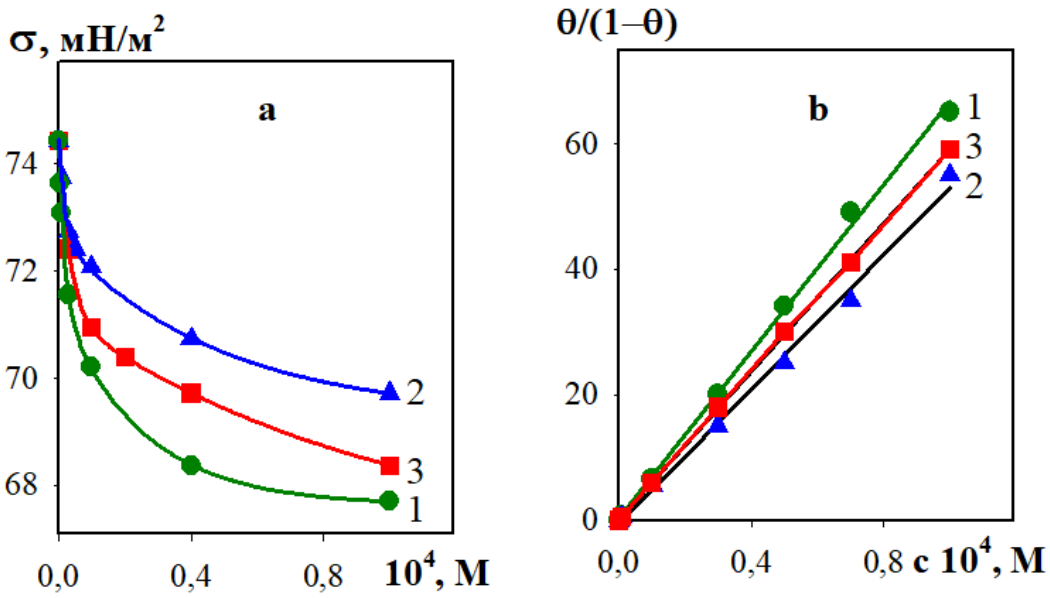


Figure-1. The dependence of surface tension vs concentration of polyelectrolytes (a) and adsorption isotherms (b) at the $NaCH_3SO_3$/air phase interface: 1- PG; 2 - PG-K; 3 - PG-F.

Table-1. The adsorption characteristics of modified polyelectrolytes at the $NaCH_3SO_3$/air phase interfaces.

Adsorbate	B·10⁻⁶, l/mol	$-\Delta\overline{G}_0^0$, kJ/mol
PG	0.653	43.1
PG-K (α=0,5)	0.559	42.7
PG-F (α=0,3)	0.610	42.9

With an increase in the content of carboxyl groups in the polyelectrolyte, a decrease in surface activity and the adsorption equilibrium constant at the $NaCH_3SO_3$/air interface was observed (Table-1). The obtained values of the adsorption limit of modified polyelectrolytes (Γ_∞) decreased as the degree of macromolecule modification increased (Table-2), which is related to an increase in the area occupied by the molecule at the phase boundary.

The decrease in adsorption of macromolecules modified with monochloroacetic acid may be due to an increase in their hydrophilicity and a decrease in solvent repulsion at the phase boundary. To verify this assumption, the hydrophilic-lipophilic balance (HLB_A) of the surface-active substance of elementary polyelectrolyte links was calculated [29]:

$$HLB_A = 7 + \sum(HLB)_G - \sum(HLB)_L \quad (10)$$

where $\sum(HLB)_G$ is the sum of the HLB values of all hydrophilic groups; $\sum(HLB)_L$ is the sum of the HLB values of lipophilic (hydrophobic) groups.

Table-2. Adsorption parameters of polyelectrolytes with different degrees of carboxyl group attachment at the $NaCH_3SO_3$/air phase interface.

Parameters	Degree of attachment, α					
	0	0.1	0.3	0.5	0.7	0.9
B·10⁻⁶, l/mol	0.653	0.649	0.626	0.565	0.382	0.275
$\Gamma_\infty \cdot 10^6$, mol/m²	1.03	0.99	0.94	0.74	0.69	0.64
$-\Delta\overline{G}_{A/air}^0$, kJ/mol	43.1	43.0	42.9	42.7	41.7	40.9
HLB	3.68	3.87	4.25	4.64	5.02	5.41

It turned out that with an increase in the content of carboxyl groups, the HLB value for the elementary unit of the polyelectrolyte increases by almost 1.5 times (Table-2).

3.2 Adsorption of Polyelectrolytes on the Surface of Polycrystalline Electrodes

Figure-2 shows the adsorption isotherms of modified polyelectrolytes on the surface of zinc and iron

(Armco) electrodes. The dependencies are linear in Langmuir coordinates, which indicates the formation of a monomolecular adsorption layer on the electrode surface with a fixed number of active centers.

Based on the obtained isotherms, adsorption equilibrium constants (B) were calculated for each of the studied polyelectrolytes. It was found that modified derivatives of polyhexamethyleneguanidine hydrochloride exhibit significantly higher values of these constants compared to the unmodified form of polyhexamethyleneguanidine (Table-3), indicating an increased affinity of functionalized molecules to the metal surface.

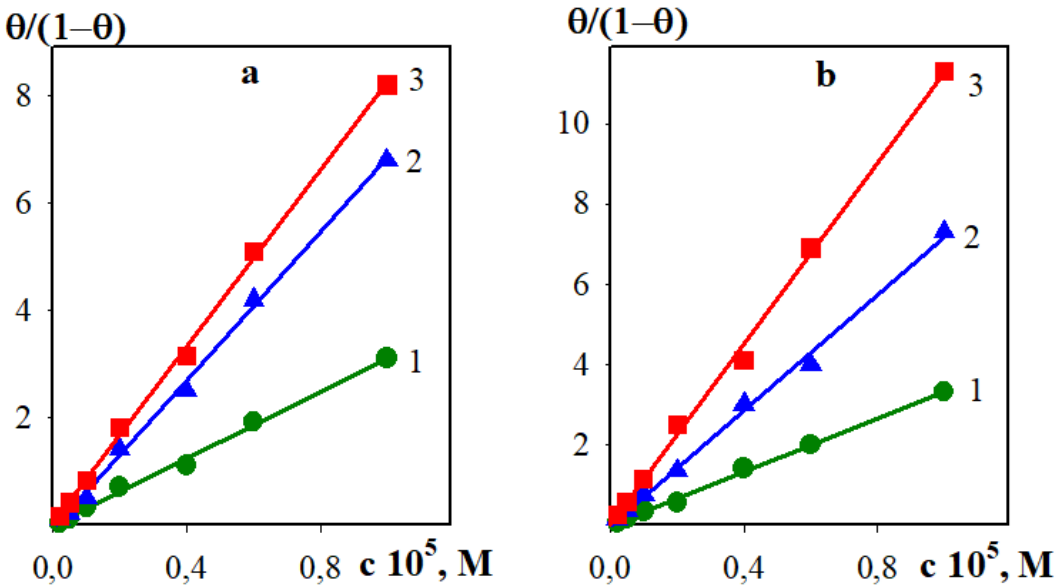


Figure-2. Adsorption isotherms of polyelectrolytes on zinc (a) and Armco-iron (b) electrodes in methanesulfonate electrolyte: 1 - PG; 2 - PG-K; 3 - PG-F.

Polyelectrolytes with attached aromatic groups (PG-F) showed more pronounced adsorption activity, providing not only electrostatic but also π-π interaction with the metal surface [30]. These structures exhibited the highest adsorption capacity on both zinc and iron electrodes, indicating the important role of the spatial and electronic characteristics of functional groups in the adsorption mechanism.

Table-3. The adsorption characteristics of modified polyelectrolytes at the various phase interfaces.

Phase interfaces	PG		PG-K (α=0.5)		PG-F (α=0.3)	
	B·10^{-6}. l/mol	$-\Delta\overline{G}_0^0$. kJ/mol	B·10^{-6}. l/mol	$-\Delta\overline{G}_0^0$. kJ/mol	B·10^{-6}. l/mol	$-\Delta\overline{G}_0^0$. kJ/mol
CH_3SO_3Na /Fe	0.339	41.5	0.735	43.4	1.138	44.5
CH_3SO_3Na /Zn	0.137	39.2	0.712	43.3	0.846	43.7

The values of the adsorption equilibrium constants of polyelectrolytes on the zinc electrode were significantly lower than the corresponding values obtained for the Armco iron electrode. This difference may indicate that the nature of the metal surface significantly affects the adsorption efficiency of polyelectrolytes, in particular due to the different interaction energy of functional groups with the electronic structure of the metal surface.

It is probable that the decrease in the adsorption equilibrium constant on zinc is associated with less favorable energy interaction between the functional groups of the polymer chain and the zinc surface, as compared to the more active interaction on the iron surface. In addition, the influence of the structure of the hydrate shell and the molecular organization of the solvent in the pre-electrode layer cannot be excluded; these may vary depending on the type of metal, thereby affecting the availability of active centers for adsorption.

The energy of interaction between the adsorbate and the surface of metal electrodes was calculated using equation (4), taking into account the values of $\Delta\overline{G}_{A/air}^0$ (Table-1) found based on the data (Figure-1) and using the values of the energy of interaction between the solvent and the surface of iron and zinc, which are equal to -57.8 and -

10.7 kJ/mol, respectively [31], [32], [33]. Analysis of the results obtained showed (Table 4) that this interaction is greater for modified polyelectrolytes and increases significantly when changing from a zinc electrode to an iron one.

Analysis of the results obtained (Table-4) showed that the intensity of interaction between polyelectrolytes and metal surfaces significantly depends on the chemical structure of the polymer. Modified polyelectrolytes, in particular, exhibit a higher ability to interact with the metal surface, which is due to the presence of functional groups capable of specific adsorption. In addition, a significant increase in this interaction is observed when changing from a zinc electrode to an iron one, which is probably due to the higher hydrophilicity of the iron surface.

Table-4. Energy of the polyelectrolyte interactions with the surface of metal electrodes.

Adsorbate	$-\Delta\overline{G}^0_{Zn/A}$, kJ/mol	$-\Delta\overline{G}^0_{Fe/A}$, kJ/mol
PG	9.8	56.2
PG-K	11.3	58.5
PG-F	11.5	59.4

To assess the influence of the degree of attachment of functional groups on the adsorption characteristics of polyelectrolytes on a zinc electrode, adsorption isotherms of carboxyl-containing compounds with different attachment degrees α were obtained. It was found that with an increase in α, the value of the adsorption equilibrium constant of polyelectrolytes first increases, passes through a maximum at α=0.5, and then decreases (Table-5). The extreme dependence of B and $\Delta\overline{G}^0_0$ on α can be associated with different trends in the changes in the values of $\Delta\overline{G}^0_{A/sol}$ and $\Delta\overline{G}^0_{A/Me}$.

Calculations of the energy of interaction between macromolecules and the zinc surface using equation (9) showed that this interaction increases with an increase in the content of carboxyl groups in the polyelectrolyte (Table-5).

Table-5. Adsorption parameters of polyelectrolytes with different degrees of attachment of carboxyl groups on a zinc electrode.

Parameters	Degree of attachment α					
	0	0.1	0.3	0.5	0.7	0.9
B 10^{-6}, l/mol	0.13	0.34	0.56	0.7	0.48	0.45
$-\Delta\overline{G}^0_0$, kJ/mol	38.5	40.8	42.0	42.6	41.7	41.5
$-\Delta\overline{G}^0_{A/Me}$, kJ/mol	6.78	9.16	10.41	11.29	11.33	11.94

Obviously, the extreme dependence of the free energy of adsorption of polyelectrolytes ($\Delta\overline{G}^0_0$) on α (Table 5) is associated both with an increase in the interaction energy of carboxyl-containing polyguanidines with zinc (Table-4) and with a decrease in the repulsion of macromolecules by the solvent (Table-2).

3.3 Fitting of the Data

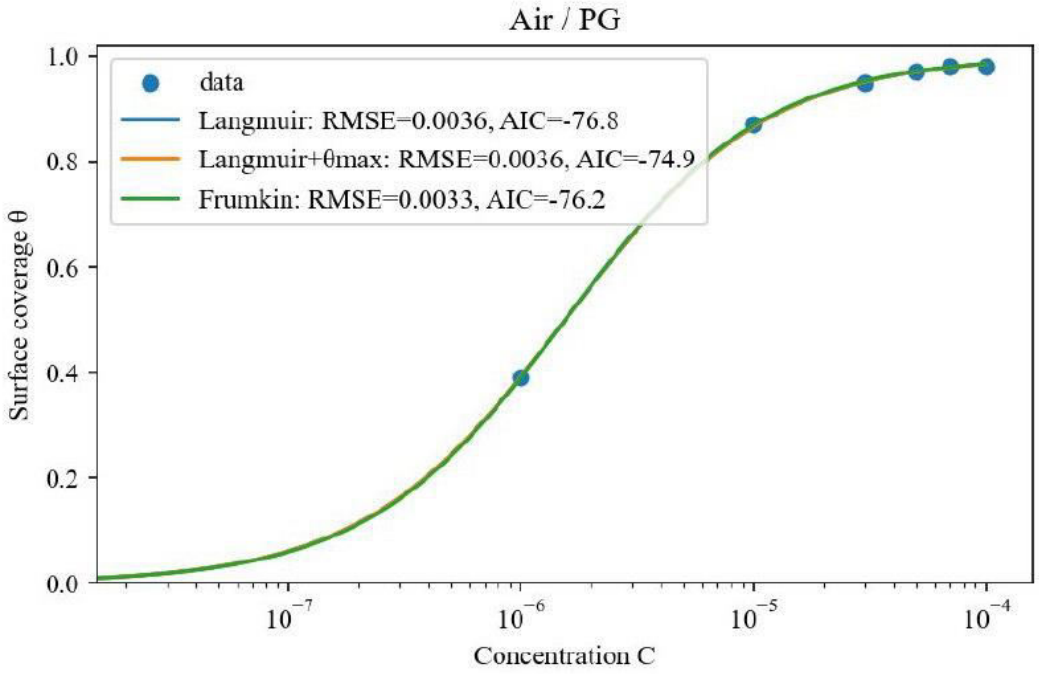
In addition to the linearized Langmuir treatment, the experimental θ(c) dependences were analyzed using nonlinear fitting procedures to verify the applicability of the Langmuir model and to assess possible deviations from ideal monolayer adsorption. The adsorption data were fitted using physically motivated monolayer models of increasing complexity, including the classical Langmuir isotherm, a modified Langmuir model with finite maximum surface coverage (θmax), and the Frumkin isotherm accounting for lateral interactions between adsorbed species. Model parameters were obtained by nonlinear least-squares fitting, while the quality of the fits and the statistical significance of additional fitting parameters were evaluated using the root-mean-square error (RMSE) and the Akaike information criterion (AIC) (Table-6).

Table-6. RMSE and AIC parameters for all isotherms in the investigation.

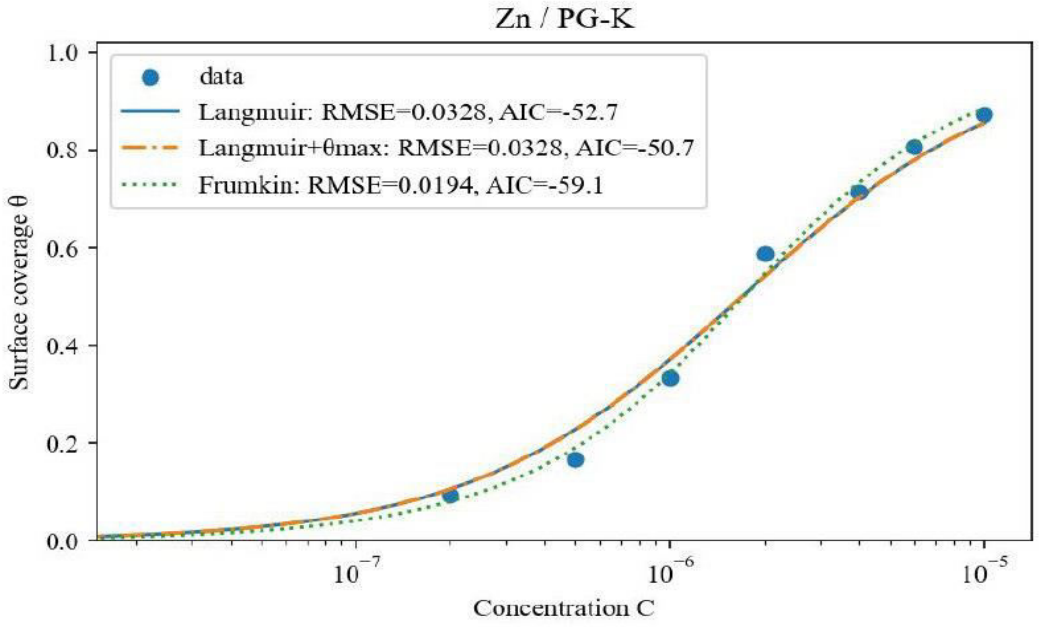
#	Isotherm	Langmuir (RMSE / AIC)	Langmuir+θmax (RMSE / AIC)	Frumkin (RMSE / AIC)
1	Air /PG	0.0036 / -76.8	0.0036 / -74.9	0.0033 / -76.2
2	Air /PG-K	0.0086 / -64.7	0.0048 / -70.9	0.0059 / -67.8
3	Air / PG-F	0.0054 / -71.1	0.0041 / -73.0	0.0054 / -69.2
4	Zn / PG	0.0234 /-58.1	0.0234 / -56.1	0.0229 / -56.4
5	Zn / PG-K	0.0328 / -52.7	0.0328 /-50.7	0.0194 / -59.1
6	Zn / PG-F	0.0092 / -73.0	0.0087 / -71.9	0.0085 / -72.3
7	Fe / PG	0.0163 / -63.9	0.0163 / -61.9	0.0121 / -66.7
8	Fe / PG-K	0.0088 / -73.8	0.0084 / -72.4	0.0079 / -73.5
9	Fe / PG-F	0.0095 / -72.5	0.0094 / -70.7	0.0095 / -70.5

Based on the goodness-of-fit, the classical Langmuir model is comparable to the modified Langmuir and Frumkin models. In most cases, the difference in AIC values among the three models is less than 4. Simultaneously, low RMSE values, indicate that the simplest model is more suitable for comparison. Only in the 5th case for the Zn/PG-K case do both RMSE and AIC differ across models. Still, RSMEs remain low, allowing us to use the simplest model. As mentioned above, for all models, RSMEs remain low, allowing us to use the simplest model (Figure-3).

Analysis of the RMSE and AIC values obtained by fitting the experimental isotherms with the three models shows that the classical Langmuir isotherm yields consistently good agreement with the experimental data across all systems studied. The RMSE values for the Langmuir model range from 0.0036 to 0.0328, indicating satisfactory accuracy in describing the adsorption process.



(a)



(b)

Figure-3. Experimental adsorption isotherm (θ vs C) for the Zn/PG-K system. Symbols represent experimental data, while solid lines correspond to fits using the Langmuir isotherm, the modified Langmuir isotherm with finite surface coverage (θmax), and the Frumkin adsorption isotherm for: a -Air/PG; b - Zn/PG-K.

Introducing the additional parameter θmax or employing the more complex Frumkin model does not yield a significant improvement in fit quality: in most cases, the reduction in RMSE is minimal, and the AIC values often become less favorable due to the increased number of adjustable parameters. Despite the above, the Frumkin model yielded a calculated parameter for the Zn/PG-K case, g = 0.696 (Frumkin interaction parameter), attributed to lateral interactions between adsorbed species. In this model, the adsorption free energy depends on surface coverage, reflecting interactions between neighboring adsorbed species.

3.4 Kinetics of Metal Ion Discharge in the Presence of Polyelectrolytes

The change in the corrosion rate of iron and the discharge of zinc ions on the zinc electrode during the adsorption of polyelectrolytes was evaluated using the polarization resistance values measured by the coulostatic method.

Analysis of the obtained data shows (Figure-4) that with an increase in the concentration of polyelectrolytes, the coefficient of damping zinc ion discharge increases, and more intensively in the case of macromolecules modified with aromatic groups.

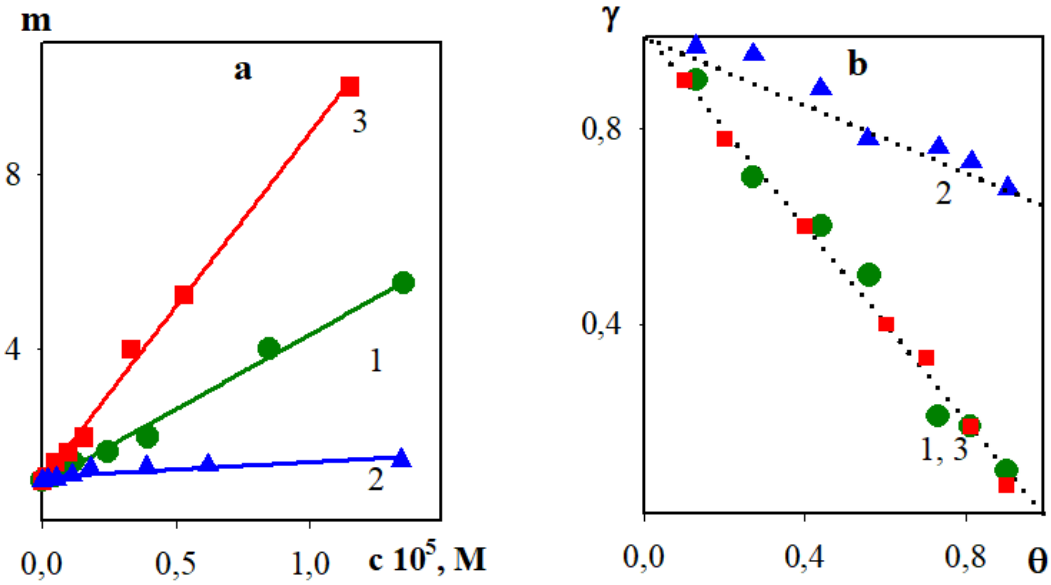


Figure-4. Dependences of the inhibition coefficient on the concentration of polyelectrolytes (a) and the activation factor on the surface coverage (b) during the discharge of Zn(II) ions on a zinc electrode: 1 - PG; 2 - PG-K; 3 - PG-F ($C_{Zn(II)}$=4·10^{-3} M).

The minimum effect was observed during metal ionization discharges in the presence of polyelectrolytes with attached carboxyl groups in solution, despite the fact that their adsorption capacity is significantly higher than that of PG. Similar patterns were observed during the dissolution of Armco iron in the presence of modified polyelectrolytes. For a correct interpretation of the observed effects, it is necessary to compare the kinetic parameters of electrochemical reactions under conditions of constant filling of the electrode surface with organic adsorbate. A comparison of γ values under θ=const conditions showed a significant decrease in the activation factor of carboxyl-containing polyelectrolytes compared to the base polyelectrolyte (Fig. 4). The observed effect may be associated with a change in the charge of macromolecules due to the possible dissociation of carboxyl groups in a neutral medium and a decrease in the activation component of the inhibitory action [26].

CONCLUSIONS

Attachment of carboxyl and aromatic groups to polyhexamethyleneguanidine hydrochloride leads to an increase in the adsorption capacity of polyelectrolytes on zinc and iron electrodes, which is associated with enhanced interaction of macromolecules with the metal surface. This effect is more pronounced in the case of compounds with attached aromatic groups.

An extreme dependence of the adsorption equilibrium constant of modified polyelectrolytes on a zinc electrode on the degree of attachment of carboxyl groups has been established; this is due, on the one hand, to an increase in the interaction of functional groups with the electrode, and, on the other hand, to a decrease in the expulsion of macromolecules to the phase interface due to an increase in their hydrophilicity.

Under the same conditions of electrode filling with organic adsorbate, a significant decrease in the activation factor of modified polyelectrolytes was observed as compared to the base polyelectrolyte, which is associated with the dissociation of carboxyl groups in a neutral medium and a change in the electrostatic component of metal ion discharge damping.

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