

Corrosion inhibition of iron in hydrochloric acid by polyacrylamide

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Abstract: The corrosion protection and/or adsorption of polyacrylamide (PAA) of number average molecular weight, \overline{M}_n , between 15,000 – 1,350,000 g mol⁻¹ on mild steel and iron (99.99 % Fe) in 3 M HCl at room temperature was studied using spectrophotometry (the phenanthroline method), the weight loss method and EIS (Electrochemical Impedance Spectroscopy). It was found that the corrosion protection efficiency of the PAA – adsorbed layers strongly depends on both the molar concentration of PAA in the solution and its molecular weight, reaching limiting values between 85 and 96 %. Simultaneously, it was also concluded that a relatively high surface coverage could be obtained with very low PAA concentrations (0.5 – 2 ppm), indicating the good adsorption characteristics of PAA on mild steel and iron in hydrochloric acid. The experimentally obtained results follow a Langmuir adsorption isotherm. According to the best fitting parameters, the adsorption coefficient B ranged between 2×10^7 and 4×10^8 mol⁻¹ and depended strongly on the molecular weight of the PAA: $B = k \overline{M}_n^\alpha$ (for $\alpha \approx 0.67$ and $k = 2.95 \times 10^4$) or the size of the polymer coil. As was found by EIS, the thickness of the adsorbed PAA layer was approx. 1.1 nm (for $\epsilon_r = 15$) and corresponded only to the polymer segments attached to the metal surface. On the other hand, as was found by ellipsometry, the limiting layer of the adsorbed PAA molecules was highly voluminous and relatively thick (100 – 200 nm), containing entangled polymer coils.

Keywords: mild steel, corrosion inhibition, polyacrylamide, electrochemical impedance spectroscopy, adsorption isotherm.

INTRODUCTION

The adsorption of macromolecules at the solid/solution interface differs in many respects from that of small molecules.¹ For example:

- i) segments may be “adsorbed” although they are not in direct contact with the surface, *i.e.*, as loops or tails rather than trains;
- ii) the nature of the adsorption isotherm differs, *i.e.*, polymer adsorption leads in general to high affinity isotherms;
- iii) the polydispersity of polymers affects the adsorption;

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iv) the adsorption rates are much slower, particularly in the case of higher polydispersity.

It has been observed that a very small amount of certain water soluble polymers, which are effective as flocculating agents, are extremely effective in inhibiting corrosion of ferrous materials in contact with water. Thus, it was found that such polymers in an amount ranging from 5×10^{-6} to 2 wt. % remove the products of corrosion formed prior to treatment and effectively prevent further corrosion.²

Therefore, it was of interest to explain the specificity of adsorption of macromolecules and to study their conformational behavior in solution, especially at the metal/solution interface.^{3,4} It was shown that using a statistical-mechanical treatment it is possible to estimate the number of conformations during the adsorption of polymer molecules.⁵⁻⁷

Previous work on this subject was focused on the conformational behavior of polyacrylamide (PAA) adsorbed on silver and titanium.⁶ As shown by ellipsometry, the chemisorption of PAA on a bare silver surface is more pronounced compared with that on a Ti/TiO₂ interface. The presence of PAA in boric-borate buffer, pH 8.4, mostly inhibits the processes in the active region of passivation of iron.⁸ These results show that PAA adsorbs mainly on the bare active metal surface.

Double-layer capacitance measurements of the metal/solution interface can give valuable additional information about the adsorption of polymers. An attempt to correlate the adsorption and/or inhibition characteristics of polyacrylamide with various molecular weights on iron from acidic solutions of HCl (a very important industrial process for the removal of scales from steel surfaces) with its conformational behavior in solution⁹ was made in this study.

EXPERIMENTAL

The corrosion protection efficiency of PAA was followed on mild steel coupons (70 mm × 15 mm × 2 mm) (0.1 % C, 0.012 % S, 0.015 % P, 0.01 % Si, 0.4 % Mn and 0.07 % Cu) in 3 M HCl at room temperature using the weight loss method and the spectroscopic phenanthroline method at 508 nm for the determination of the Fe(II)-ion concentration in the solution. The duration of the corrosion tests was 5 hours.

The impedance measurements for iron in 3 M HCl at the corrosion potential ($E = -250 \pm 10$ mV/SHE) were carried out in the frequency range from 100 kHz to 10 mHz (with an a.c. signal of 5 mV). An iron rod (99.99 % Fe; 0.18 cm²) mounted in a Teflon holder and platinum foil (10 cm²) were used as the working electrode and auxiliary electrode, respectively. The potentials were measured *versus* saturated calomel electrode and are referred to the standard hydrogen electrode (SHE). The aqueous solutions of 3 M HCl were prepared from 36 wt % HCl (*p.a.*, Merck) and redistilled water ($\kappa < 2 \times 10^{-7}$ S cm⁻¹). PAA was obtained by the redox-initiated polymerization of acrylamide. Six fractions of PAA with molecular weights from 15,000 to 1,350,000 g mol⁻¹ were used in this study. The polydispersity index of the employed PAA samples ranged from 1.2 to 1.35.

The experimental results were fitted using the Boukamp program.¹⁰

RESULTS

Spectrophotometric and gravimetric measurements

As it was stated in the Experimental, the rate of corrosion of mild steel in 3 M HCl was following by spectrophotometry and weight loss measurements. PAA with molecular weights from 15,000 to 1,350,000 g mol⁻¹ and concentrations from 0.2 to 100 ppm in the solution were used as the corrosion inhibitors. Using the obtained experimental results, the protection efficiency coefficient, η_{prot} , was calculated by means of Eqs. 1 and 2. It should be noted that the assumption $\eta_{\text{prot}} = \theta$ (where θ is the relative surface coverage with adsorbed PAA molecules or segments), usually used for the adsorption of organic molecules at a metal/solution interface,¹¹ was made in the present case as well:

$$\eta_{\text{prot}} = \theta = (\Delta m - \Delta m^c) / \Delta m \quad (1)$$

where Δm and Δm^c represent the weight loss of the steel coupons (mg cm⁻²) in the absence or in the presence of PAA (with the concentration c_{PAA} in mol dm⁻³), respectively.

Using the spectrophotometric results for the concentration of Fe(II)-ions in the solution, the corrosion protection efficiency of PAA, or surface coverage (θ) of the steel surface with adsorbed PAA-molecules (or segments) was calculated by means the equation:

$$\eta_{\text{prot}} = \theta = (c_{\text{Fe(II)}}^0 - c_{\text{Fe(II)}}^c) / c_{\text{Fe(II)}}^0 \quad (2)$$

where $c_{\text{Fe(II)}}^0$ and $c_{\text{Fe(II)}}^c$ represent the concentration of Fe(II)-ions in the solution after the corrosion test ($\mu\text{g cm}^{-3}$) in the absence and in the presence of PAA of concentration c (mol dm⁻³), respectively.

It should be mentioned that both methods showed fairly good agreement as far as the protection efficiency of PAA is concerned. The experimentally obtained results are presented in Fig. 1, from which it can be seen that the surface coverage of the steel surface (θ) or the corrosion protection efficiency of PAA adsorbed layer depends both on the concentration of PAA in the solution and its molecular weight, reaching limiting values between 0.85 and 0.96. Simultaneously, it can be concluded that a relatively high value of θ can be obtained using very low PAA concentrations (0.5 – 2 ppm), indicating the very good adsorption characteristics of PAA onto mild steel in aqueous solutions of HCl. As it was shown in previous papers,^{6,12,13} PAA and/or poly(acrylic acid) are better anodic inhibitors than cathodic ones. The adsorbed polymer layers which inhibit the corrosion process are relatively thick, 100 – 250 nm, and highly voluminous, containing a small amount of solid material (approx. 1 wt. %).

The presented results in Fig. 1 are in good accordance with a Langmuir adsorption isotherm:

$$\theta / (1-\theta) = Bc \quad (3)$$

where B is the adsorption coefficient (mol^{-1}) and c is the concentration of PAA (mol dm^{-3}) in the solution.

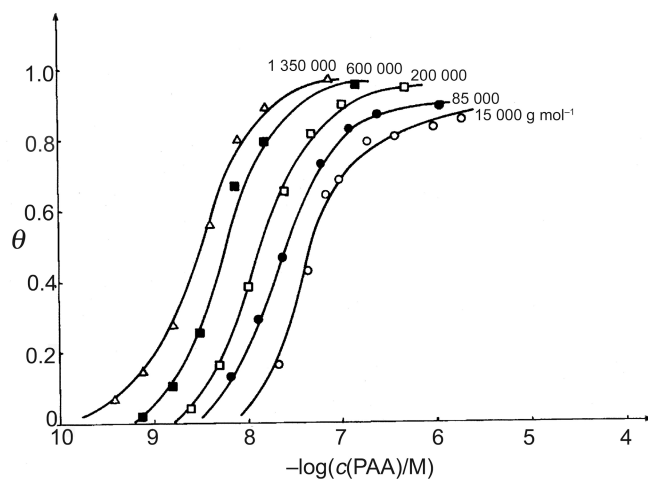


Fig. 1. Adsorption isotherms for PAA from 3 M HCl on mild steel at 293 K.

The best fitting parameters of the obtained experimental results are presented in Table I.

TABLE I. Best fitting parameters for the adsorption of PAA on mild steel from 3 M HCl at 293 K; using a Langmuir adsorption isotherm

$\overline{M}_n / \text{g mol}^{-1}$	B / mol^{-1}	$-\Delta G^\ominus / \text{kJ mol}^{-1}$	r
15,000	2.0×10^7	50.74	0.978
85,000	6.25×10^7	53.51	0.987
200,000	9.8×10^7	54.61	0.995
600,000	2.4×10^8	56.80	0.992
1,350,000	4.1×10^8	58.09	0.997

The values of ΔG^\ominus were calculated using the equation:¹²

$$-\Delta G^\ominus = RT \ln (55.5B) \quad (\text{J mol}^{-1}) \quad (4)$$

where 55.5 is the concentration of water (mol dm^{-3}) in the solution.

It can be concluded that the adsorption coefficient B and ΔG^\ominus depend on the molecular weight of the PAA and follow the empirical Equation:¹⁴

$$B = k \overline{M}_n^\alpha \quad (\text{for } \alpha \approx 0.67 \text{ and } k = 2.95 \times 10^4) \quad (5)$$

The same type of empirical Equations describe the relationship between the molecular weight of a polymer and its dilute solution viscosity (η),¹⁵ between the adsorbed quantity of the polymer (m)¹⁶ and the radius of gyration of the polymer coil in the solution (R_G).⁹

Electrochemical Impedance Spectroscopy (EIS) study

The adsorption and/or corrosion protection efficiency of PAA on iron from 3 M HCl at room temperature was examined using Electrochemical Impedance Spectroscopy (EIS) at the corrosion potential in the frequency range from 100 mHz to 100 kHz with a.c. signal of 5 mV. These experiments were performed for several molecular weights of PAA (from 15,000 to 1,500,000 g mol⁻¹), usually in the concentration range of PAA from 0.5 to 200 ppm.

Analyzing the obtained Bode plots ($\log Z - \log f$ and $\varphi - \log f$) for PAA adsorption on iron presented in Fig. 2, the following can be concluded:

i) The $\log Z - \log f$ and $\varphi - \log f$ dependences indicate the existence of three main regions. In the first one, at high frequencies (from 25 – 100 kHz), the measured impedance (Z) of approx. 2 Ω or 0.34 $\Omega \text{ cm}^{-2}$, as well as the phase angle (up to 5 degree) are very low, corresponding to an ohmic resistance of the electrolytic solution (3 M HCl) between the working and the reference electrode.

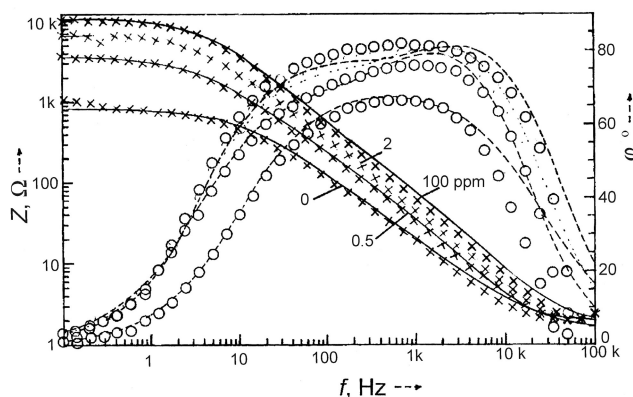


Fig. 2. Bode plots for the adsorption of PAA ($\overline{M}_n = 15,000 \text{ g mol}^{-1}$) on iron ($A = 0.18 \text{ cm}^2$) from 3 M HCl at room temperature and the corrosion potential.

ii) The second region (from $\approx 8 \text{ kHz}$ to 20 Hz) shows a linear $\log Z - \log f$ dependence with a slope, $\partial(\log Z)/\partial(\log f)$, ranging from 0.84 to 0.944 and phase angles between 65 and 82 (non-ideal condenser), depending on the concentration of PAA in the solution and corresponding to the capacitance of the iron/solution interface (in the absence or in the presence of PAA in the solution).

iii) At low frequencies (from 5 Hz to 100 mHz) the measured impedances Z are practically again not influenced by the frequency accompanied with an abrupt decrease of the phase angle ($\varphi \rightarrow 0$). Thus, the measured impedances in this region corresponds to the sum of charge transfer and electrolytic resistance ($Z = R_{\text{ct}} + R_{\text{el}}$).

Evidently, regions 1 and 3 show typical ohmic behavior with $Z_1 = R_{\text{el}}$ and $Z_3 = R_{\text{ct}} + R_{\text{el}}$, respectively. As far as the second region is concerned (linear $\log Z - \log f$ dependences), the impedance for a non-ideal condenser can be represented as:

$$Z = 1/Q(j\omega)^n \quad (6)$$

and for an ideal condenser ($n = 1$) as:

$$Z = 1/C_{dl}(j\omega) \quad (7)$$

where C_{dl} is a capacitance of the electrochemical double layer.

The Fe/3 M HCl-interface is presented in Fig. 3, without (case a) and with PAA in the solution (case b), respectively. The simple equivalent electric circuit ($R(QR)$) can be used in two cases:

i) For impedance characterization of the Fe/3 M HCl-interface, by determination of R_{ct} (or $j_{corr} = (RT/zF)(1/R_{ct})$) and the values of Q and n (CPE) in the absence of PAA in the solution.

ii) For impedance characterization of the Fe/adsorbed polymer layer/3 M HCl ($\theta \geq 0.7$) with PAA in the solution, which form a compact and stable inhibition layer on the metal surface, Figs. 4 and 5.

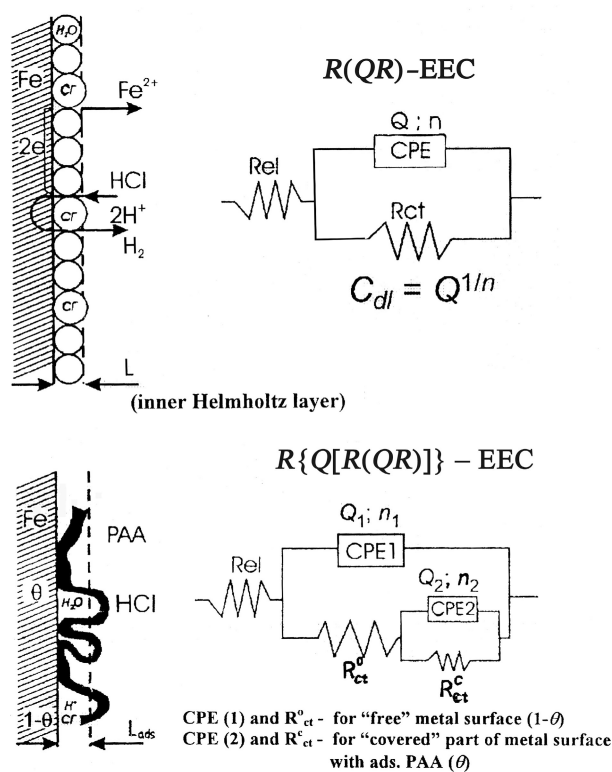


Fig. 3. Schematic representation of the Fe/HCl interface in the absence (a) and in the presence (b) of PAA in the solution.

On the other hand, the more complex $EEC - R\{Q[R(QR)]\}$ takes into account a parallel existence of covered parts of iron surface ($0.1 < \theta < 0.7$) with adsorbed PAA molecules or segments and uncovered parts of the metallic surface ($1-\theta$) which are in direct contact with the electrolyte. In this case, the experi-

mentally obtained impedance results should indicate the existence of two RC constants (Q_1R_{ct1} and Q_2R_{ct2}) or two relaxation times ($\tau_1 = 1/C_1R_{ct1}$ and $\tau_2 = 1/C_2R_{ct2}$), Figs. 6 and 7.

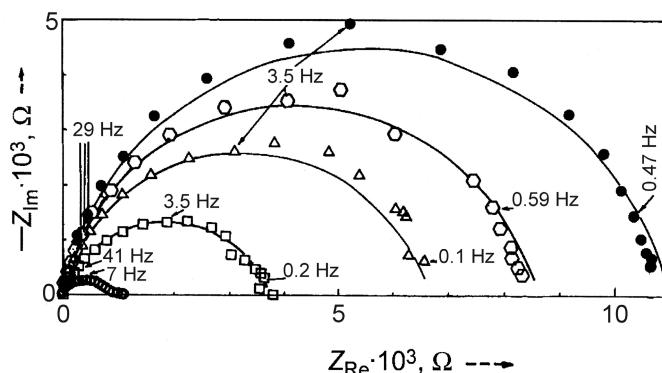


Fig. 4. Experimental (O; □; △; ○; ●) and theoretical (—) Nyquist plots for 0, 0.5, 2, 10 and 100 ppm PAA ($15,000 \text{ g mol}^{-1}$) adsorption on iron ($A = 0.18 \text{ cm}^2$) from 3 M HCl at room temperature using $R(QR)$ EEC.

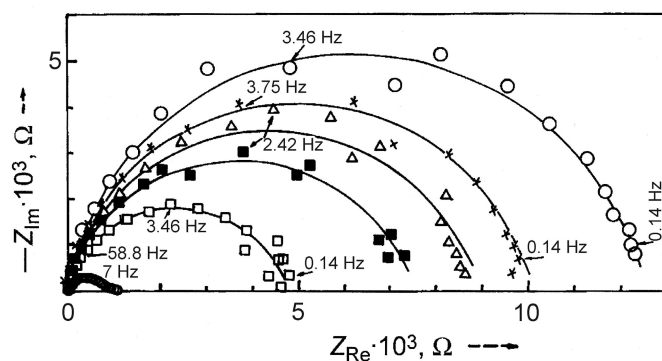


Fig. 5. Experimental (●; □; ■; △; ★; ○) and theoretical (—) Nyquist plots for 0, 0.5, 1, 2, 5 and 100 ppm PAA ($600,000 \text{ g mol}^{-1}$) adsorption on iron ($A = 0.18 \text{ cm}^2$) from 3 M HCl at room temperature using $R(QR)$ EEC.

The best fitting parameters for PAA adsorption on iron from 3 M HCl at the corrosion potential and room temperature were obtained using the impedance data and the Boukamp program.¹⁰ The results are presented in Tables II and III. These data indicate the following:

i) The values of Q (or C) are strongly influenced by the PAA concentration in the solution and/or by the coverage of the metal surface (θ) with adsorbed PAA molecules (segments).¹⁷ The limiting values of Q (or C) for $\theta \rightarrow 1$ are $\approx 26 \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$ or $\approx 12 \mu\text{F cm}^{-2}$ (for $n \approx 0.945$) and they were found to be slightly influenced by the molecular weight of the PAA. According to the two-con-

denser model ($\theta = (C^{\theta=0} - C^{\theta}) / (C^{\theta=0} - C^{\theta=1})$), the limiting values of θ (for $c_{\text{PAA}} \rightarrow \infty$) in these cases should be between 0.91 and 0.95.

ii) The obtained values of the charge transfer resistance (R_{ct}) strongly increase in the presence of PAA in the solution, clearly indicating a significant inhibition of the corrosion process. In the absence of PAA in the solution, $R_{\text{ct}} = 150 \Omega \text{ cm}^2$ corresponding to $j_{\text{corr}} = 84 \mu\text{A cm}^{-2}$, which in a very good agreement with literature data for corrosion rate of iron in 3 M HCl.¹⁸ The limiting value of R_{ct} in the present cases were $\approx 1800 \Omega \text{ cm}^2$ and $\approx 2200 \Omega \text{ cm}^2$ for $15,000 \text{ g mol}^{-1}$ and $600,000 \text{ g mol}^{-1}$ PAA, respectively, indicating again the high degree of coverage θ of the metallic surface ($\theta > 0.9$).

iii) The value of exponent n (degree of surface homogeneity) also increases in the presence of PAA adsorbed at the metal surface by decreasing its micro inhomogeneity.

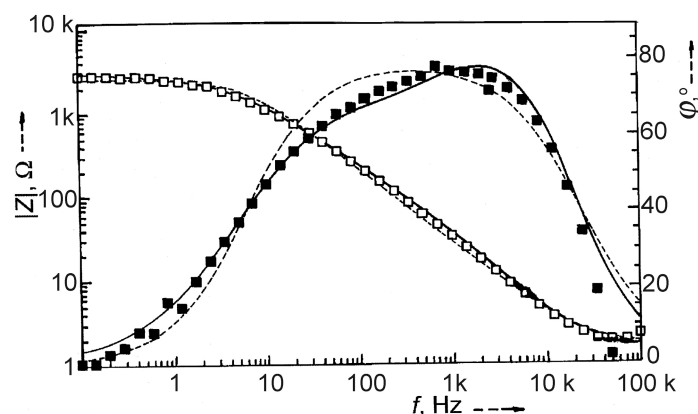


Fig. 6. Experimental and theoretical Bode plots for PAA ($600,000 \text{ g mol}^{-1}$; 0.5 ppm) adsorption on iron ($A = 0.18 \text{ cm}^2$) from 3 M HCl at room temperature; --- $R(QR)$ EEC and — $R\{Q[R(QR)]\}$ EEC.

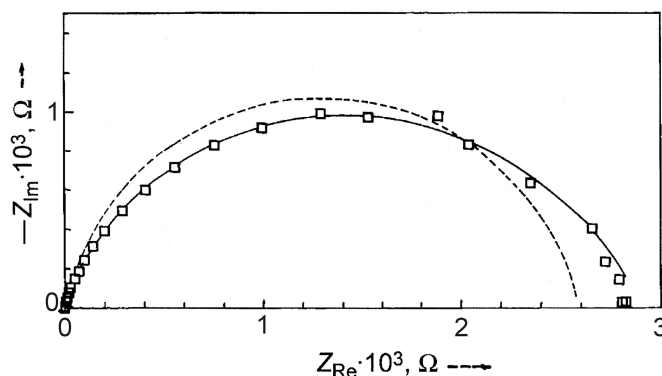


Fig. 7. Experimental and theoretical Nyquist plots for PAA ($600,000 \text{ g mol}^{-1}$; 0.5 ppm) adsorption on iron ($A = 0.18 \text{ cm}^2$) from 3 M HCl at room temperature; --- $R(QR)$ EEC and — $R\{Q[R(QR)]\}$ EEC.

TABLE II. Best fitting parameters for the adsorption of PAA ($15,000 \text{ g mol}^{-1}$) on iron from 3 M HCl at the corrosion potential; 293 K

EEC	Elements of EEC	$C_{\text{PAA}} / \text{ppm}$								
		0	0.5	1.0	2.0	5.0	10.0	20.0	100.0	200.0
R(QR)	$R_{\text{el}} / \Omega \text{ cm}^2$	0.34	0.31	0.30	0.31	0.31	0.31	0.32	0.32	0.32
	$Q \times 10^6 / \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	220.6	83.6	59.9	47.0	40.7	35.1	31.0	27.3	25.3
	n	0.840	0.883	0.905	0.919	0.928	0.936	0.942	0.943	0.944
	$R_{\text{ct}} / \Omega \text{ cm}^2$	151	618	906	1125	1302	1471	1633	1793	1894
R{Q[R(QR)]}	$R_1 / \Omega \text{ cm}^2$	0.36	0.34	0.35	0.34	0.35	0.48	0.36	0.37	
	$Q_1 \times 10^6 / \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	24.0	20.3	17.4	17.0	13.4	10.9	11.1	8.5	
	n_1	1	1	1	1	1	0.998	1	1	
	$R_2 / \Omega \text{ cm}^2$	31.7	41.9	47.0	2.3×10^{-16}	43.7	2.5×10^{-16}	51.8	31.5	
	$Q_2 \times 10^6 / \Omega^{-1} \text{ s}^n \text{ cm}^{-2}$	131.7	89.2	60.6	66.8	40.4	34.2	29.9	28.8	
	n_2	0.706	0.715	0.743	0.652	0.768	0.791	0.775	0.790	
	$R_3 / \Omega \text{ cm}^2$	648	952	1157	1482	1511	1737	1836	1980	

TABLE III. Best fitting parameters for the adsorption of PAA ($600,000 \text{ g mol}^{-1}$) on iron from 3 M HCl at the corrosion potential; 293 K

EEC	Elements of EEC	$C_{\text{PAA}} / \text{ppm}$							
		0	0.5	1.0	2.0	5.0	10.0	20.0	100.0
R(QR)	$R_{\text{el}} / \Omega \text{ cm}^2$	0.34	0.30	0.31	0.30	0.31	0.30	0.32	0.32
	$Q \times 10^6 / \Omega^{-1} \text{s}^n \text{cm}^{-2}$	220.6	85.6	44.4	41.4	36.1	32.2	30.0	28.9
	n	0.840	0.887	0.930	0.930	0.938	0.945	0.944	0.943
	$R_{\text{ct}} / \Omega \text{ cm}^2$	151	450	1152	1503	1710	1980	2088	2160
R{Q[R(QR)]}	$R_1 / \Omega \text{ cm}^2$		0.35	0.38	0.34	0.34	0.34	0.35	0.35
	$Q_1 \times 10^6 / \Omega^{-1} \text{s}^n \text{cm}^{-2}$		20.6	9.6	15.7	15.1	14.0	13.4	14.1
	n_1		1	0.990	1	1	1	1	1
	$R_2 / \Omega \text{ cm}^2$		21.8	2.2×10^{-16}	40.5	43.6	42.7	47.2	61.7
	$Q_2 \times 10_6 / \Omega^{-1} \text{s}^n \text{cm}^{-2}$		176.1	81.7	52.8	42.2	36.1	29.9	28.8
	n_2		0.681	0.690	0.735	0.747	0.755	0.733	0.758
	$R_3 / \Omega \text{ cm}^2$		497	1413	1586	1795	2034	2151	2205

DISCUSSION

As was shown by the EIS measurements of the Fe/3 M HCl (PAA) interface, Tables II and III, the value of the minimum capacitance depends mainly on the concentration and molecular weight of the polymer. On the other hand, it was also confirmed that the limiting value of the minimum capacitance ($12 \mu\text{F cm}^{-2}$ for $\theta = 1$) and the effective thickness of the adsorbed layer ($1.1 \pm 0.05 \text{ nm}$; for $\epsilon_r = 15$) are insignificantly affected by the molecular weight of the polymer.

In accordance with these statements, it follows that impedance measurements are not sufficient for the determination of the surface concentration (mol cm^{-2}) of the polymer adsorbed at the metal surface (or the surface area occupied by each adsorbed PAA molecule, $\sigma_{\text{PAA}} / \text{nm}^2$), nor the thickness of the adsorbed layer.

However, assuming the same conformations for polymer coil in the solution and in the adsorbed state at the metal surface, several basic parameters, such as surface concentration of the adsorbed polymer (c_s for $\theta = 1$), volume and/or weight of the adsorbed polymer coil (v_c and/or m_c) and the polymer concentration in the coil (wt \% PAA_c) can be calculated ($R_G = 7.49 \times 10^{-3} \times \bar{M}_n^{0.64} / \text{nm}^9$; $R_G^2 \times \pi / \text{nm}^2$; $v_c = 4/3 R_G^3 \times \pi$; $m_c = \bar{M}_n / N$; $\text{wt. \% PAA}_c = m_c / (v_c \rho_{\text{sol}}) \times 100$). These values are presented in Table IV.

TABLE IV. Basic parameters for the statistical polymer coil in solution and/or at the metallic surface (assuming a spherical polymer coil)

$\bar{M}_n / \text{g mol}^{-1}$	R_G / nm	σ / nm^2	$c_s / \text{mol cm}^{-2}$	$(\theta=1) / \text{mg cm}^{-2}$	v_c / cm^3	m_c / g	w % PAA _c
15,000*	3.53*	39.0*	4.28×10^{-12} *	6.42×10^{-5} *	1.84×10^{-19} *	2.49×10^{-20}	≈ 13 *
85,000*	10.7*	359.6*	4.62×10^{-13} *	3.93×10^{-5} *	5.13×10^{-18} *	1.41×10^{-19}	≈ 2.6 *
200,000	18.5	1075	1.54×10^{-13}	3.09×10^{-5}	2.65×10^{-17}	3.32×10^{-19}	≈ 1.19
600,000	37.37	4387	3.78×10^{-14}	2.27×10^{-5}	2.19×10^{-16}	9.96×10^{-19}	≈ 0.43
1,350,000	62.8	12386	1.34×10^{-14}	1.81×10^{-5}	1.04×10^{-15}	2.24×10^{-18}	≈ 0.2

It should be mentioned that empirical equation for calculating R_G (given above) was obtained using viscosimetric and/or sedimentation data of dilute solutions of relatively high molecular weight PAA⁹ and consequently its application for much lower values of \bar{M}_n (such as 15,000 and 85,000 g mol^{-1} *, Table IV) is questionable.

Evidently, the surface concentration of adsorbed polymer (c_s) is a function of the molecular weight of the polymer and follows the equations:

$$c_s = 9.6 \times 10^{-7} \times \bar{M}_n^{-1.28} \text{ or } c_s = 5.313 \times 10^{-11} / R_G^2 (\text{mol cm}^{-2}) \quad (8)$$

where R_G is given in nm.

The same type of empirical equation has already been obtained for the adsorption of many other polymers, mainly at non-metallic surfaces,¹⁶ and implies that the quantity (c_s) of the adsorbed layer, as well as its thickness should depend on the molecular weight of the polymer (Table IV).

On the other hand, the thickness of the adsorbed polymer layer of about 1.1 nm, determined by impedance measurements (for $\epsilon_r = 15$) corresponds only to the polymer segments directly attached to the metal surface. The other parts of the adsorbed polymer coils (loops and tails) do not significantly contribute to the value of the measured capacitance due to the very low participation of the polymer material ($\leq 1\%$) in the overall volume of the coil ($\epsilon_{r,\text{coil}} \approx \epsilon_{r,\text{sol}}$). Thus, the

sharp decrease of the dielectric constant (from $\varepsilon_{r,sol} \approx 80$ to $\varepsilon_{r,ads} \approx 15$) occurs in the thin layer of polymer segments adsorbed at the metallic surface.

Relatively high degree of coverage ($\theta > 0.7$) or high “protection” efficiency of the metallic surface most probably results from further involvement of the polymer molecules in the adsorbed layer causing its additional structuring (slow process). Therefore, in the state of limiting coverage, the adsorbed layer is highly voluminous and relatively thick (100 – 200 nm), as it was found by ellipsometry,^{6,19} and contains entangled polymer coils.

CONCLUSIONS

1. It was found that the efficiency of corrosion protection by adsorbed layers of PAA strongly depends both on the molar concentration of PAA in the solution and its molecular weight, reaching the limiting values between 85 and 96 %. Simultaneously, it was also concluded that a relatively high value of surface coverage can be obtained with very low concentrations of PAA (0.5 – 2 ppm), indicating the good adsorption characteristics of PAA on mild steel and iron in hydrochloric acid.
2. The experimentally obtained results follow a Langmuir adsorption isotherm. According to the best fitting parameters, the adsorption coefficient B ranged between 2×10^7 and $4 \times 10^8 \text{ mol}^{-1}$ and strongly depended on the molecular weight of the PAA, $B = k \times \overline{M}_n^\alpha$ (for $\alpha \approx 0.67$ and $k = 2.95 \times 10^4$), or the size of the polymer coil.
3. As found by EIS, the thickness of the adsorbed PAA layer was approx. 1.1 nm (for $\varepsilon_r = 15$), which corresponds only to the polymer segments attached to the metal surface. On the other hand, as found by ellipsometry, the limiting layer of adsorbed PAA molecules was highly voluminous and relatively thick (100 – 200 nm), containing entangled polymer coils.
4. It was also found that the degree of coverage or inhibition efficiency of the metal surface with adsorbed PAA molecules (segments) was strongly influenced by the molecular weight of the PAA, following the relation:

$$B_1/B_2 \equiv (\theta_1/\theta_2)_c \equiv R_{G1}/R_{G2} \equiv (\overline{M}_{n1}/\overline{M}_{n2})^{0.67}$$

where B is the adsorption coefficient and R_G the radius of gyration of the statistical polymer coil in solution.

ИЗВОД

ИХИБИЦИЈА КОРОЗИЈЕ ГВОЖЂА У ХЛОРОВОДОНИЧНОЈ КИСЕЛИНИ ПОЛИАКРИЛАМИДОМ

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Испитивана је корозиона заштита и/или адсорпција полиакрил-амида (ПАА) средње моларне масе $\overline{M}_n = 15000 - 1350000 \text{ g mol}^{-1}$ на меком челику и гвожђу (99,99 % Fe) у 3 М НСI на собној температури коришћењем спектрофотометрије (фенантролинска метода), методе губитка масе и спектроскопије електрохемијске импеданције (СЕИ). Утврђено је да

ефикасност корозионе заштитите адсорбованог слоја ПАА јако зависи од концентрације ПАА у раствору и његове молекулске масе, достижући граничну вредност између 85 и 96 %. Такође је показано да се релативно високе вредности степена покривености могу добити при веома ниским концентрацијама ПАА (0,5 – 2 ppm), што указује на добре адсорпционе карактеристике ПАА на меком челику и гвожђу у раствору HCl. Експериментално добијене вредности степена покривености следе Ленгмирову адсорпциону изотерму. Адсорпциони коефицијент, B , се креће од 2×10^7 до $4 \times 10^8 \text{ mol}^{-1}$ и зависи од величине полимерног клупка, односно од средње моларне масе ПАА према једначини $B = k \times \overline{M}_n^\alpha$ (где је $\alpha \approx 0,67$ и $k = 2,95 \times 10^4$). Као што су мерења методом СЕИ показала, дебљина адсорбованог слоја ПАА је око 1,1 nm (за $\varepsilon_r = 15$) и одговара сегментима полимерног ланца адсорбованим на површини метала. С друге стране, раније је показано елипсометријском методом да је гранични слој адсорбованих молекула ПАА изразито волуминозан и релативно дебео (100 – 200 nm) и да садржи замршене полимерне ланце.

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