

ADSORPTION OF POLYACRYLAMIDE ON GOLD AND IRON FROM ACIDIC AQUEOUS SOLUTIONS

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Abstract—The adsorption behaviour of polyacrylamide (PAA) on gold, and mild steel from sulphuric and hydrochloric acid was studied using cyclic voltammetry with simultaneous monitoring of the double layer capacity. Adsorption isotherms, obtained by capacity measurements (using the two-condenser model), and corresponding thermodynamic parameters of the adsorption processes strongly depend upon the molecular mass of the polymer, electrode potential and temperature. In all cases the experimentally-obtained results show the best fit with Frumkin's isotherm (Langmuir and Flory–Huggins isotherms were tested as well).

It was found that nearly complete coverage ($\theta = 1$) can be reached at extremely low polymer concentrations in the solution (10^{-8} – 10^{-7} M) which can be explained by a significant participation of the directly attached segments of the polymer molecules (trains) at the metallic surface and weak lateral interactions. This conclusion was proved by comparison of the polymer adsorption with the adsorption behaviour of the monomer itself.

Capacity measurements predict flat orientation of the polymer molecules at the metal/solution interface with an average thickness of the adsorbed layer of about 0.8 nm.

Thermodynamic parameters of the polymer adsorption on gold, at low anodic potentials, are comparable with those obtained from corrosion measurements on iron and mild steel. At high anodic potentials adsorption of PAA on gold is an endothermic process which can be explained by a substitutional adsorption ($\text{Polym}_{(\text{aq})} + x\text{H}_2\text{O}_{(\text{s})} = \text{Polym}_{(\text{s})} + x\text{H}_2\text{O}_{(\text{aq})}$) and conformation changes of the adsorbed polymer molecule. Thus, the calculated values of ΔH_{ads}^0 and ΔS_{ads}^0 correspond to the whole process; adsorption of polymer molecules and desorption of x -water molecules per polymer molecule.

Key words: adsorption of polyacrylamide, acidic aqueous medium, gold and iron surfaces, capacity measurements, corrosion protection.

1. INTRODUCTION

The adsorption of macromolecules on metallic surfaces has been extensively studied in the last 2 decades, both from theoretical (effect of length and different conformation towards adsorption of "small" organic molecules) and practical (corrosion inhibition, drag reduction, machining and tempering of metals and alloys) points of view[1–11].

As we have shown in our previous work polyacrylamide (PAA) strongly adsorbs on silver and titanium[12] and gold and iron[13] from aqueous neutral solutions. The adsorption of PAA on iron, from boric–borate buffer, pH = 8.45, considerably inhibits the processes of electrochemical passivation in the active region. The current in the passive region was not affected at all[14].

The aim of the present study was to examine, in more detail, the influence of the polymer molecular mass, temperature and potential on the mechanism of PAA adsorption on gold and iron towards its corrosion inhibition properties in acidic aqueous solutions.

2. EXPERIMENTAL

The measurements were carried out in the classical thermostat electrochemical cell using a gold wire

($d = 0.5$ mm; 0.35 cm²) as a working electrode and gold foil (app. 25 cm²) as an auxiliary electrode. The potentials were measured against saturated calomel (*see*) and Hg/HgSO₄ reference electrodes and are referred to the hydrogen electrode in the same solution (*hess*).

Cyclic voltammetry ($dE/dt = 25$ and 100 mV s⁻¹) with simultaneous monitoring of double layer capacity (at 1 kHz and 1 mV *ac* signal) was used to follow the adsorption of polymers as well as the processes taking place in the potential range studied (0 – 2 V/*hess* for the gold electrode in 0.5 M H₂SO₄ and $E_{\text{corr}} \pm 50$ to 150 mV, with $dE/dt = 5$ mV s⁻¹, for iron electrode in 1.6 M HCl). The electric circuit used has been described previously[15].

The corrosion protection efficiency of PAA was followed on the mild steel coupons ($70 \times 15 \times 2$ mm) (0.1% C, 0.012% S, 0.015% P, 0.01% Si, 0.4% Mn and 0.07% Cu) in 1.6 M (6%) HCl using a usual spectroscopic, phenantroline, method for Fe(II)-ion concentration determination in the solution at 508 nm. The duration of corrosion tests was 30 min.

PAA was obtained by a redox-initiated polymerization of acrylamide (AA) (twice recrystallized from benzene; melting point 84 – 85°C), using an Fe(III)–IDA–Na₂S₂O₅ redox couple [Fe(III)–IDA is an Fe-complex of iminodiacetic acid]. Different molecular masses were obtained using various molar

ratios between reducer ($\text{Na}_2\text{S}_2\text{O}_5$) and oxidant $[\text{Fe(III)-IDA}]$.

3. RESULTS AND DISCUSSION

3.1. $\text{Au}/\text{H}_2\text{SO}_4$; PAA

Voltammograms and capacitance spectra for gold in $0.5\text{ M H}_2\text{SO}_4$, and in the presence of PAA, were recorded in the temperature range between 20 and 80°C . Five different PAA molecular masses (5×10^3 ; 2.2×10^4 ; 2.25×10^5 ; 6.80×10^5 and $1.5 \times 10^6\text{ g mol}^{-1}$) were studied in order to determine their adsorption behaviour on gold in sulphuric acid at a given temperature.

The usual types of voltammograms and capacitance spectra were obtained (Figs 1 and 2) in the potential range from 0 to 2 V/hess [15]. Three different regions can be easily resolved, both from voltammograms and capacitance spectra: double layer charging; oxide formation and reduction.

In the presence of PAA (Figs 1 and 2) drastic changes can be seen in the whole potential range: gold-oxide formation is anodically shifted, its reduction peak significantly decreases (as a result of the thinner Au_2O_3 film formed) and the reorientation processes of water molecules in the Helmholtz part of the double layer (0 to about 1.4 V/hess) are suppressed and shift towards more anodic potentials.

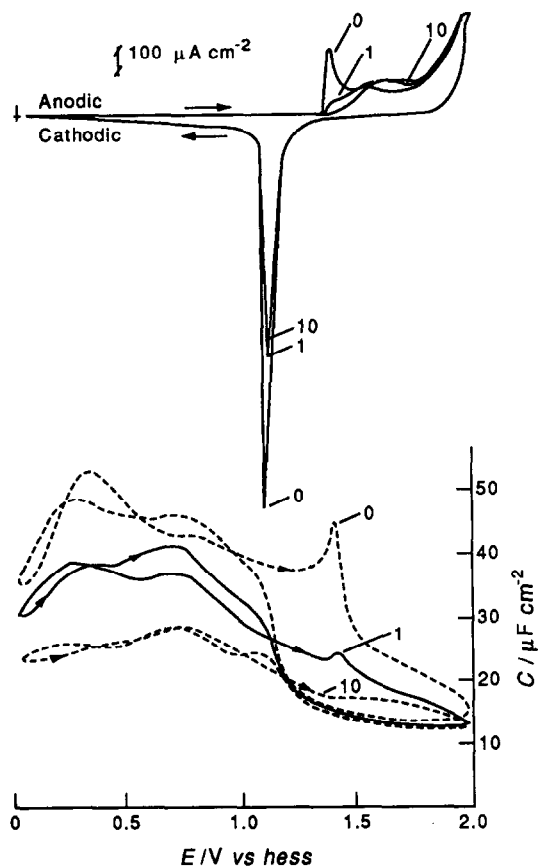


Fig. 1. Voltammograms and capacitance spectra for gold in $0.5\text{ M H}_2\text{SO}_4$ and the presence of PAA ($\bar{M}_n = 5 \times 10^3\text{ g mol}^{-1}$); $dE/dt = 100\text{ mV s}^{-1}$; 40°C .

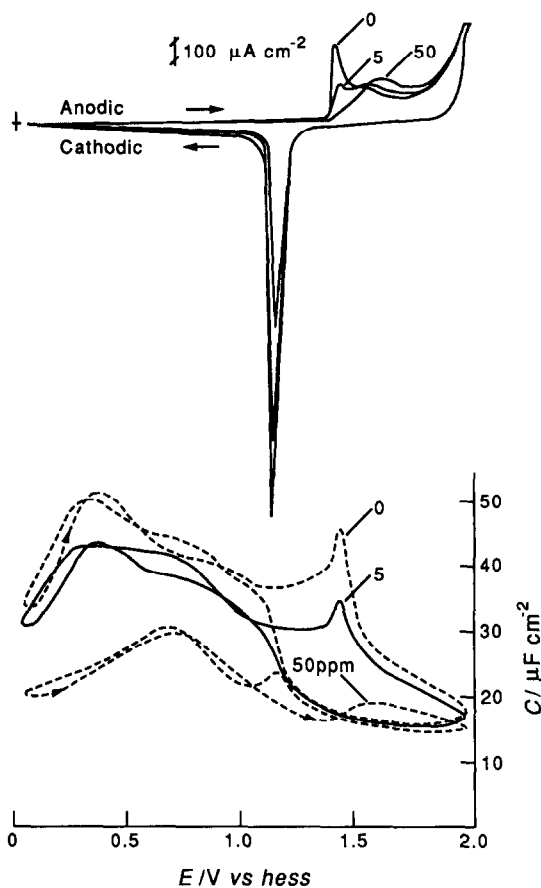


Fig. 2. Voltammograms and capacitance spectra for gold in $0.5\text{ M H}_2\text{SO}_4$ and the presence of PAA ($\bar{M}_n = 1.48 \times 10^6\text{ g mol}^{-1}$); $dE/dt = 100\text{ mV s}^{-1}$; 40°C .

It can be seen that PAA with the lowest molecular mass ($5 \times 10^3\text{ g mol}^{-1}$) starts to act with the metallic surface, even at less than 1 ppm (about 10^{-7} M) in the solution. All these capacity changes indicate a strong PAA adsorption mainly at the $\text{Au}/\text{solution}$ interface. On the other hand PAA adsorption on the $\text{Au}_2\text{O}_3/\text{solution}$ interface is not so pronounced (capacity decreases only by $3\text{--}5\text{ }\mu\text{F cm}^{-2}$).

As can be seen from the results presented (Figs 1 and 2), two capacity minima (at 0 and 1.3 V/hess) at the $\text{Au}/\text{solution}$ interface are present. These effects are much more pronounced with the presence of polymer on the metal surface. Thus, we examined in more detail the adsorption of PAA at these two particular potentials.

Using a two-condenser model for the inner part of the double layer at the metal/solution interface, partially covered with adsorbed polymer molecules:

$$C = C^0(1 - \theta) + C^p\theta \quad (\text{for } E = \text{const}) \quad (1)$$

$$\theta = (C^0 - C)/(C^0 - C^p) = \Delta C/\Delta C_{\text{max}} \quad (2)$$

we obtain $\theta - C_{\text{PAA}}$ isotherms supposing that at 1.3 V and room temperature limiting coverage is very close to 1 ($\theta \leq 1$). In this case $\Delta C_{\text{max}} = 27$ and $C^p = 17\text{ }\mu\text{F cm}^{-2}$ which, according to the condenser model and $D = 16$ [15, 16], gives an acceptable value for the thickness of the adsorbed polymer layer of

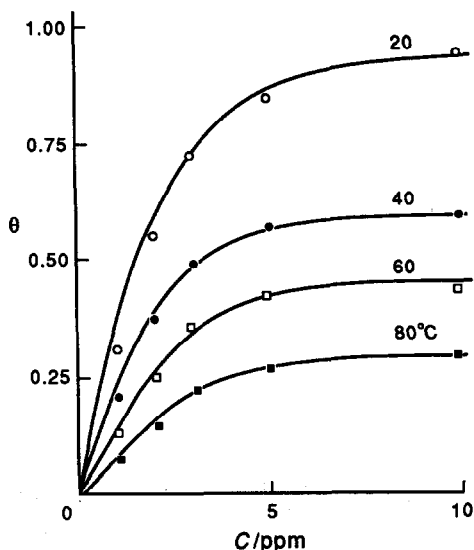


Fig. 3. Adsorption isotherms for PAA ($\bar{M}_n = 5 \times 10^3 \text{ g mol}^{-1}$) on gold from 0.5 M H_2SO_4 at 0 V/hess.

about 0.8 nm. At the same time in the absence of PAA in the solution the minimum capacity (C^0) is approximately $40 \mu\text{F cm}^{-2}$ corresponding to the thickness of the Helmholtz layer, with adsorbed water molecules, of about 0.35 nm which is a reasonable value as well[16].

As far as the obtained adsorption isotherms are concerned we can conclude the following:

(i) Adsorption of PAA at the Au/solution interface ($E = 0 \text{ V}$) strongly depends on both the temperature and the polymer molecular mass (Figs 3 and 4).

(ii) Nearly complete coverage ($\theta = 1$) can only be achieved at room temperature ($E = 0 \text{ V}$); Fig. 3. At elevated temperatures limiting coverages such as 0.6,

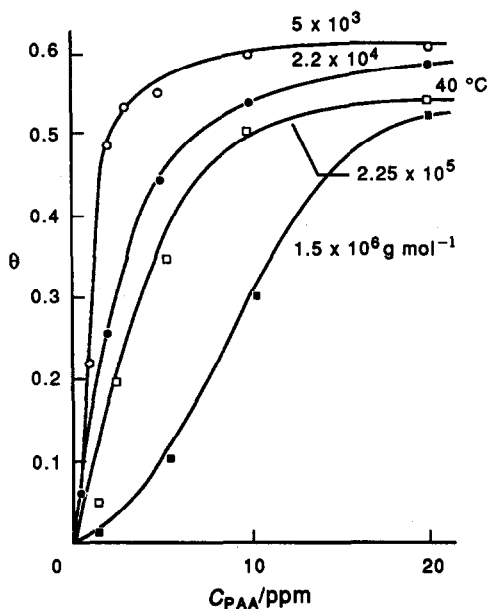


Fig. 4. Adsorption isotherms for PAA on gold from 0.5 M H_2SO_4 at 0 V/hess; 40°C.

Table 1. Thermodynamic parameters (according to Frumkin's isotherm) for PAA adsorption on gold from 0.5 M H_2SO_4 at 0 V and 40°C

$\bar{M}_n/\text{g mol}^{-1}$	$-\Delta G^0/\text{kJ mol}^{-1}$	f
5×10^3	48.08	-1.04
2.2×10^4	50.65	-1.33
2.25×10^5	54.94	-0.50
1.48×10^6	55.03	2.64

0.45 and 0.3 have been obtained for 40, 60 and 80°C, respectively; Fig. 3.

(iii) The polymer molecular mass has a strong influence on the shapes (or thermodynamic parameters) of the adsorption isotherms; Fig. 4 and Table 1.

(iv) The value of ΔC_{max} or a limiting coverage (θ), at a given temperature, is almost not affected by a polymer molecular mass. It could be an indication that the thickness of the adsorbed layer is not influenced by a polymer molecular mass and consequently flat orientation of adsorbed parts of polymer molecules on the metal surface is most probable.

(v) It appears that for higher values of PAA molecular mass a limiting degree of coverage is obtained at a higher polymer concentration (in parts per million). Thus, for PAA with $\bar{M}_n = 5 \times 10^3 - 2.2 \times 10^4 \text{ g mol}^{-1}$, limiting θ is obtained for only 2-3 ppm and that of PAA with $\bar{M}_n = 6.8 \times 10^5 - 1.48 \times 10^6 \text{ g mol}^{-1}$, for more than 20 ppm PAA in the solution; Fig. 4.

However, taking into account the molar concentration of PAA (with their \bar{M}_n values) it is just opposite (about $5 \times 10^{-7} \text{ mol dm}^{-3}$ for 5×10^3 and $1.3 \times 10^{-8} \text{ mol dm}^{-3}$ for $1.48 \times 10^6 \text{ g mol}^{-1}$). This is in very good agreement with some literature data[1] and with calculated thermodynamic parameters (Table 2) of the adsorption processes as well.

As far as the double layer capacity measurements are concerned it can be stressed that only directly

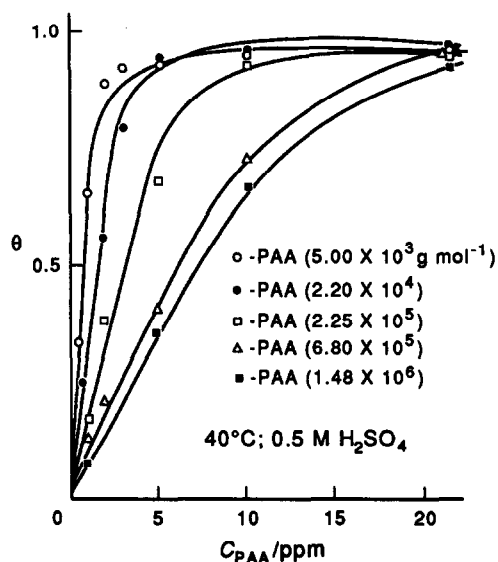


Fig. 5. Adsorption isotherms for PAA on gold at 1.3 V/hess.

Table 2. Thermodynamic parameters (according to Frumkin's isotherm) for PAA ($5 \times 10^3 \text{ g mol}^{-1}$) adsorption on gold from $0.5 \text{ M H}_2\text{SO}_4$ at 0 V/hess

20	$-\Delta G_{\text{ads}}^0/\text{kJ mol}^{-1}$			80°C	f				$\Delta H/\text{kJ mol}^{-1}$	$\Delta S/\text{J mol}^{-1} \text{ K}^{-1}$
	40	60			20	40	60	80°C		
45.1	48.1	49.5	51.2	1.2	-1.04	-0.85	-1.6	-17.0	98.0	

attached parts of macromolecules contribute to the decrease of capacity. It should be noted that it is rather difficult to determine the particular contribution of trains, loops and tails of the polymer molecules at the metallic surface (it is difficult by ellipsometry, as well[3, 12]) which depends on the electrode potential and macromolecular conformations. On the other hand conformational behaviour is closely related to polymer structure, concentration, presence of other species in the solution and temperature (thermal motion energy and different kinds of mutual interactions; intra- and intermolecular). All these relations can be additionally complicated by a polymer polydispersion (PAA is not fractionated; $M_w/M_n = 2-2.5$).

The adsorption isotherms (Figs 3 and 4) were analysed using Langmuir, Frumkin and Flory-Huggins equations [equations (3), (4) and (5), respectively]:

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

$$\frac{\theta}{1-\theta} \exp(-f\theta) = KC \quad (4)$$

$$\frac{\theta}{e^{x-1}(1-\theta)^x} = KC, \quad (5)$$

where the K -equilibrium constant of the adsorption process is:

$$K = (1/55.5)\exp(-\Delta G^0/RT). \quad (6)$$

It is well known that the Frumkin isotherm (4) takes into account the lateral interactions between adsorbed molecules or the influence of θ on ΔG_{ads}^0 [parameter f in equation (4)], and the Flory-Huggins isotherm (5), modified by Dahr *et al.*[17], introduces the configurational term x —being a number of desorbed water molecules from the surface replaced by adsorption of one organic molecule.

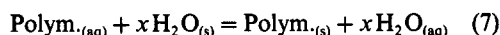
Fitting of the obtained experimental results, $\theta = f(C)$, with equations (3) and (5) is relatively simple because the slope of the linear dependences, $(\theta/(1-\theta))$ or $\theta/[e^{x-1}(1-\theta)^x]$ upon C in a double logarithmic plot, should be 1.

Thermodynamic parameters for PAA (with $M_n = 5 \times 10^3 \text{ g mol}^{-1}$) adsorption on gold from $0.5 \text{ M H}_2\text{SO}_4$, at 0 V/hess , as a function of temperature are presented in Table 2. In this case the experimental results (Fig. 3) were tested

with Frumkin's isotherm. The obtained values for the interaction parameter f seem to be reasonable, indicating attraction between adsorbed polymer molecules at 20°C and repulsion at elevated temperature ($40-80^\circ\text{C}$). On the other hand $-\Delta G_{\text{ads}}^0$ increases with temperature indicating an irreversible process.

The average values for ΔH^0 and ΔS^0 were obtained using the equation: $\Delta G^0 = \Delta H^0 - T \Delta S^0$. The obtained values of ΔH_{ads}^0 (-17 kJ mol^{-1}) and ΔS_{ads}^0 ($98 \text{ J K}^{-1} \text{ mol}^{-1}$) can be explained by a substitutional adsorption of PAA [equation (7)].

The experimental results from Fig. 4 were tested using Langmuir, Frumkin and Flory-Huggins isotherms, for several values of x , and the results obtained are presented in Tables 1 and 3. Evidently only in a few cases are the log/log slopes close to 1 and the result is that Frumkin's isotherm gives the best fit. On the other hand, the calculated values for ΔG_{ads}^0 (or K of the adsorption process):



increase with increasing polymer molecular mass (Table 1), which seems to be consistent with experimental results.

The Flory-Huggins isotherm for $x \geq 2$, as can be seen from the calculated parameters, Table 3, cannot be applied in our case. As far as the more pronounced capacity minimum, at about 1.3 V , for PAA adsorption on gold, is concerned (Figs 1 and 2), we can stress the following:

(i) The values for $\Delta C_{\text{max}}(C^0 - C^p)$ at this particular potential are almost not affected by a polymer molecular mass and very slightly decrease at elevated temperatures. These values range between 24 and $28 \mu\text{F cm}^{-2}$.

(ii) The limiting coverages, very close to $\theta = 1$, are obtained for polymer concentrations between 2 and 20 ppm , depending on the polymer molecular mass; Fig. 6.

(iii) At elevated temperatures, for $0 < \theta < 0.7$, adsorption of PAA on gold is even more pronounced which can be related with decreased time of relaxation and increased possibility for a more convenient conformation of macromolecular chains at the metallic surface. At high anodic potentials these effects can be strengthened.

Table 3. Testing of the experimentally-obtained results (Fig. 4) with Langmuir and Flory-Huggins isotherms

Adsorption isotherm	M_n	$\log[\theta/e^{x-1}(1-\theta)^x]/\log C$ -slopes			
		5×10^3	2.2×10^4	2.25×10^5	$1.48 \times 10^6 \text{ g mol}^{-1}$
Langmuir:		1.29	0.86	0.99	1.37
Flory-Huggins:	$x = 2$	1.41	1.10	1.11	1.95
	$x = 3$	1.75	1.33	1.41	2.25
	$x = 4$	2.10	1.57	1.51	2.50

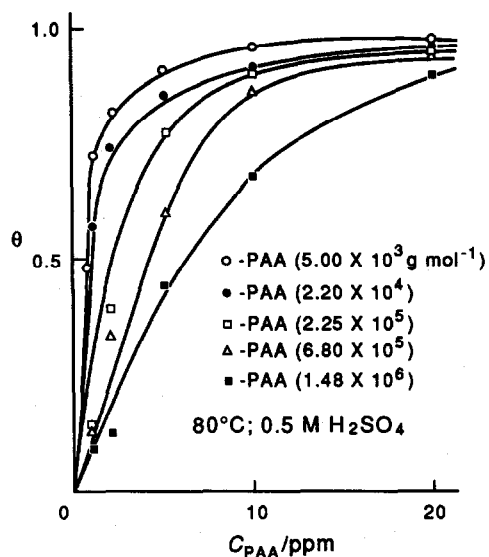


Fig. 6. Adsorption isotherms for PAA on gold at 1.3 V/hess.

The adsorption isotherms (Fig. 6) were tested and again showed best fitting with the Frumkin isotherm. The free energy of the adsorption process (Fig. 7) depends on both temperature and polymer molecular mass. Fairly good, linear, $-\Delta G-T$ dependences were found, and ΔH and ΔS were estimated (Table 4). To get, eventually, some more information about the specificity of polymer adsorption, we examined the adsorption behaviour of the monomer (AA) as well.

Voltammograms and capacitance spectra are similar at first glance, but they differ substantially in several important ways:

(i) Acrylamide does not adsorb at 0 V/hess and has a negligible influence on the reorientation processes in the Helmholtz part of the double layer (from 0 to about 1 V/hess).

(ii) A significant decrease of the double layer capacity was only observed at 1.3 V. ΔC_{\max} was reached at extremely (compared with those of PAA) high concentrations (over 500 ppm) of AA

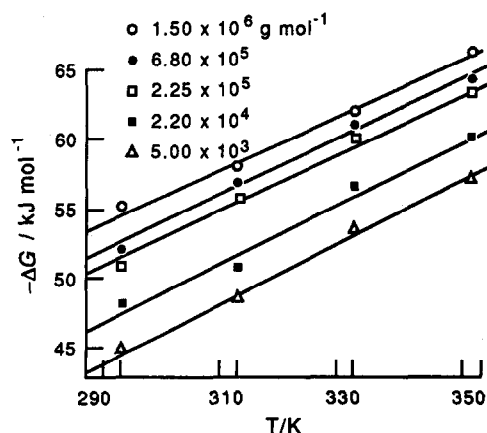


Fig. 7. $\Delta G^0_{\text{ads}}-T$ dependences (calculated from Frumkin's isotherm) for PAA adsorption on gold at 1.3 V/hess from 0.5 M H_2SO_4 .

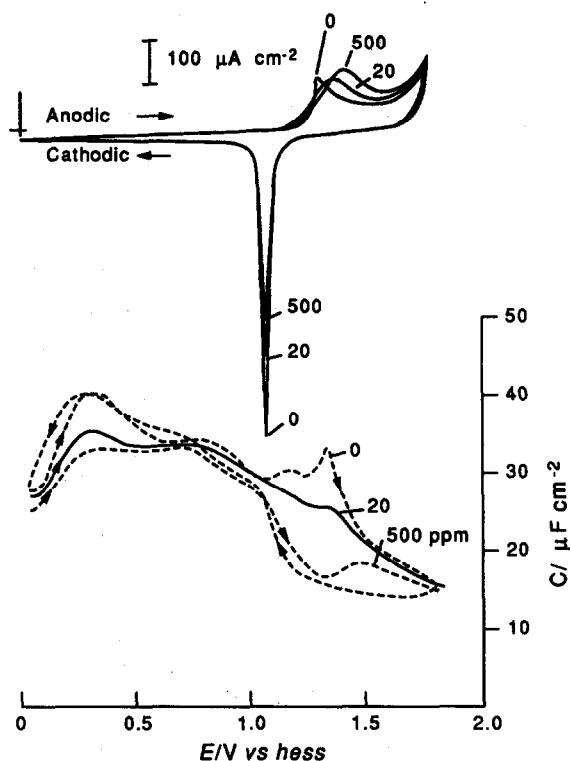


Fig. 8. Voltammograms and capacitance spectra for gold in 0.5 M H_2SO_4 and the presence of acrylamide (AA); $dE/dt = 100 \text{ mV s}^{-1}$; 40°C.

with an average value of about $21 \mu\text{F cm}^{-2}$ and $C_{\min} = 20 \mu\text{F cm}^{-2}$. Taking into account this value it can be concluded that complete covering ($\theta = 1$) of the metal surface does not occur, which was confirmed by a subsequent addition of only 10 ppm PAA with $\bar{M}_n = 5 \times 10^3 \text{ g mol}^{-1}$. In the solution with 1000 ppm AA this amount of PAA decreases the capacity (at 1.3 V) for an additional $5-6 \mu\text{F cm}^{-2}$ and in the whole potential region, between 0 and 1 V, for about $10 \mu\text{F cm}^{-2}$.

It can be explained with a complete exchange of the adsorbed AA molecules by PAA macromolecules or by a filling of the unoccupied sites on the surface with polymer molecules (coadsorption). The adsorption isotherms for AA on gold (at 1.3 V) (Fig. 9), were obtained using ΔC_{\max} [equation (2)] for PAA. These isotherms obey both the Langmuir and Frumkin isotherms. The calculated values for ΔG^0_{ads} are 25 (20°C) and 32 kJ mol^{-1} (60°C) from the Langmuir isotherm and about 29 kJ mol^{-1} from the Frumkin isotherm.

Such a substantial difference in the adsorption behaviour of the monomer (AA) towards its polymer

Table 4. Enthalpy and entropy values for PAA adsorption on gold at 1.3 V in the temperature range 20–80°C

\bar{M}_n (PAA)/ g mol^{-1}	$\Delta H^0_{\text{ads}}/\text{kJ mol}^{-1}$	$\Delta S^0_{\text{ads}}/\text{J mol}^{-1} \text{K}^{-1}$
5×10^3	18.20	215
2.2×10^4	17.00	219
2.25×10^5	11.10	213
6.8×10^5	9.00	210
1.48×10^6	0.50	190

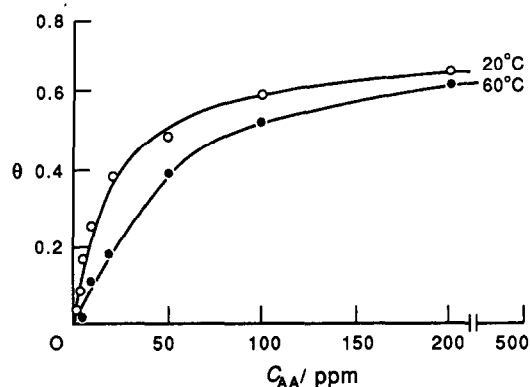


Fig. 9. Adsorption isotherms for AA on gold at 1.3 V/hess from 0.5 M H₂SO₄.

(PAA) can be due to several reasons:

(i) The amide group in acrylamide takes part in the strong hydrogen bond formation with water molecules and/or AA itself. In this case the ability of the amide to approach the metal surface can be significantly decreased which, besides great differences in sizes between the monomer and polymer molecules, can be the main reason for such an adsorption behaviour of acrylamide.

(ii) Flat or nearly flat orientation of the adsorbed polymer molecules at the metal surface represents a maximum "close-packed" unit with almost no lateral interactions between neighbouring functional groups attached to the metal surface.

Almost all of the above stressed conclusions or statements concerning the question of electrosorption of PAA on gold from acidic (H₂SO₄) aqueous solution were confirmed on a "real" corrosion system such as iron or mild steel in hydrochloric acid (the usual case for a pickling corrosion of steel).

3.2. Fe/HCl; PAA

The adsorption behaviour of PAA on mild steel, from 1.6 M HCl (6% HCl), was studied by following the corrosion protection efficiency; Figs 10 and 11. A classical inhibitor such as hexamethyltetramine (HMTA) and a commercial one Qwene 3125 (Qwecker Chimica) were studied as well as comparative systems. It was shown that the corrosion protection efficiency (η_{prot}) or degree of coverage (θ) depends on the inhibitor concentration (C_i), temperature (T) and the polymer molecular mass (\bar{M}_n); $\eta_{\text{prot}}(\theta) = f(C_i, T, \bar{M}_n)$. It should be noted that all these experiments, with the above-mentioned inhibitors, were undertaken in order to determine their application ability for pickling corrosion of mild steel in hydrochloric acid. On the other hand, it was also of interest to examine the mechanisms of inhibition or adsorption of PAA on mild steel. Even at a first glance (Figs 10 and 11) it can be seen that very similar adsorption behaviour of PAA was found, in comparison with electrosorption on gold (Figs 4 and 6).

Analysing these curves (Figs 10 and 11) again, according to the Frumkin isotherm for $\eta_{\text{prot}} = \theta$, thermodynamic parameters for the adsorption of PAA and HMTA on mild steel were calculated. These data are given in Table 5.

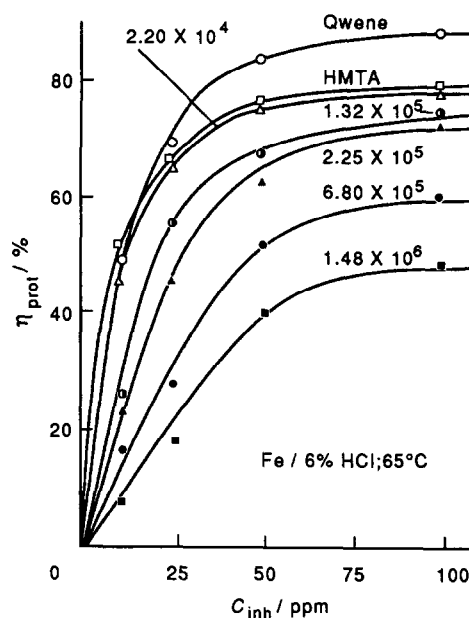


Fig. 10. Corrosion protection efficiency of PAA, HMTA and Qwene for mild steel in 6% (1.6 M) HCl.

ΔH_{ads}^0 and ΔS_{ads}^0 were calculated (for $\theta = \text{const}$; 0.1 or 0.2) using the equations:

$$\Delta H_{\text{ads}}^0 = \frac{RT_1 T_2}{(T_1 - T_2)} \ln(C_2/C_1) \quad (8)$$

$$\Delta G_{\text{ads}}^0 = \Delta H_{\text{ads}}^0 - T \Delta S_{\text{ads}}^0 \quad (9)$$

It can be concluded that for relatively small organic molecules and/or macromolecules (such as HMTA or PAA with lower molecular mass) the adsorption process is exothermic and for a PAA with a higher value of \bar{M}_n the process is endothermic. Such behaviour can be explained, mainly, by a substitutional adsorption process [equation (7)] on the bare metal surface. The values of ΔH_{ads}^0 and ΔS_{ads}^0 (Table 5)

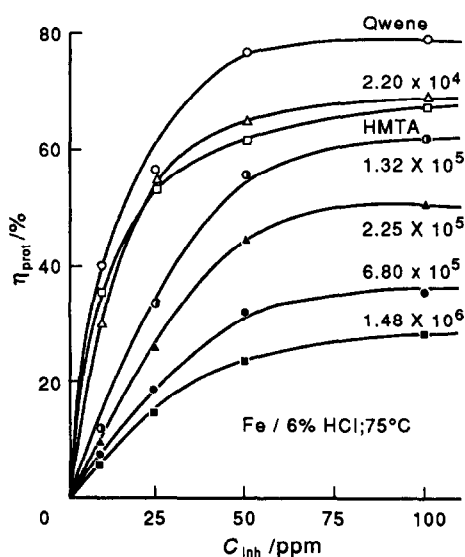


Fig. 11. Corrosion protection efficiency of PAA, HMTA and Qwene for mild steel in 6% (1.6 M) HCl.

Table 5. Thermodynamic parameters for PAA and HMTA adsorption on mild steel from 1.6 M HCl

Thermodynamic parameter	$T/^\circ\text{C}$	HMTA	PAA, \bar{M}_n			
			2.2×10^4	2.25×10^5	6.8×10^5	1.48×10^6
$-\Delta G^0/\text{kJ mol}^{-1}$:	65	41.5	52.6	55.4	56.2	57.0
	75	39.3	50.5	54.9	56.8	59.3
$\Delta H^0/\text{kJ mol}^{-1} \text{K}^{-1}$:		-82.9	-67.8	-61.4	-45.4	-29.6
$\Delta S^0/\text{kJ mol}^{-1} \text{K}^{-1}$:		-125.4	-47.3	-18.2	32.4	78.9

strongly depend on the enthalpy and entropy of the desorption and on the number of water molecules desorbed from the metallic surface. So, it can be supposed that an increase in the polymer molecular mass (or length of macromolecular chain) increases the number of desorbed water molecules (per molecule) which leads to a decrease in ΔH_{ads}^0 and an increase in the solvent entropy. It means that the enthalpy of PAA adsorption on mild steel is indeed greater than the estimated values, by an amount equal to the enthalpy of desorption of x -water molecules. Very similar behaviour was found for adsorption of thiourea on mild steel.

Our further electrochemical measurements on iron (99.99% Fe) in 1.6 M HCl, Fig. 12, clearly show that PAA mainly acts as an anodic inhibitor which considerably decreases the rate of electrochemical dissolution of iron. Its influence on the cathodic side (hydrogen evolution) is much less obvious. At the same time the corrosion potential is slightly shifted in the anodic direction and the DL-capacity decreases to about $15 \mu\text{F cm}^{-2}$. After that (in the presence of 100 ppm PAA in the solution) HMTA was added (20, 100 and 1000 ppm) and a drastic decrease in the cathodic current was observed (Fig. 12). Thus, it is very clear that HMTA is a typical cathodic inhibitor which can be coadsorbed with PAA (a synergistic effect was found). The value of DL-capacity is almost constant in the narrow potential region (close to the E_{corr}) (Fig. 12), indicat-

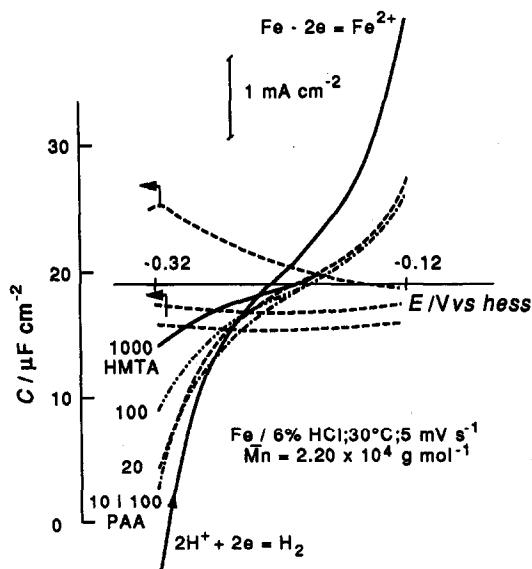


Fig. 12. Current-potential and capacity-potential curves for iron in 6% (1.6 M) HCl in the presence of PAA and HMTA.

ing a potential independence of the PAA adsorption on iron. The lower corrosion inhibition efficiency of PAA with relatively high molecular mass was also confirmed; Fig. 13.

One of the greatest disadvantages of PAA as an inhibitor for steel and iron in HCl (especially at elevated temperatures) by itself or with HMTA is its relatively low chemical stability and/or adsorption activity as a function of time. Our experiments, Fig. 13, clearly indicated that adsorption activity (corrosion inhibition efficiency) of PAA decreases with time depending on temperature and the polymer molecular mass.

Voltammograms and capacitance spectra (Fig. 14) for Au/H₂SO₄ in the presence of PAA are very illustrative. The decreases of PAA adsorption with time can be seen from both j/E and C/E curves. Such behaviour of PAA in acidic media at elevated temperatures can be explained by its hydrolysis followed by NH₃ formation and/or cross-linking of the polymer molecules *via* NH bridges, which both lead to the decrease of the adsorption ability. On the other hand these processes are very slow at room temperature. It was found that η_{prot} of PAA (mild steel/HCl) decreases for 4–6% after a 30-day treatment in 1.6 M HCl.

4. CONCLUSIONS

Electrochemical studies of polyacrylamide (PAA) adsorption on gold, mild steel and iron from acidic aqueous solutions (H₂SO₄ and HCl) as a function of

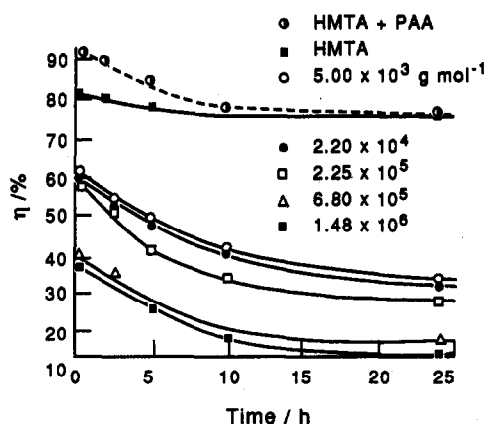


Fig. 13. Corrosion protection efficiency of PAA (0.05 g dm^{-3}), HMTA (1 g dm^{-3}) and HMTA-PAA ($5 \times 10^3 \text{ g mol}^{-1}$) for mild steel in 6% (1.6 M) HCl as a function of time at 70°C .

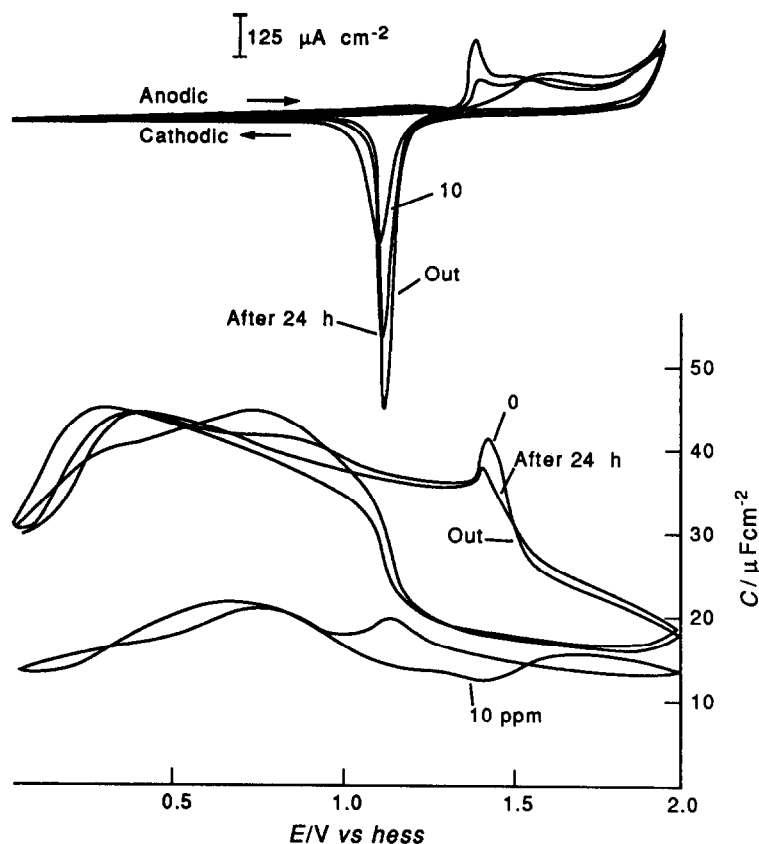


Fig. 14. Voltammograms and capacitance spectra for gold in 0.5 M H₂SO₄ and the presence of PAA (5×10^3 g mol⁻¹); solution containing 10 ppm PAA was treated for 24 h at 80°C.

polymer molecular mass and temperature, indicate the following:

(i) PAA is strongly adsorbed on the Au/solution interface in a wide potential range (0 to 1.3 V/hess) reaching almost complete coverage ($\theta = 1$) of the bare metal surface at very low polymer concentrations (10^{-7} – 10^{-8} mol dm⁻³). The average or effective thickness of the adsorbed polymer layer at the metal surface, as being determined from capacity measurements, ranged from 0.8 to 1.0 nm. At high anodic potentials (such as 1.3 V) the thickness of this layer does not depend on the polymer mass or on the temperature, predicting a flat orientation of the adsorbed parts of polymer molecules.

(ii) At room temperature the influence of potential (0 and 1.3 V) on the adsorption behaviour of PAA on gold can almost be neglected. However, at elevated temperatures (40–80°C) and high anodic potentials adsorption of PAA on gold is even more pronounced indicating an endothermic adsorption process.

(iii) Thermodynamic parameters for PAA adsorption on gold were calculated using the Frumkin isotherm which shows the best agreement with experimental results (compared with Langmuir and Flory–Huggins adsorption isotherms).

(iv) The adsorption behaviour of the monomer (AA) is considerably different and indicates much more distinct lateral interactions between adsorbed

molecules. In this case complete coverage ($\theta = 1$) was not obtained and a limiting value of θ of about 0.7 was determined for relatively high monomer concentration (about 10^{-3} M AA) and at relatively high anodic potentials.

(v) PAA adsorption on mild steel from hydrochloric acid considerably inhibits the corrosion process. Thermodynamic parameters of the adsorption process, determined again from Frumkin's isotherm, depend in a very similar way (as in the case of PAA adsorption on gold) upon the polymer molecular mass. These effects were explained in terms of substitutional adsorption of the polymer on a bare metal surface followed by significant desorption of water molecules from the surface.

(vi) As was shown by our electrochemical measurements on iron in HCl, PAA acts as a "classical" anodic inhibitor which can be improved in the presence of hexamethylenetetramine (coadsorption)—a well-known cathodic inhibitor for iron in HCl.

(vii) Thermal and chemical stability of PAA (closely related to its adsorption/inhibition ability) in HCl, especially at elevated temperatures (60–80°C), was found to be poor. Its inhibition efficiency drastically decreases after 5–10 h.

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