The Kinetics of Polyacrylamide Adsorption on Polycrystalline Gold

Dragica Chamovska, Maja Cvetkovska, and Toma Grchev*

Faculty of Technology and Metallurgy, »St. Cyril and Methodius« University, 1000 Skopje, R. Macedonia

Keywords
potentiostatic pulses
adsorption kinetics
polyacrylamide
polycrystalline gold

Fast potential step measurements ($0.9 \rightarrow 1.9 \rightarrow 0.9$ V, *E vs.* she) with simultaneous monitoring of the double layer capacity were applied in the study of the kinetics of PAA adsorption on gold from 0.5 M H_2SO_4, at 293 K. It was shown that the addition of PAA to the solution at 1.9 V (in the presence of a very thin oxide layer at the gold surface of ≈ 1 nm) does not affect the value of the capacity of the Au/Au_2O_3/PAA-solution interface, which was also confirmed by Electrochemical Impedance Spectroscopy. After the very fast cathodic reduction of the thin oxide layer (step $1.9 \rightarrow 0.9$ V) for several milliseconds, the initial adsorption of PAA molecules at the bare gold surface reappeared in ≈ 10 ms, causing exhaustion of the metal/solution boundary layer. The induction region ($d\theta/dt \approx 0$) as well as the diffusion controlled region ($d\theta/dt = $ const. $= f \overline{M}_n((PAA); c_{PAA})$ are characteristic of low concentrations in the solution. According to the experimentally obtained linear parts of the ($\theta / \log t$)-dependences, values of the diffusion coefficient of PAA-molecules with different molecular weights were calculated. These values follow fairly well the empirical equation: $D_{PAA} = 7.03 \times 10^{-4} \overline{M}_n^{-0.66}$ cm^2 s^{-1}. Using the same procedure, the diffusion coefficient of 9×10^{-6} cm^2 s^{-1} for adsorption of »small« organic molecules, such as HMBT, was calculated.

INTRODUCTION

The electrochemist is, naturally, primarily interested in the kinetics and the mechanisms of electrode processes with time as the fundamental variable.[1–12] Although adsorption is often a major step in overall electrode reactions, it is remarkable to note that the double layer has been considered merely as a static structure.

In the past, most adsorption studies were directed to the thermodynamics of adsorption and to the inhibiting properties displayed by a surfactant toward faradaic processes, while very little attention was paid to the kinetic aspects.

Studies of the kinetics of the establishment of adsorption equilibrium are of fundamental importance for understanding its mechanism and for evaluating the reliability of the obtained data on adsorption. The rate of establishment of equilibrium during adsorption depends on the chemical nature of the polymer and its molecular weight, the solvent, and the type of adsorbent. In most cases, kinetic curves indicate an increase in the amount of adsorbed polymer with time, with an asymptotic approximation to the equilibrium value.

Diffusion of polymers to the surface of the adsorbent or into its pores is almost always the stage that determines the adsorption rate.

Polyelectrolyte adsorption on interfaces also concerns various applications such as flocculation and steric stabilization of colloidal particles in an aqueous phase, oil re-

---

* Author to whom correspondence should be addressed. (E-mail: toma@tmf.ukim.edu.mk)

covery, and soil conditioning. In these cases, both the ad-sorbance of polyelectrolytes and the conformation of the adsorbed polymer, which is connected with the thickness of the adsorbed layer, are very important.

The aim of this study is to investigate and to compare the kinetics of adsorption of macromolecules (poly-acrylamide, PAA, M_n = 5 000–1 500 000 g mol^{-1}) with that of some small organic molecules, such as 1-hydroxy-methyl-1,2,3-benzotriazole, HMBT) on polycrystalline gold from sulfuric acid.[11]

EXPERIMENTAL

Experiments were carried out in a classical thermostated electrochemical cell, at 293 K, using a gold wire (d = 0.5 mm, 0.25 cm^2) as a working electrode and a gold foil (10 cm^2) as an auxiliary electrode. Potentials were measured against the Hg/Hg$_2$SO$_4$ reference electrode and were referred to the standard hydrogen electrode (she).

The kinetics of PAA adsorption on gold from 0.5 M H$_2$SO$_4$ were studied using the potentiostatic method with simultaneous monitoring of the dl-capacity.[13] The program applied in these investigations is shown in Figure 1.
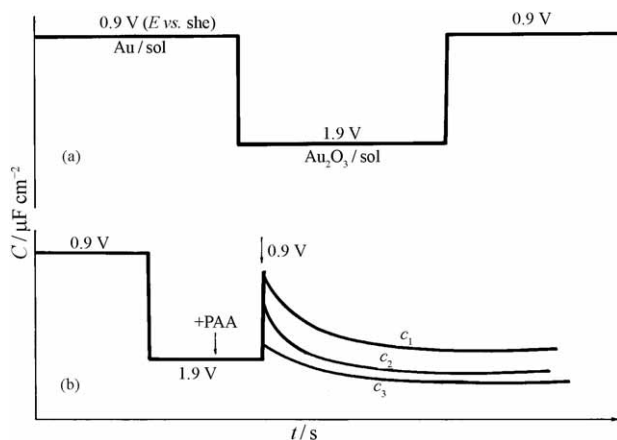

Figure 1. Schematic representation of the capacity-time (C/t)-profiles during the process of formation (1.9 V) and reduction (0.9 V) of Au$_2$O$_3$ at the gold/solution interface; (a) without PAA; (b) with PAA in the solution; (PAA was added at 1.9 V, E *vs.* she).

The method of fast (potential) pulse measurements, following the current (t > 10^{-7} s) and capacity (t > 10^{-3} s) transients[14,15] was also used in this study. This method allows us to look into the very fast processes (microseconds) taking place at the metal/solution interface.

Aqueous solutions of 0.5 M H$_2$SO$_4$ were prepared from 98 % (w) *p.a.* H$_2$SO$_4$ (Merck) and redistilled water (κ < 2 × 10^{-7} S cm^{-1}). PAA was obtained by redox-initiated polymerization of acrylamide. Six fractions of PAA with molecular weights from 5 000 to 1 500 000 g mol^{-1} were used in the study. The polydispersity index of PAA ranged from 1.2 to 1.35.

RESULTS AND DISCUSSION

Processes gold oxidation and formation of a thin oxide film (*ca.* 0.9 ± 0.1 nm), stepping from 0.9 to 1.9 V (with 100 V/s), and especially its reduction (1.9 V → 0.9 V), are fast processes (5–10 ms), as determined by log j / log t profiles (not shown in this paper) and confirmed later from C / log t data.
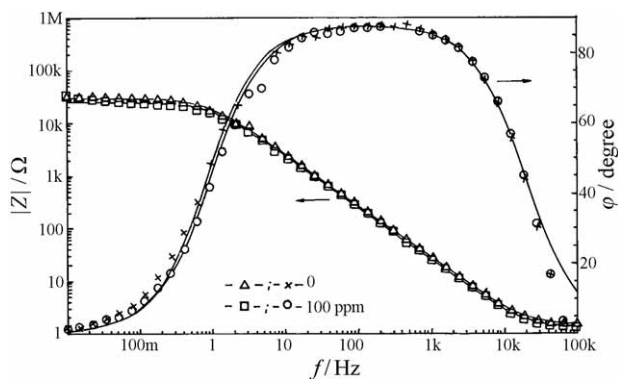

Figure 2. Experimental and fitted Bode-plots (using the Boukamp program)[17] for the system: Au/0.5 M H$_2$SO$_4$ at E vs. she = 1.9 V and 293 K; –△– and –×– without PAA in the solution; –○– and –□– in the presence of PAA (w_{PAA} = 100 ppm, M = 1 500 000 g mol^{-1}).

These steps (0.9 V → 1.9 V → 0.9 V, E *vs.* she) were repeated at least 10 times, and after that a given quantity of PAA was added into the solution at the potential of 1.9 V (in the presence of Au$_2$O$_3$ film, Figure 1b). The capacity was practically constant after the PAA addition into solution, and this is additional evidence that PAA does not adsorb at the gold oxide/solution interface. This fact was also confirmed by EIS (Electrochemical Impedance Spectroscopy), Figure 2. After a certain period of time (≥ 100 s), the potential was stepped from 1.9 to 0.9
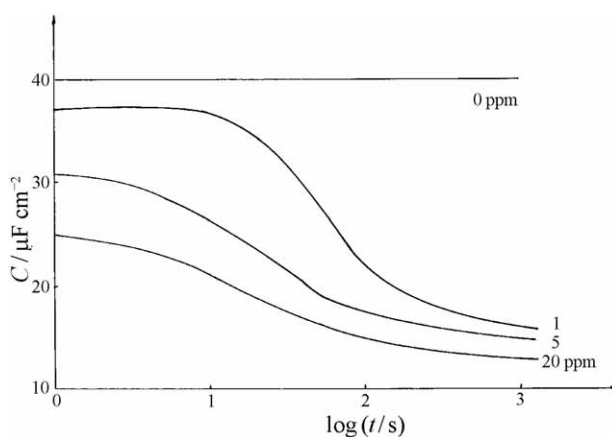

Figure 3. Capacity-time (C/t)-profiles for PAA (5 000 g mol^{-1}) adsorption at the gold/solution interface (0.9 V, E vs. she) for several PAA concentrations (w = 1, 5, 20 ppm) in the solution.

V (reduction of gold oxide and simultaneous adsorption of PAA at the bare gold surface) and capacity-time profiles were registered (Figure 3).

It can be seen that the capacity values (after fast reduction of Au_2O_3) for $t \leq 1$ s are significantly lower than those obtained in the absence of PAA and regularly depend on the PAA-concentration in solution. After that, the capacity monotonically decreases reaching a limiting value for $t \to \infty$ (Figure 3).

Kinetic (θ vs. time) curves for PAA adsorption on gold shown in Figures 4 and 5 were obtained using previously determined values for capacity, in the absence ($C^{\theta=0}$) or in the presence of PAA (C_m^{θ}) in the solution (as a function of time, Figure 3) and two-condenser model. This model assumes parallel existence of covered parts of a metallic surface with adsorbed PAA molecules (θ) and an uncovered part ($1 - \theta$). Thus, the measured value of the overall capacity can be given as:

$$C_m^{\theta} = C_m^{\theta=0}(1 - \theta) + C_m^{\theta=1}\theta \qquad \text{or} \qquad (1)$$

$$\theta = (C_m^{\theta=0} - C_m^{\theta}) / (C_m^{\theta=0} - C_m^{\theta=1}) \qquad (2)$$

It should be mentioned that the value of $C_m^{\theta=1}$ was determined as a limiting (minimum) value of the capacity for $c_{PAA} \to \infty$ and $t \to \infty$ at 0.9 V, E vs. she (12 ± 0.5 μF cm^{-2} in our case).

Four regions (steps) can be observed on these curves (Figures 4 and 5):

(i) The initial adsorption step, point A.

(ii) The induction period, region A–B.

(iii) The diffusion controlled PAA adsorption, region B–C.

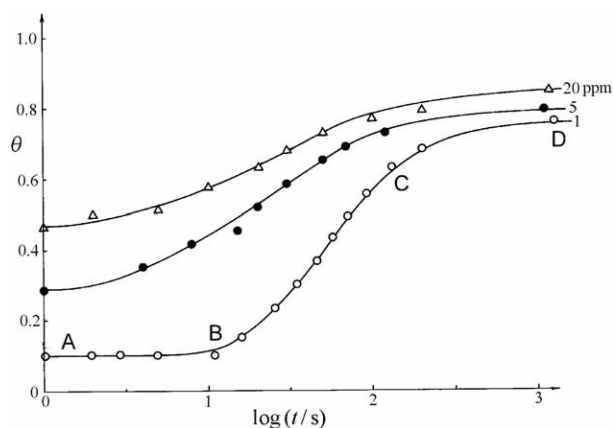(iv) The saturation of the gold surface with adsorbed PAA-molecules, C–D region.

Figure 4. Surface coverage (θ) vs. time dependences for PAA (5 000 g mol^{-1}) adsorption on gold from 0.5 M H_2SO_4 (w_{PAA} = 1, 5, 20 ppm) at E vs. she = 0.9 V; point A, initial adsorption; A–B induction period; B–C diffusion controlled adsorption and C–D saturation of the adsorbed layer.
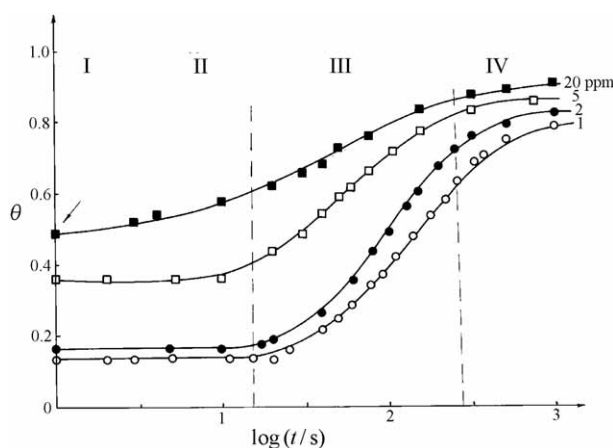

Figure 5. Surface coverage (θ) vs. time dependences for PAA (1 500 000 g mol^{-1}) adsorption on gold from 0.5 M H_2SO_4 (w_{PAA} = 1, 2, 5, 20 ppm) at E vs. she = 0.9 V.

TABLE I. Parameters for adsorption kinetics of PAA on gold at 0.9 V (E vs. she) and 293 K

$\overline{M_n}$(PAA) / g mol^{-1}	w_{PAA} / ppm	c_{PAA} / mol dm^{-3}	θ ($\tau \to 0$)	θ ($\tau \to \infty$)	$(d\theta / d\tau) \cdot 10^{3}$ [a] / s^{-1}	v_{ads} [b] / mol cm^{-2} s^{-1}	$\delta_{exh} \cdot 10^3$ / cm
5 000	1	(2×10^{-7})	0.08	0.767	4.24	7.38×10^{-14}	6.9
	5	(1×10^{-6})	0.31	0.798	4.47	7.73×10^{-14}	5.4
	20	(4×10^{-6})	0.48	0.853	3.57	6.18×10^{-14}	2.1
225 000	1	(4.44×10^{-9})	0.123	0.780	1.78	2.37×10^{-16}	3.7
	2	(8.88×10^{-9})	0.224	0.805	2.30	3.06×10^{-16}	3.4
	5	(2.22×10^{-8})	0.434	0.830	2.17	2.90×10^{-16}	2.6
	20	(8.88×10^{-8})	0.470	0.845	1.34	1.78×10^{-16}	0.7
1 500 000	1	(6.7×10^{-10})	0.114	0.782	1.69	1.98×10^{-17}	2.00
	2	(1.34×10^{-9})	0.170	0.811	2.48	2.90×10^{-17}	1.50
	5	(3.33×10^{-9})	0.360	0.849	2.53	2.96×10^{-17}	1.26
	20	(1.34×10^{-8})	0.520	0.855	1.45	1.70×10^{-17}	0.45

[a] B–C region.
[b] Calculated by $v_{ads} = (d\theta/dt) \cdot c_s^{\theta=1}$.

Point A (Figure 4) represents the initial coverage (θ) of the metal/solution interface with adsorbed polymer molecules for $t < 1$ s. Fast pulse measurements, represented in the Figures 6 and 7, confirm these findings.

On the other hand, the values of the initial surface coverage also depend on the PAA-concentration in the solution (Figures 3, 4 and Table I) and it can be assumed that the adsorption process during this step is under kinetic control. Otherwise, the transport of PAA molecules through a very thin layer of solution, after electrochemical fast reduction of Au_2O_3 film (≈ 1 nm), is an extremely fast process (for $D_{PAA} \approx 10^{-8}$ cm^2 s^{-1}; $t = x^2 / 2D = (10^{-7})^2 / 2 \times 10^{-8} = 5 \times 10^{-7}$ s).[16]

As can been seen from Figures 4 and 5, the induction period A–B ($d\theta/d\tau \approx 0$) appears only for very low values of PAA mass fraction, $w_{PAA} \leq 5$ ppm and its duration depends both on the concentration and molecular weight of PAA. This period is necessary for the transport of PAA-molecules from the bulk of solution to the metal/solution-boundary layer exhausted in the process of the initial step of adsorption; $t_{AB} / s = \delta_{exh}^2 / 2D$, Table I.

The values of $c_s^{\theta=1}$ were calculated with regard to the size of polymer coils in dilute polymer solutions, as given in the paper of Schwartz[16] ($R_G / nm = 7.49 \times 10^{-3} \times \overline{M}_n^{0.64}$ or $\sigma / nm^2 = R_G^2 \pi$). These values are presented in Table II.

Region B–C (Figures 4 and 5) shows fairly good linear parts whose slope ($d\theta / dt$) and duration also depend on the PAA-concentration in the solution and/or the size of the uncovered part of the metal surface ($1 - \theta_{in}$). For lower PAA concentrations, this step (B–C) is relatively slow and the limiting values of surface coverage can be achieved after about 10 minutes. For higher values of PAA mass fraction ($w \geq 5$ ppm), this region is shorter and the rate of adsorption (under diffusion control) mainly depends on the available bare metal surface ($1 - \theta_{in}$).

The thickness of the exhausted layer (δ_{exh}) close to the metal surface, after the initial step of adsorption (for $t \approx 10$ ms), can be also approximately determined (Table I) from the equation:

$$\delta_{exh} / cm = \frac{\theta_{t \to 0} \cdot c_s^{\theta=1}}{c_{sol}^{PAA}} \quad (3)$$

where $c_s^{\theta=1}$ is the limiting surface concentration of PAA molecules (expressed in mol cm^{-2}) and c_{sol}^{PAA} is the PAA concentration in the solution (expressed in mol cm^{-3}).

Assuming the diffusion controlled adsorption process in region B–C, especially for low initial coverage (θ_{in}), it follows:

$$\left(\frac{d\theta}{dt}\right)_{III} \cdot c_s^{\theta=1} = v_{ads} = -D \frac{\partial c}{\partial x} \quad mol\ cm^{-2}\ s^{-1} \quad (4)$$

where $\partial c \approx c^0_{PAA}$ and $\partial x \approx \delta_{exh}$.

TABLE II. Basic parameters for statistical polymer coils (assuming ball-shaped polymer coils, both in solution and at metallic surface)

$\overline{M}_n$	R_G	σ	$c_s^{\theta=1}$	
g mol^{-1}	nm	nm^2	mol cm^{-2}	mg cm^{-2}
5 000	1.75	9.6	1.74×10^{-11}	8.7×10^{-5}
22 000	4.50	64	2.6×10^{-12}	5.72×10^{-5}
225 000	20.0	1 250	1.33×10^{-13}	3.0×10^{-5}
680 000	40.5	5 150	3.22×10^{-14}	2.19×10^{-5}
1 500 000	67.0	14 170	1.17×10^{-14}	1.76×10^{-5}

Thus, the calculated values of the diffusion coefficient for PAA (using data from Table I; for $w_{PAA} = 1$ ppm) are:

$D_{5\ 000} = 2.54 \times 10^{-6}$ cm^2 s^{-1}; $D_{225\ 000} = 1.97 \times 10^{-7}$ cm^2 s^{-1}; $D_{1\ 500\ 000} = 5.9 \times 10^{-8}$ cm^2 s^{-1}.

Evidently, the calculated values of the diffusion constants for PAA significantly depend on its molecular weight, or the size of the statistical polymer coils in the solution, and they are in a good agreement with the literature data for a similar system.[16]

The limiting value of the surface coverage (θ_{lim}), for steady-state conditions, can be obtained from region C–D, Figure 4; where: $(d\theta / dt)_{C-D} << (d\theta / dt)_{B-C}$, and $(d\theta / dt)_{C-D} \to 0$. These values are also presented in Table I (θ for $t \to \infty$).

All the above considerations can be additionally confirmed by means of fast (potential) pulse measurements following the current and capacity transients (Figures 6 and 7).

The same experimental and calculation procedure was, also applied for the adsorption of »small« organic molecules (HMBT) at the gold/H$_2$SO$_4$ interface. The obtained results are presented in Figure 8 and Table III.
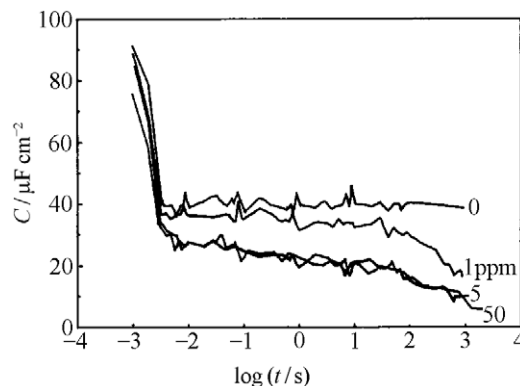

Figure 6. Capacity-time (C/t) dependences for adsorption of PAA (5 000 g mol^{-1}) at the gold/solution interface during a fast potential step from 1.9 to 0.9 V (E vs. she) and the presence of several concentrations of PAA ($w_{PAA} = 1$, 5, 50 ppm) in the solution.
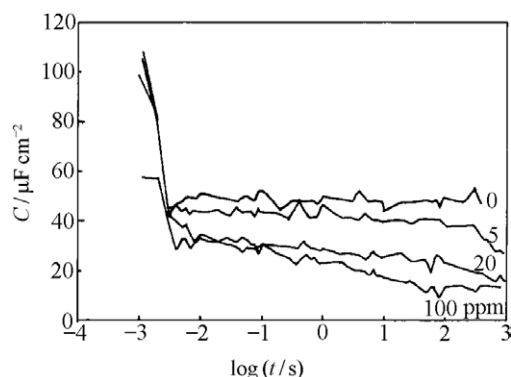
Figure 7. Capacity-time (C/t) dependences for adsorption of PAA (1 500 000 g mol^{-1}) at the gold/solution interface during the fast potential step from 1.9 to 0.9 V (E vs. she) and the presence of several concentrations of PAA (w_{PAA} = 5, 20, 100 ppm) in the solution.

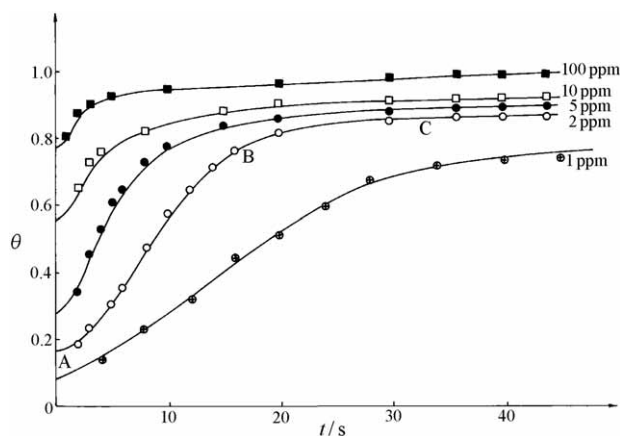Figure 8. Surface coverage (θ) vs. time dependences for HMBT adsorption on gold from 0.5 mol dm^{-3} H$_2$SO$_4$ (w_{HMBT} = 1, 2, 5, 10, 100 ppm) at 0.9 V and 293 K.

TABLE III. Parameters for adsorption kinetics of HMBT on gold at 0.9 V, E vs. she, and 293 K

$\dfrac{w_{HMBT}}{ppm}$	$\left(\dfrac{c_{HMBT}}{mol\ dm^{-3}}\right)$	$\theta(\tau \to 0)$	$\theta(\tau \to \infty)$	$\dfrac{d\theta / d\tau}{s^{-1}}$	$\dfrac{v_{ads} \cdot 10^{11}}{mol\ cm^{-2}\ s^{-1}}$ [a]
1	(6.70×10^{-6})	0.080	0.720	0.026	1.14
2	(1.34×10^{-5})	0.170	0.850	0.049	2.17
5	(3.36×10^{-5})	0.280	0.885	0.074	3.26
10	(6.72×10^{-5})	0.552	0.915	0.0585	2.59
30	(2.02×10^{-4})	0.740	0.930	0.055	2.42
100	(6.72×10^{-4})	0.777	0.970	0.057	2.51

[a] σ_{HMBT} = 0.375 nm^2 (for θ = 1; c^s_{HMBT} = 4.4 × 10^{-10} mol cm^{-2}).[11]

On the basis of the experimentally obtained linear (θ / log t)-dependences, for the diffusion controlled region B–C, values of the diffusion coefficient of PAA molecules with different molecular weights were calculated. These values follow fairly well the empirical equation: D_{PAA} / cm^2 s^{-1} = 7.03 × 10^{-4} $\overline{M}_n^{-0.66}$ and are in good agreement with the literature values for the diffusion coefficient of PAA-molecules with similar molecular weights.[16]

Using the same procedure, the diffusion coefficient of 9 × 10^{-6} cm^2 s^{-1} for adsorption of "small" organic molecules such as HMBT was calculated.

Comparing Figures 4 and 5 (for PAA) with that for HMBT (Figure 8) it can be concluded that the rate of HMBT adsorption is significantly faster. The calculated value of the diffusion coefficient for HMBT molecules was about 9 × 10^{-6} cm^2 s^{-1}, which is in good accord with literature data for many other "small" organic molecules.

CONCLUSIONS

The study of PAA adsorption kinetics on polycrystalline gold from 0.5 M H$_2$SO$_4$ (at E vs. she = 0.9 V and 293 K) clearly indicates the existence of four regions: initial, induction, diffusion controlled regions and saturation of the metal surface with adsorbed PAA-molecules.

The initial step is very fast ($t \leq$ 10 ms) and kinetically controlled. The following three regions are diffusion controlled; $d\theta / dt = f((1 - \theta_{in}) ; \overline{M}_n(PAA), c_{PAA}))$.

REFERENCES

1. M. Beier and J. W. Schultze, *Electrochim. Acta* **37** (1992) 2299–2307.
2. M. Beier, M. M. Lohrengel, and J. W. Schultze, *J. Appl. Electrochem.* **23** (1993) 606–614.
3. D. M. Drazic, Lj. Vracar, and V. J. Drazic, *Electrichim. Acta* **39** (1994) 1165–1170.
4. A. Takahashi, M. Kawaguchi, K. Hayashy, and T. Kato, *Ellipsometric Study of Adsorption of Polyelectrolyte onto a Metal Surface*, in: *Polymer Adsorption and Dispersion Stability*, Am. Chem. Soc., 1984, pp. 39–51.
5. G. Bereket, A. Yurt, and H. Turk, *Anti-Corrosion Methods and Materials* **50** (2003) 422–435.
6. A. El-Sayed, *Corrosion Prevention and Control* **43** (1996) 27–34.
7. B. Vincent, *Polymers in Disperse Systems*, in: E. D. Goddard and B. Vincent (Eds.), *Polymer Adsorption and Dispersion Stability*, ACS Symposium Series 240, Am. Chem. Soc., Washington, 1984, pp. 3–20.
8. M. Mekki Daouadji and N.Chelali, *J. Appl. Polym. Sci.* **91** (2004) 1275–1284.
9. K. S. Khairou and A. El-Sayed, *J. Appl. Polym. Sci.* **88** (2003) 866–871.
10. T. Grchev, M. Cvetkovska, T. Stafilov, and J. W. Schultze, *Electrochim. Acta* **36** (1991) 1315–1323.
11. D. Chamovska, M. Cvetkovska, and T. Grchev, *Bull. Chem. Technol. Macedonia* **18** (1999) 187–197.

12. B. Muller, *Reactive and Functional Polymers* **39** (1999) 165–177.

13. M. M. Lohrengel, K. Shubert, and J. W. Schultze, *Werkst. Korros.* **32** (1981) 13–18.

14. U. Konig, M. Beier, and J. W. Schultze, *J. Electroanal. Chem.* **330** (1992) 615–635.

15. M. M. Lohrengel, *Principles and Applications of Pulse Techniques to Corrosion Study*, in: M. G. S. Ferreira and C. A. Melenres (Eds.), *Electrochemical and Optical Techniques for Study and Monitoring of Metallic Corrosion*, Kluwer Academic Publishers, Netherlands, 1991, pp. 69–121.

16. T. Schwartz, J. Francois, and G. Weill, *Polymer* **21** (1980) 247–249.

17. B. A. Boukamp, *Solid State Ionics* **20** (1986) 31.

SAŽETAK

Kinetika adsorpcije poliakrilamida na polikristaliničnom zlatu

Dragica Chamovska, Maja Cvetkovska i Toma Grchev

Kinetika adsorpcije poliakrilamida na zlato u otopini 0,5 M H_2SO_4 pri 293 K mjerena je uz brzu promjenu potencijala (0,9 → 1,9 → 0,9 V, *E vs.* she), a simultano je određivan kapacitet dvostrukog sloja. Pokazano je da dodatak PAA u otopinu pri 1.9 V (u prisustvu tankog oksidnog sloja na površini zlata, ≈ 1 nm) ne utječe na kapacitet $Au/Au_2O_3/PAA$ međupovršine, što je također potvrđeno elektrokemijskom impedancijskom spektroskopijom. Nakon vrlo brze (nekoliko milisekundi) katodne redukcije tankog oksidnog sloja (korak 1,9 → 0,9 V), dolazi do adsorpcije molekula PAA na površinu zlata (≈ 10 ms). Područje indukcije ($d\theta/dt \approx 0$), kao i područje difuzijske kontrole ($d\theta/dt \approx$ konst $= f \overline{M}_n$((PAA); c_{PAA}), karakteristični su za niske koncentracije u otopini. Vrijednosti difuzijskog koeficijenta PAA različitih molarnih masa izračunate su prema eksperimentalno utvrđenoj linearnoj ovisnosti ($\theta / \log t$). Dobivene vrijednosti se prilično dobro slažu s empirijskom jednadžbom: $D_{PAA} = 7,03 \times 10^{-4} \overline{M}_n^{-0.66}$ cm^2 s^{-1}. Difuzijski koeficijent za adsorpciju "malih" organskih molekula kao HMBT određen je istim postupkom i iznosi 9×10^{-6} cm^2 s^{-1}.