The Impact of Polyacrylamide Molecular Weight on Its Adsorption Behavior at the Gold/Acidic Solution Interface

Dragica B. CHAMOVSKA, Toma P. GRCHEV[*]**, Maja V. CVETKOVSKA**
Faculty of Technology and Metallurgy, Sv. Kiril & Metodij University,
1000 Skopje-REPUBLIC OF MACEDONIA
e-mail: toma@tmf.ukim.edu.mk

Adsorption isotherms for polyacrylamide (PAA) on polycrystalline gold, from sulfuric acid (potential range 0-2.0 V/she; 293 K), were obtained by means of cyclic voltammetry with simultaneous monitoring of the double-layer capacity. The Frumkin isotherm indicates that relatively strong attractive forces are present (a = 0.8-1.0), and the Gibbs energies range between 43 and 56 kJ mol^{-1}. The coverage (θ) of the metal surface with polymer molecules depends on the molar concentration of PAA, as well as on its molecular weight, and the size of the statistical polymer coil in the solution ($R_G = 7.49 \times 10^{-3} \times \bar{M}_n^{0.64}$ / nm). The adsorption coefficient B also strongly depends on the polymer molecular weight ($B = k\ \bar{M}_n^{\alpha}$), indicating, once more, that the size of the polymer coil and its conformation at the metal surface and/or in solution are the main factors determining the polymer adsorption at the metal/solution interface.

Key Words: Electrosorption, polyacrylamide, polycrystalline gold, adsorption isotherms, radius of gyration.

Introduction

Polymer adsorption onto solid surfaces is important for a wide range of applications, and is relevant to many issues in biology and medicine. Adsorbed polymer layers are used widely in the stabilization of colloidal suspensions and are essential for the formulation of paints, coatings, printing inks, drilling needs, and ceramic processing.[1,2] They also play a crucial role in corrosion protection[3−9] as well as in many tribological applications such as boundary lubricants.[2]

The ultimate goal of research in polymer adsorption is to facilitate the manipulation of the properties of adsorbed polymer layers (or polymer-solid interfaces) so that materials with required properties can be obtained. To take steps toward this goal, understanding how the nature of the polymer, the substrate, and the other prevailing conditions (such as the type of solvent) affect the macroscopic properties of the interface is crucial.

[*]Corresponding author

In a given situation, many macroscopic properties are directly determined by the polymer chains conformations. Thus, if we want to understand the relationships between the properties of adsorbed polymer layers and the nature of the polymer, substrate, and other conditions, we have to elucidate the molecular conformations of the polymer chains in a given situation. Appropriate choice of the molecular features of polymeric agents offers the opportunity to control macroscopic surface and interfacial properties.[1]

The aim of this study was to correlate the adsorption behavior of PAA on polycrystalline gold substrate in sulfuric acid with its molecular characteristics.

Experimental

The measurements were carried out in the classical thermostated electrochemical cell 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. The potentials were measured vs. Hg/Hg_2SO_4 – reference electrode and referred to the standard hydrogen electrode (she).

Cyclic voltammetry ($dE/dt = 10$ mV s^{-1}) with simultaneous monitoring of the double layer (dl) capacity (at 100 Hz and 1 mV ac signal) was used for an adsorption study of polyacrylamide (PAA). The electric circuit used has been described elsewhere.[10]

PAA was synthesized for this work by redox-initiated polymerization of acrylamide using $Na_2S_2O_5$-Fe(III)-complex of iminodiacetic acid as the redox couple. For this study, 6 fractions (of 18) of PAA with the lowest polydispersity index (1.2 to 1.35), obtained by classical fractionation (aqueous solution/methanol), were used. Molecular weights and polydispersity indexes were determined by GPC (Waters instrument; 410 Differential Refractometer; THF; styragel column HTGE and polystyrene standards).

Results and Discussion

Voltammograms and capacitance spectra for gold in 0.5 mol dm^{-3} H_2SO_4 and the presence of PAA (1,500,000 g mol^{-1}), taken after at least 10 cycles, are presented in Figure 1.

Several potential regions can be distinguished, both on voltammetric and capacity curves:

– A-B and H-A - regions of double-layer charging

– B-C-D-E – Au-O chemisorbtion, $Au(OH)_3$ or Au_2O_3 formation[11,12]

– F-G-H – reduction of the surface products formed in the previous region

As can be easily observed, the voltammetric and capacitance profiles are strongly influenced by the presence of PAA in the solution. The effects seen can be summarized as follows:

1. The processes of anodic oxidation of gold, represented in a simple form as:

   $2Au + 3H_2O = Au_2O_3 + 6H^+ + 6e^-$, as well as its reduction(regions B-D-E and F-G-H, respectively), are strongly inhibited.

2. The dl-capacity significantly decreases in the whole potential range ($0 \rightarrow 1.9 \rightarrow 0$ V), by increasing PAA concentration in the solution, indicating that PAA adsorbs at the gold/solution interface.

3. Capacity maxima observed at about 0.3 V/she shifts anodically for more then 200 mV in the presence of a higher concentration of PAA. It should be noted that these capacities' maxima appear very close

to the reorientation processes of adsorbed water molecules at the gold surface and/or p.z.c (potential of zero charge).[13−15]

4. The higher concentration of PAA in the solution (>20 ppm) does not cause further significant changes, on j/E or C/E curves. On the other hand, the potentiodynamic curves shown in Figure 1 indicate that the process of surface oxidation of gold is not completely blocked as in the case of adsorption of some small organic molecules with similar or the same functional groups.[16,17] That means that only a certain number of segments of the long polymer chain directly contact with the metal surface while the other parts form loops and/or tails in the solution.[18]
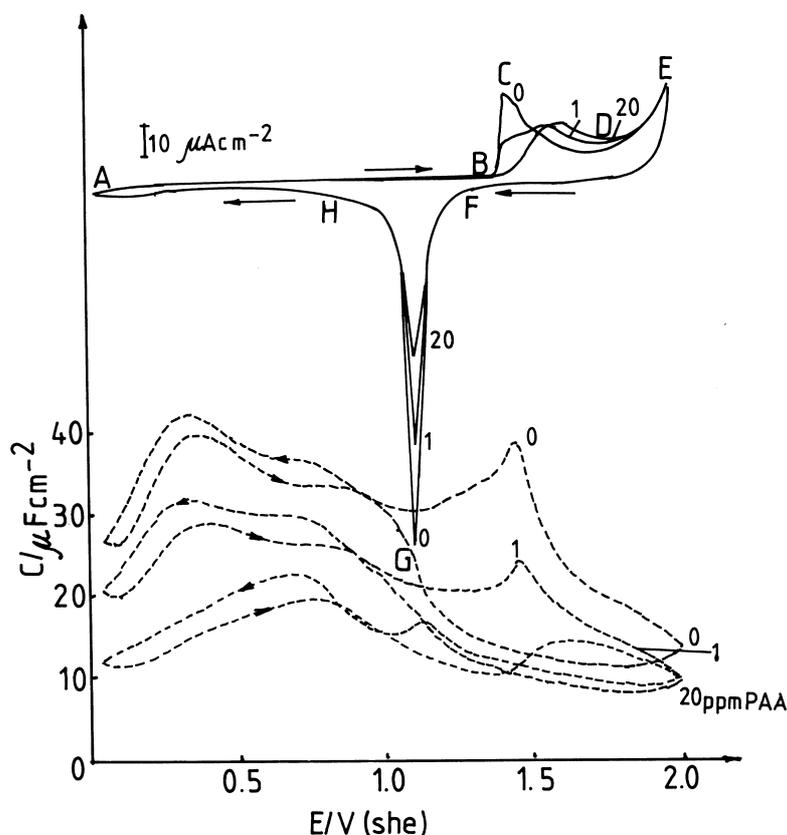
Figure 1. Voltammograms and capacitance spectra for gold in 0.5 M H_2SO_4 and in the presence of polyacrylamide (PAA; 1,500,000 g mol^{-1}; 1 and 20 ppm); 293 K.

Accordingly, the decrease in dl-capacity at a given potential is mainly a result of directly adsorbed segments of the polymer molecule on the metal surface and in the case of adsorption of small organic molecules a well packed adsorbed layer is formed (see Figure 3).

The loops of the polymer molecule (chain) contain a significant quantity of electrolyte (Figure 2a), and thus the dl-capacity on that part of the metal surface is mainly determined by the adsorbed layer of water molecules and (bi)sulfate anions.[19] Therefore, the formation of oxide (in the B-C-D-E region) takes place at the uncovered part of the metal surface (for $\theta < 1$), as well as on the "screened" surface under loops (Figure 2).

a) E = 0-1.2 V/she
A-B and H-A regions (Figure 1)

b) E > 1.25 V/she
B-C-D-E and E-F-regions (Figure 1)
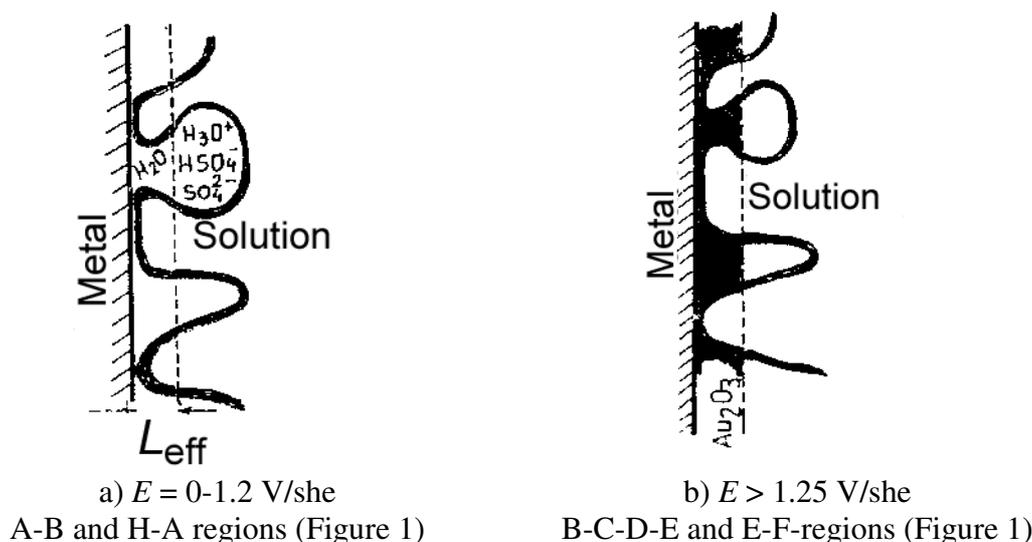
Figure 2. Schematic representation of the metal/solution interface (a), and metal/oxide/solution interface (b) in the presence of PAA.

Thus, according to the two-condenser model, the surface coverage (θ) with adsorbed polymer molecules (PAA) in the region of double layer charging (A-B), in the vicinity of p.z.c. (E $\approx$ 0.2 V/she), can be determined by experimentally measured values of capacities; Table 1 and Eq. (3):

$$C_m^\theta = C_m^{\theta=0}(1 - \theta) + C_m^{\theta=1}\theta \tag{1}$$

or

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

$$\theta = (C_m^{\theta=0} - C_m^\theta)/(C_m^{\theta=0} - C_m^{\theta=1}) \tag{3}$$

C_m^θ is the experimentally measured minimum capacity (at 0.2 V/she) in the presence of PAA, and $C_m^{\theta=0}$ is the capacity in the same point, in the absence of PAA.

The limiting capacity $C_m^{\theta=1}$ (for $c_{PAA} \to \infty$) in our case is approximately 12 μF cm^{-2}.

Table 1. Electrochemical parameters for adsorption of PAA (M = 1,500,000 g mol^{-1}) on gold from 0.5 M H$_2$SO$_4$ at 293 K.

c_{PAA}		C_{min}/μF cm^{-2}		θ^*
		$E/$ V(she)		
ppm	mol dm^{-3}	~ 0.2	~ 1.95	~ 0.2
0	0	27.0	11.7	0
0.5	3.33×10^{-10}	23.48	11.3	0.235
1	6.67×10^{-10}	19.95	9.2	0.47
2	1.33×10^{-9}	15.45	9.0	0.77
5	3.33×10^{-9}	13.05	8.7	0.93
10	6.67×10^{-9}	12.45	8.4	0.97
20	1.33×10^{-8}	12.23	8.3	0.985
50	3.33×10^{-8}	12.15	8.2	0.99

$*$-calculated by Eq. (3), assuming $C_m^{\theta=1} = 12$ μF cm^{-2}

In order to illustrate and confirm the above-mentioned considerations, Figure 3 shows the j/E and C/E spectra for the Au/0.5 M H_2SO_4 system, in the absence and presence of the limiting concentration of PAA (500 ppm), as well as in the presence of 100 ppm DBTO [dibenztriazole-1-yl-methyloctylamine] and 5 ppm TMS [1-triazol-1-yl-methylstearate], which create relatively thick films (by adsorption and precipitation, respectively) on the gold surface.
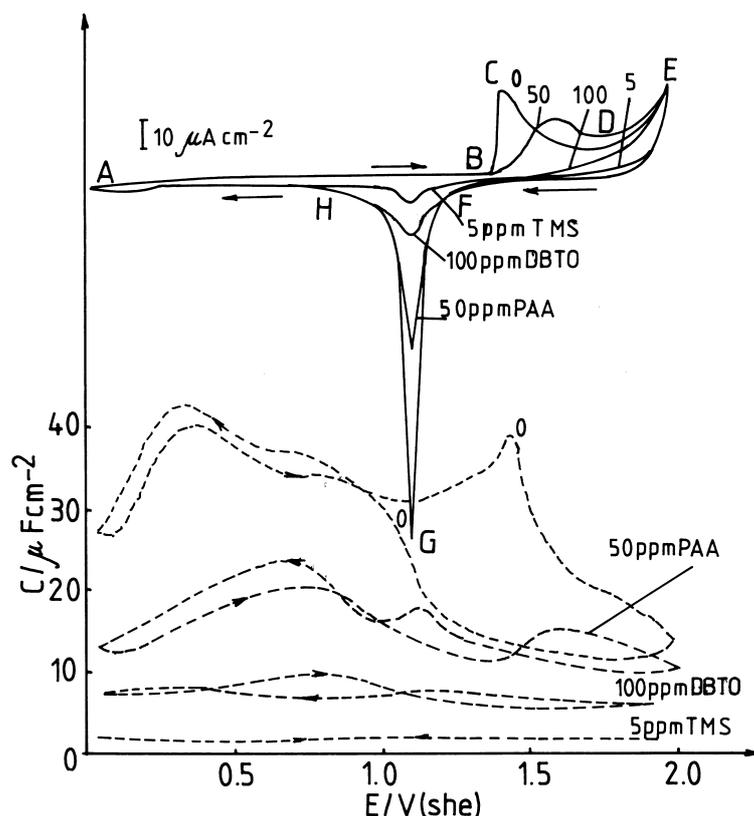
Figure 3. Voltammograms and capacitance spectra for gold in 0.5 M H_2SO_4 and the presence of PAA (1,500,000 g mol^{-1}), DBTO and TMS.

As can be concluded from Figure 3, in the presence of relatively thick and compact adsorption (and/or precipitation) films at the gold/solution interface (DBTO and TMS) the Faradaic processes of oxide formation are very strongly inhibited and measured capacities are very low and practically constant in the whole potential range.

Thus, using a simple condenser model ($C_{min}^{\theta=1} = \varepsilon \times \varepsilon_o/L$), for $\varepsilon = 15$,[8,20] the following effective thicknesses (L) of these layers were calculated: $\sim$1.1 nm (for PAA), $\sim$ 2 nm (for DBTO) and $\sim$ 7 nm (for TMS-precipitation layer).

The adsorption isotherms shown in Figure 4 were obtained using experimental data (such as those given in Table 1) and Eq. (3) (based on a two-condenser model).
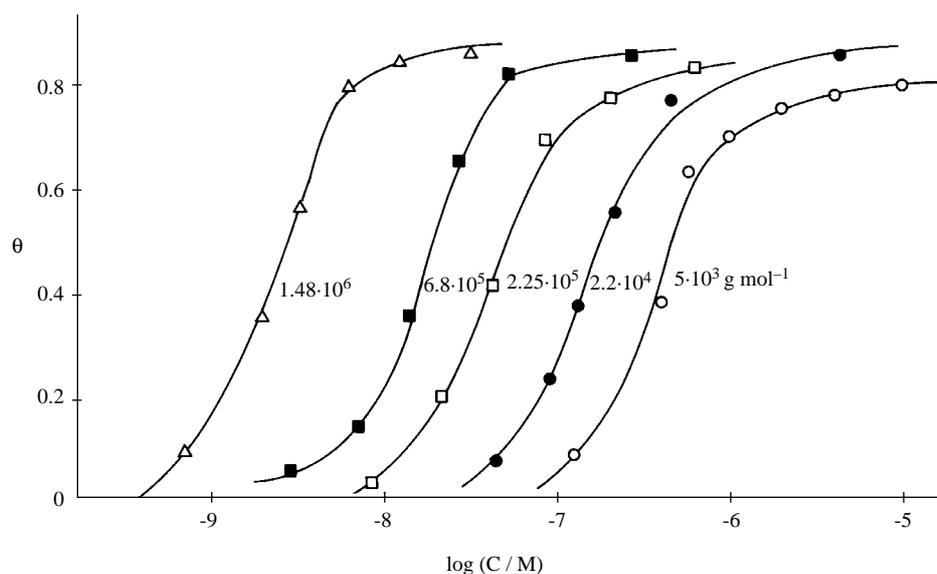
Figure 4. Adsorption isotherms for PAA on gold from 0.5 M H_2SO_4; at 0.2 V/she; 293 K.

The best fit of these experimental results (Figure 4) can be achieved with the Frumkin isotherm:

$$[\theta/(1-\theta)]\exp(-2a\theta) = B \cdot c \qquad (4)$$

or

$$\ln\left[\frac{\theta}{1-\theta}\cdot\frac{1}{c}\right] = \ln B + 2a\theta \qquad (5)$$

which takes into account the lateral interactions between adsorbed molecules at the metal surface (parameter a).

The best fit parameters (given in Table 2) were determined from the $\ln\{[\theta/(1-\theta)]1/c\}/\theta$-linear plots (Eq. (5) and Figure 5). Thus the value of adsorption coefficient B was determined from the intercept (for $\theta = 0$) and the interaction parameter (a) from the slopes of these linear plots. Gibbs energies of the adsorption, referred to $\theta = 0$, were calculated using the equation

$$\Delta G_{ads} = -RTln(55.5B) \qquad (6)$$

Table 2. Thermodynamic parameters for adsorption of PAA on gold from 0.5 M H_2SO_4, at 293 K, in accordance with the Frumkin isotherm (Eqs. (4) and (5)).

$M_n/$ g mol^{-1}	$E = 0.2$ V/she		
	α	B/M^{-1}	$-\Delta G^0/$kJ mol^{-1}
5×10^3	1.05	7.5×10^5	42.74
2.2×10^4	0.8	2.3×10^6	45.45
2.25×10^5	0.9	6.5×10^6	48.00
6.8×10^5	1.0	1.7×10^7	50.34
1.5×10^6	0.82	1.5×10^8	55.70
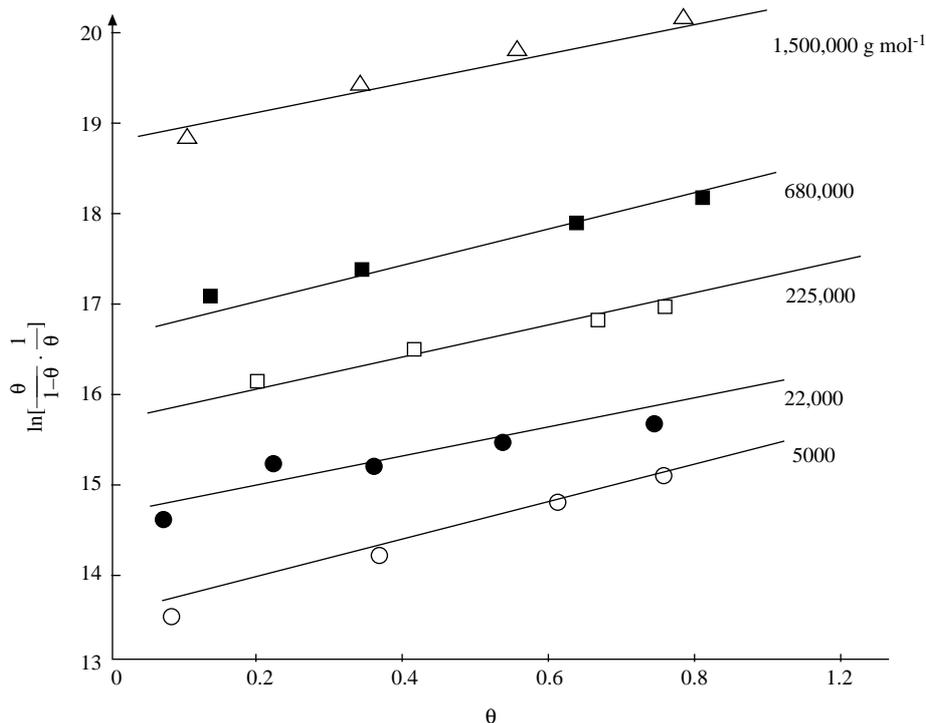
Figure 5. Evaluation of experimental results given in Figure 4 according to the Frumkin isotherm (Eq. (5)).

It can be concluded that the adsorption coefficient B as well as $\Delta G°C$ depends on the molecular weight of PAA. On the other hand, the positive values of the interaction parameter a, obtained in all cases, indicate the existence of considerable attraction forces between adsorbed molecules and/or segments of the polymer on the gold surface.

It was found that the calculated values for B, given in Table 2, follow the empirical equation

$$\mathbf{B} = \mathbf{k} \times \bar{M}_n^{\alpha} \qquad (\text{for} \quad \alpha \sim 0.80 \quad \text{and} \quad k = 6.7 \times 10^2) \tag{7}$$

The same type of empirical equation describes the relationship between polymer molecular weight and viscosity η[21] (for dilute polymer solutions), and between the adsorbed quantity of the polymer (m)[22] and the radius of gyration of the polymer coil in the solution (R_G).[23]

The thickness of the adsorbed polymer layer of about 1.1 nm, determined by capacity measurements (for $\varepsilon = 15$), corresponds only to the directly attached polymer segments to the metal surface. Other parts of the adsorbed polymer coils (loops and tails), do not significantly contribute to the value of the measured capacity due to the very low participation of the polymer material ($\leq 1\%$) in the overall volume of the coil ($\varepsilon_{coil} \approx \varepsilon_{sol}$). Thus the sharp decrease in the dielectric constant (from $\varepsilon_{sol} \approx 80$ to $\varepsilon_{ads} \approx 15$) occurs in the thin adsorbed layer of polymer segments at the metallic surface.

On the other hand, as found by elipsometry[24,25] (for much longer exposures of gold in the solution containing PAA), the process of further involvement of polymer molecules in the adsorbed layer causes its additional structuring (most probably creating entangled polymer coils). The measured thickness of the PAA-adsorbed layers in this case ranged between 100 and 200 nm.

Conclusions

Polyacrylamide (PAA) strongly adsorbs at the gold/acidic solution interface in a wide potential range (from 0 to approx. 1.1 V/she) at a negatively and/or positively charged metallic surface. The adsorption isotherms obtained experimentally (for $E = 0.2$ V/she; very close to the p.z.c.) follow the Frumkin isotherm, indicating the existence of relatively strong attractive forces between adsorbed segments of polymer molecules. The Gibbs energies of the adsorption process ($-\Delta G_{ads}$) range between 43 and 56 kJ mol^{-1} (for $\overline{Mn} = 5000$ and 1,500,000 g mol^{-1}, respectively). The adsorbed PAA-molecules at the metal/solution interface significantly inhibit the processes of surface oxidation of gold.

It was found that the surface coverage (θ) depends on the molar concentration of PAA in the solution, as well as on its molecular weight (or the size of the statistical polymer coil in the solution). The adsorption coefficient, B, also depends strongly on the polymer molecular weight, indicating, once more, that the size of the polymer coil and its conformation on the metal surface are the determining factors for polymer adsorption at the metal/solution interface. These findings can be represented by the following relation:

$$B_1/B_2 \equiv (\theta_1/\theta_2)_c \equiv (\bar{M}_{n_1}/M_{n_2})^{0.80} \tag{8}$$

The thickness of the adsorbed layer, calculated from the capacity data, is approx. 1.1 nm and is almost unaffected by the polymer molecular weight.

Acknowledgments

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