Electrochemical Determination of Organic Surface Active Substances in Model and Natural Sea Water with Au(111) Monocrystal Electrode

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The applicability of Au(111) monocrystal electrode for the determination of the amount of surface active organic substances was investigated using cyclic voltammetry, CV, and phase selective alternating current voltammetry, PSACV. The behaviour of the electrode was tested in a simple sea water model solution (0.55 M NaCl or 0.55 M NaCl plus 9.6×10^{-4} M KBr), as well as in natural sea water samples from the northern Adriatic. Surface active organic molecules used for model adsorption investigations were Triton X-100, T-X-100, and humic acid, HA. Their behaviour in NaCl medium is discussed and typical CV and PSACV curves are compared for Cl^- and Br^- media. The characteristic of Au(111) surface reconstruction to be lifted by the adsorption of anions such as Cl^- or Br^- was used for analytical purposes, since competition in adsorption between inorganic anions and organic molecules changes strongly the reconstruction behaviour of Au(111). Calibration curves for T-X-100 and HA in model sea water were constructed and were used for determination of the relative concentrations of surface active molecules in natural sea water samples. The PSACV method was chosen as more reproducible and practical since no deaeration of the solution was necessary.

Key words: surface active substances, electrochemical determination, sea water, gold(111) electrode, Triton X-100, humic acid.

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INTRODUCTION

Organic matter in natural waters determines the fate of many trace substances. Complexation of dissolved organic matter with trace metals has been the subject of numerous papers.[1–3] Due to their surface active properties, organic substances are adsorbed on different phase boundaries.[4–7] Their fate in natural aquatic environments and the flux of dissolved organic carbon (DOC) from continents to oceans, and subsequently to sediments, is largely influenced by adsorption reactions. Adsorbed organic compounds at the mineral/water interface influence dissolution processes and crystal growth as well as adsorption and the scavenging processes of microconstituents and contaminants.[8,9]

Adsorption of organic molecules on different metal electrodes has been the subject of intense electrochemical studies for many years. It was mainly the mercury electrode with its defect-free surface that allowed detailed experimental investigations and interpretations. Although the mercury electrode is a simple and very practical model of a charged interface, solid electrodes resemble natural interfaces more closely.

Surface active characteristics of organic substances were also employed for analytical purposes. Again, mercury electrodes were used almost exclusively for determining the amounts and nature of the naturally present organic matter, including pollutants.[10–13] Ironically, mercury by itself is one of the most toxic pollutants of natural habitat.

For the above mentioned reasons, the aim of this work was to substitute mercury with a non-toxic solid electrode and investigate its possibilities for the analysis of organic substances in sea water. Au(111) monocrystal electrode was chosen mainly because of its relatively easy handling in a reactive ambient, such as air or aqueous solutions, and its wide double-layer charging region. The behaviour of Au(111) face in electrolytic solutions has been investigated in considerable detail to date.[14–24] One of the basic characteristics of gold surfaces is that they undergo surface reconstruction. This means that surface atoms are displaced laterally due to the imbalance of forces on surfaces where atoms find an environment that is highly asymmetric, compared to that in the bulk.[23] This phenomenon was originally suggested by Hamelin[15] and was followed by detailed studies of Kolb.[18,19] The (111) face of Au readily reconstructs and the $Au(111) - (\sqrt{3} \times 22)$ reconstruction results in compression of the surface atoms by about 4%. The specific adsorption of anions lifts the reconstruction and this is related to the shift of the potential of zero charge, p.z.c. The sudden shift in p.z.c with the lifting of reconstruction requires additional charging of the electrode surface in order to maintain the applied potential during the structural transition, and this gives rise to a concomitant current peak in voltammetry.[18,23] The above characte-

ristic of the gold electrode was used in this work for analytical purposes, as it will be discussed later.

Electrochemical methods coupled with other techniques were used to investigate the adsorption of HSO_4^-,[25] Br^-,[26,27] Cl^-,[27–29] I^-,[30] and SO_4^{2-},[27,31–33] on the Au(111) surface. Recently, the adsorption of these anions on Au(111) was reviewed by Lipkowski *et al.*[34] The strength of gold-anion interaction is $I^- > Br^- > Cl^- > OH^- > SO_4^{2-} > ClO_4^- \approx F^-$.[19] All of these anions are of special interest since they are present in sea water, which was the subject of investigation in this work.

Adsorption of organic substances can also have a profound influence on the stability of the reconstructed gold surface.[23] Generally, they can lift the reconstruction by themselves, which usually decreases the potential range within which the reconstruction structure is stable. On the other hand, the adsorbed organic molecules can retard the specific adsorption of anions and thereby somewhat extend the stability range of the reconstructed surface. The high sensitivity of the electrochemical response to this behaviour can be used for the analytical determination of organic surface active substances in sea water or other natural waters.

EXPERIMENTAL

The Au(111) electrode was a monocrystal rod of a 3 mm diameter and 5 mm length. It was connected by a gold wire attached to its rear. The surface was oriented to the better of 1°, and was polished down to 0.03 μm. Before measurements, the electrode was annealed in the flame of a small Bunsen burner to a light red heat for about 30 s. After cooling in air for 30 s it was quenched in ultrapure water. The crystal was then transferred to the electrochemical cell with a droplet of water adhering to the polished surface to prevent contamination. It was connected with the electrolyte by the »dipping-technique«.[35]

The electrochemical cell used was a Metrohm 50 ml cell with platinum wire as counter electrode and Ag/AgCl/3 M KCl reference electrode which was connected to the solution through a supporting electrolyte bridge. The solution was stirred with a Teflon magnetic stirrer.

All solutions were prepared with water from a Milli-Q system (Millipore), except in the case when sea water was used as electrolyte. $NaClO_4$ was suprapure (Merck). NaCl was *p.a.* (Merck) and was additionally cleaned by heating at about 700 K for several hours in order to eliminate traces of organic impurities. Triton X-100 (T-X-100) was from Rohm and Haas (Milan), and humic acid (HA) was from Aldrich Chemie. It was peat HA in the form of water-soluble Na salt. Solutions were deaerated before and during the measurements with pure nitrogen, unless the measurements were performed in the presence of oxygen. All experiments were done at room temperature.

Cyclic voltammetry, CV, and phase selective alternating current voltammetry, PSACV, were performed with BAS 100A electrochemical analyzer. For PSACV, a frequency of 23 Hz and amplitude of 10 mV peak-to-peak were applied.

RESULTS AND DISCUSSION

In order to understand the behaviour of a complex electrolyte like sea water, a simplified model of sea water was designed. In Figure 1, the CV curves for various electrolytes are given. To a virtually nonadsorbing $NaClO_4$ (curve 1), 0.55 M NaCl was added (curve 2). Moving from the negative potentials in the positive direction, a sharp anodic peak at approximately 0.03 V was observed. It corresponds to the lifting up of the reconstruction of the Au(111) surface by the adsorption of Cl^- anions. This peak shifts towards negative potentials with increasing concentrations of Cl^-, which is consistent with the results reported in the literature.[27–29] A broad hump follows which corresponds to medium coverage of the electrode surface by mobile anions. At even more positive potentials, beyond the values shown in Figure 1, an ordered overlayer of adsorbed anions would form. The broad peak is basically symmetrical with the one formed when going in the negative direction. This means that the adsorption of Cl^- has an equilibrium character in this potential region. However, the sharp anodic peak at 0.03 V has no symmetric pair in the cathodic direction and the CV curve exhibits a pronounced hysteresis. This was attributed to the difference in the potential of zero charge between the reconstructed and unreconstructed surfaces.[18,26]

Addition of 9×10^{-4} M KBr, the amount approximately present in sea water,[36] to the last solution caused the anodic reconstruction peak to shift towards negative potentials (curve 3). Br^- adsorbs more strongly on the Au(111)
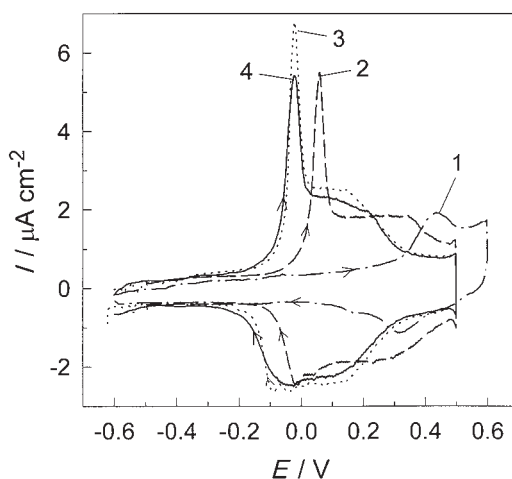

Figure 1. CV curves for (1) 0.05 M $NaClO_4$, (2) 0.05 M $NaClO_4$, 0.55 M NaCl, (3) 0.05 M $NaClO_4$, 0.55 M NaCl, 9×10^{-4} M KBr, (4) sea water. pH for solutions (1) to (3) is 6 and for (4) 8.1. Initial potential, E_i, = –0.6 V; scan rate, v, = 10 mV s^{-1}. Au(111) electrode was freshly annealed for each measurement. Second cycle was registered.

surface than Cl⁻ and this results in a potential shift as well as an increase of the peak current.[27] The general form of the CV curve remains otherwise the same as for the solution containing Cl⁻ and ClO$_4^-$ only. Finally, the reconstruction peak for natural sea water (curve 4) is at about the same potential as the solution containing Br⁻. It indicates that in sea water Br⁻ is the anion that causes the lifting of the Au(111) surface reconstruction. Organic molecules must also be taken into consideration. They certainly influence the peak height. The actual lowering of the reconstruction peak for natural sea water below that for the model sea water containing Br⁻ suggests inhibition of anion adsorption and Au(111) reconstruction by organic molecules.

Since the aim of this work was to investigate the possibilities of determining organic matter from sea water using the Au(111) electrode, one synthetic organic molecule, T-X-100, and one naturally present in sea water, HA, were chosen as models for the organic matter behaviour. The neutral surfactant T-X-100 was often used as a model substance for the organic surface active molecules present in natural waters. Its adsorption behaviour was mostly investigated on Hg/water[12,13,37–39] or air/water interface.[40] The main part of investigations was concerned with the influence upon the electrochemical processes of trace metals in natural waters.[38,39,41–49]

Being a neutral molecule, T-X-100 adsorbs on the Hg electrode on both sides of p.z.c in a wide range of potentials. Somewhat similar behaviour was observed on Au(111) electrode. In Figure 2, PSACV curves are given for in-
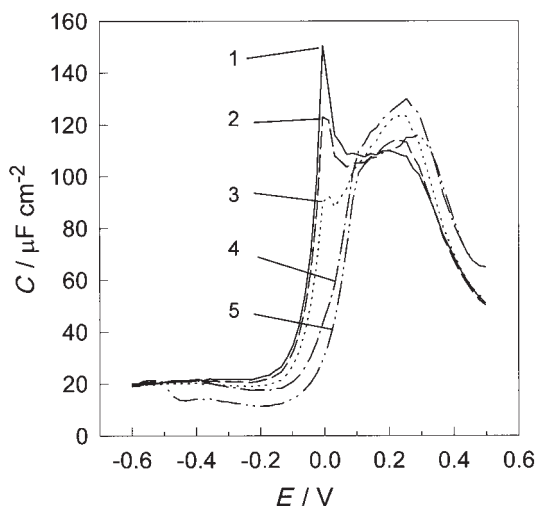

Figure 2. PSACV curves for (1) 0, (2) 0.57, (3) 0.95, (4) 1.90, and (5) 8.04 mg L⁻¹ T-X-100 in 0.55 M NaCl, pH = 6. E_i = –0.6 V, t_D = 30 s stirring, v = 10 mV s⁻¹, frequency: 23 Hz, a.c. amplitude: 10 mV peak to peak.

creasing concentrations of T-X-100 in 0.55 M NaCl. Deposition time, t_D, was 30 s with stirring at –0.6 V. 15 s after switching off the stirrer, the potential scan towards positive values commenced. At lower T-X-100 concentrations, the adsorption range is approximately –0.4 V to 0.4 V, which can be observed from the coincidence of capacity values at more negative or positive sides of this range with the values for supporting electrolyte. However, with the increase in concentration, the behaviour seems to change suddenly. The adsorption range increases drastically on both potential sides. Another important feature of these curves is that, with the increasing concentration of T-X-100, the capacity decreases at potentials more negative than 0.1 V. At more positive potentials, a broad peak, usually attributed to the loose form of Cl⁻ adsorption, increases. We suggest that this peak is either due to the reorientation and desorption of adsorbed T-X-100 or inhibition of Cl⁻ adsorption, which shifts the Au(111) reconstruction process towards more positive potentials.

In the potential range between –0.4 V and 0.1 V (Figure 2), the T-X-100 concentration may be determined from the lowering of capacity. Such a method was originally proposed for the Hg electrode by Jehring and Stolle[49] and was subsequently developed by other authors for the determination of surfactants in potable and untreated waters,[12] and for sea water.[13] The results of measurements in Figure 2 are plotted as $(C_0–C)/C_{min}$ against the T-X-100 concentration for different potentials (Figure 3). C_0 is the capacity
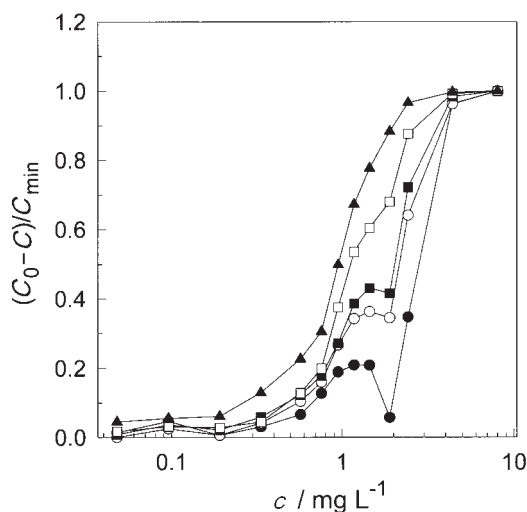

Figure 3. Plots of the relative capacity lowering from PSACV measurements in Figure 2. against T-X-100 concentration in 0.55 M NaCl, pH = 6. Capacity lowering measured at (●) –0.395, (○) –0.302, (■) –0.209, (□) –0.098, (▲) –0.005 V. Other conditions as in Figure 2.

value for the zero surfactant concentration, and C_{min} is the minimal value of capacity when it reaches a constant value at high T-X-100 concentrations. The curves have a two step form at all potentials, as it was already observed on Hg electrodes.[39] The concentration at which the second step appears on Au(111) is almost the same as on Hg. It was concluded that the first step represents the adsorption of monomers and the second step the formation of dimers or micelles on the electrode surface. Separation of the two steps is more pronounced at negative potentials, which indicates that the charge on the electrode has a strong influence on the formation of conglomerates of T-X-100 on the electrode surface. Since T-X-100 is an uncharged surfactant, it is probably the desorption of Cl⁻, with increasing negative electrode charge, that causes such T-X-100 behaviour.

As already mentioned, the adsorption of organic surface active substances on the Au(111) electrode in most cases inhibits the lifting of the reconstruction of the gold surface atoms due to the displacement of anions from the surface. This results in a lowering of the CV anodic reconstruction peak. In Figure 4, CV curves are given for increasing concentrations of T-X-100. The sharp anodic reconstruction peak around 0 V decreases with the simultaneous increase of two more positive peaks, one at approximately 0.1 V and the other at 0.3 V. As T-X-100 displaces Cl⁻ from the Au(111) surface, the lifting of reconstruction is postponed and the peak at 0.1 V is probably a partial lifting of reconstruction, which is followed by the reorientation and desorption peak of T-X–100 at 0.3 V. When the lowering of the re-
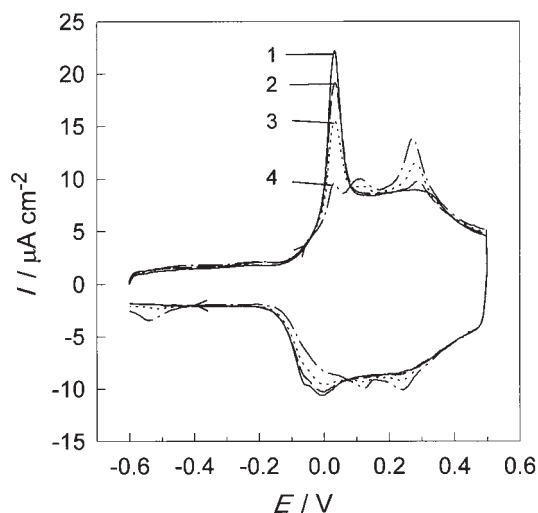

Figure 4. CV curves for (1) 0, (2) 0.19, (3) 0.76, and (4) 1.9 mg L⁻¹ T-X-100 in 0.55 M NaCl, pH = 6. E_i = –0.6 V, t_D = 30 s stirring, v = 50 mV s⁻¹.
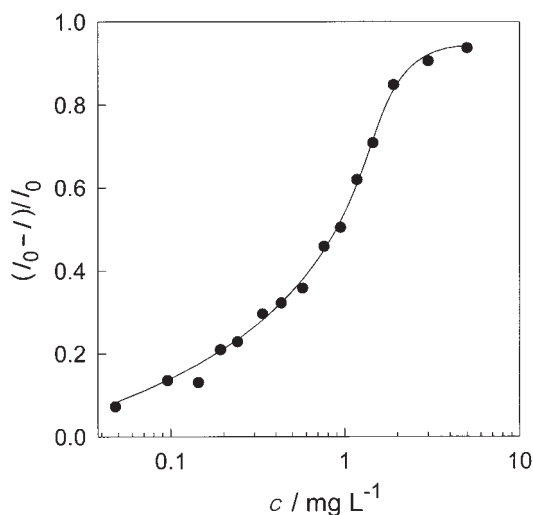
Figure 5. Normalized lowering of CV anodic reconstruction peak current against T-X-100 concentration in 0.55 M NaCl, pH = 6. Other conditions as in Figure 4. I_0 and I are anodic reconstruction peak currents for supporting electrolyte alone and with addition of T-X-100 respectively.

construction peak height or $(I_0–I)/I_0$ is plotted against concentration, a calibration curve for T-X-100 is obtained (Figure 5). I_0 and I are the anodic reconstruction peak heights in the absence and in the presence of T-X-100, respectively. No two step process can be resolved this time but it could simply be a consequence of the peak potential. The curve in Figure 5 corresponds to the curve at –5 mV in Figure 3, where the two steps are also barely discernible.

When a natural sea water sample, containing a mixture of unknown organic surface active substances, is measured, the lowering of the reconstruction peak can be read from the curve in Figure 5 and the concentration of unknown organic substances is expressed as equivalent to T-X-100. Since T-X-100 is an artificial surfactant present in natural waters only as a pollutant, sometimes it would be more realistic to use a naturally present organic substance as reference material. Humic acid, HA, could be such a choice as it is present in almost all natural waters. It is a substance of high complexity and of not very constant composition. In addition, it has a negative charge at neutral pH. In spite of that, its basic adsorption behaviour on Au(111) is similar to that of T-X-100 (Figure 6). For PSACV in Figure 6B, the alternating current was recorded at a phase angle of 90° instead of capacity. After annealing of the Au(111) electrode, the potential was cycled twice between –0.6 V and 0.5 V and was kept for 2 min at –0.8 V before accumulation at
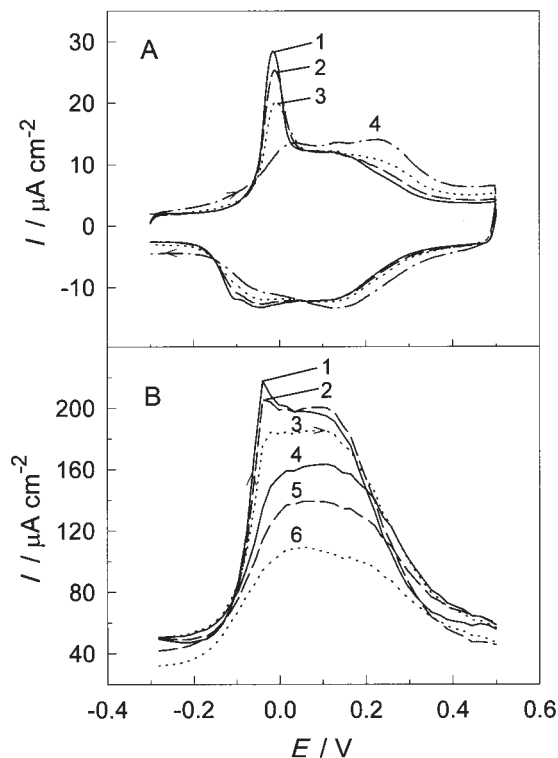
Figure 6. (A) CV and (B) PSACV curves for HA in 0.55 M NaCl and 9.6 x 10^{-4} M KBr. (A): (1) 0, (2) 0.74, (3) 2.1, (4) 9.7 mg L^{-1} HA; (B): (1) 0, (2) 0.71, (3) 2.1, (4) 5.0, (5) 8.8, (6) 47.4 mg L^{-1} HA. E_i = –0.3 V, t_D = 60 s stirring. CV: v = 50 mV s^{-1}; PSACV: v = 10 mV s^{-1}, frequency: 23 Hz, a.c. amplitude: 10 mV peak to peak, phase angle: 90° out of phase. PSACV was done in the presence of oxygen. Potential induced reconstructed electrode surface.

–0.3 V. Adsorption of HA in 0.55 M NaCl is strongest around 0 V (p.z.c) although the adsorption range is shifted somewhat towards more positive potentials as compared to T-X-100 due to the negative charge on HA. Although HA and T-X-100 lower the anodic reconstruction peak of Au(111) and capacitance values around 0 V in a similar manner, there are numerous differences in details of adsorption behaviour, but these are beyond the scope of this paper.

As expected, the CV and PSACV curves for natural sea water resemble those for HA more closely than those for T-X-100 (Figure 7). With increased deposition time, t_D, at –0.3 V, both the capacitance and anodic reconstruction peak are lowered. From PSACV curves, it seems that naturally present organic substances desorb around 0.3 V when going from negative towards

positive potentials. This, however, is not in accordance with the behaviour of HA which still adsorbs at these potentials. On the other hand, with an increased amount of adsorbed natural organic substances, no hump or appearance of new anodic peaks at potentials positive of reconstruction peak are observed. Thus, one has to recognize the fact that neither of the two substances chosen for the calibration are ideal, but this was to be expected knowing the complexity of sea water. Also, depending on the time or location of sampling, the sea water behaviour can vary considerably.
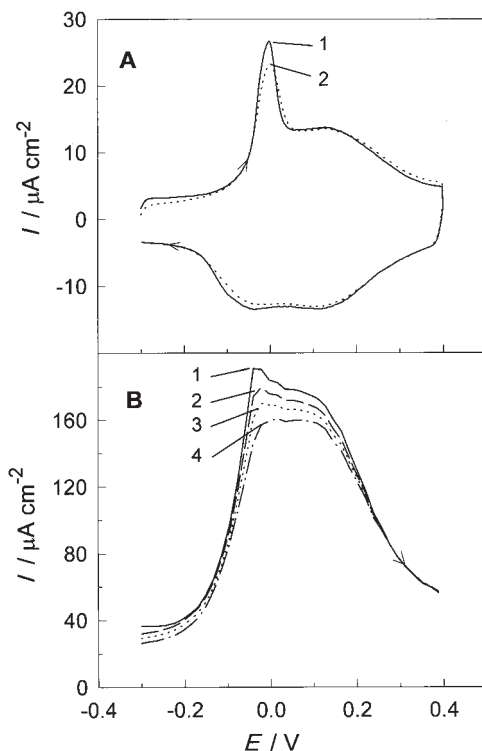

Figure 7. (A) CV and (B) PSACV curves for sea water sample from the northern Adriatic. (A) t_D = (1) 0, (2) 60 s stirring; (B) t_D = (1) 0, (2) 30, (3) 60, and (4) 120 s stirring. Other conditions as in Figure 6.

Calibration curves for model sea water were constructed using both PSACV and CV methods (Figure 8). The experiments were done for T-X-100 and HA in model sea water containing 0.55 M NaCl and 9.6×10^{-4} M KBr. With PSACV, no deaeration of the solution was necessary since oxygen reaction is sufficiently irreversible not to be observed appreciably under the given experimental conditions. The measuring procedure for model sea wa-
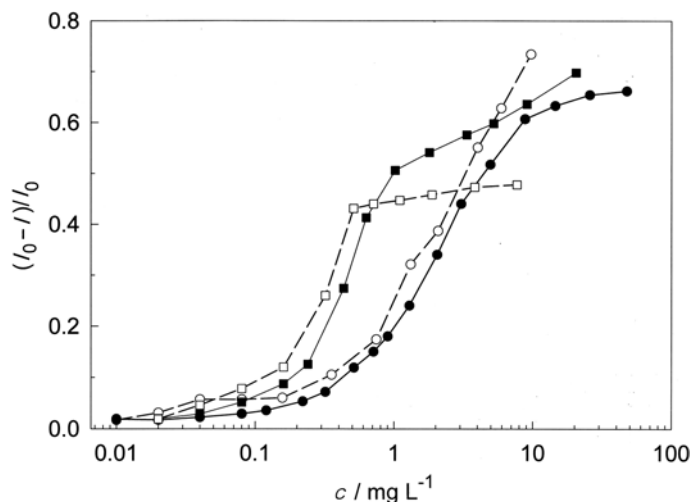
Figure 8. Calibration curves for (□), (■) T-X-100 and (○), (●) HA in 0.55 M NaCl and 9.6×10^{-4} M KBr, pH = 6. E_i = –0.3 V, t_D = 60 s with stirring. (□) and (○) CV, (■) and (●) PSACV. For CV: v = 50 mV s^{-1}, solution was deaerated. For PSACV: v = 10 mV s^{-1}, frequency = 23 Hz, amplitude = 10 mV, phase angle = 90°, solution was not deaerated. I_0 corresponds to blank solution.

ter or actual sea water samples was as follows: Au(111) electrode was annealed before measuring each solution. After the electrode was contacted to the solution, the potential was cycled twice between –0.6 and 0.5 V. This means that the measurements were done on the potential and not flame induced reconstructed Au(111) electrode. In addition, the electrode surface was thus cleaned from the adsorbed organic molecules. The potential was then changed to –0.3 V where the accumulation was performed for 60 s under stirring. The solution was allowed to settle for 15 s and the potential scan was commenced. With CV the anodic reconstruction peak, around –0.03 V, was always registered. The peak current for the model sea water solution, with t_D = 0 s, was taken as I_0, while I corresponds to the peak current value for the solutions containing organic molecules and t_D = 60 s. With PSACV, the phase angle was 90° out of phase and a.c. current at –0.039 V was measured. I_0 and I have the same meaning as in the CV method. Thus, with CV the peak height corresponds to the current due to the lifting up of the reconstruction of the Au(111) surface. Current in PSACV, in addition to being sensitive to the changes in reconstruction processes, also reacts strongly to the capacity changes due to the adsorption of organic molecules, regardless of the reconstruction.

From comparison of CV calibration curves for T-X-100 and HA (Figure 8, curves 1 and 3) it seems that HA adsorbs more strongly than T-X-100. The

concentration ranges of the curves can be misleading since they are expressed in mg L^{-1} and HA is a much larger molecule than T-X-100. The anodic reconstruction peak in the presence of T-X-100 decreases maximally to about 50% of its original height, while it is completely annihilated with the adsorption of a sufficient amount of HA. On the other hand, T-X-100 adsorption is sufficiently strong to cause almost a complete disappearance of the corresponding reconstruction peak due to Cl^- adsorption (Figs. 4 and 5). Thus, it seems that T-X-100 can displace Cl^- from the Au(111) surface but not Br^-, at least not completely. However, HA adsorption is strong enough to displace adsorbed Br^- as well.

PSACV measurements for T-X-100 (Figure 8, curve 2) indicate again a two-step process similar to the one discussed for NaCl medium in Figure 3. Presuming that the first step, up to 1 mg L^{-1} T-X-100, corresponds to the adsorption of monomers and comparing curves 1 and 2 in Figure 8, it follows that the anodic reconstruction peak (curve 1) is mainly influenced by the adsorption of monomers. The curve does not rise appreciably after that concentration. However, curve 2 continues to rise into the second step at concentrations where dimers or hemimicelles are already formed on the electrode surface, which means that they lower the capacity values of PSACV curves.

A depth profile of organic surface active substances from a station in the northern Adriatic sea was measured by the above described method. Samples were taken at the beginning of June and were not filtered. Concentrations of the surface active organic substances are given relative to T-X-100 (Figure 9, A) and HA (Figure 9, B). In both cases the general trend is the decrease of the content of surface active organic molecules from the surface towards the bottom. PSACV measurements showed better reproducibility and were less sensitive to the slight irreproducibility of the Au(111) electrode annealing procedure. Anodic reconstruction peak measured by the CV method is highly sensitive to this and if extreme care is not taken, the peak height could vary by up to 20%. In order to determine the experimental error of such measurements, a sample of the same sea water was measured five times repeating completely the whole procedure, starting with the annealing of the electrode. For PSACV, the obtained result for $(I_0 - I)/I_0$ value was 0.155 ± 0.005. This corresponds to the standard deviation of 3.3%, while with CV method the standard deviation is in the range of 12–14%. Obviously, the PSACV method, with its better reproducibility and greater speed and simplicity of measurements (no deaeration of the sample), should be the method of choice. Our further aim is to use this method for measuring the content of surface active organics from several Adriatic stations for a longer period of time and to compare the seasonal and spatial distribution results with those measured with Hg electrode as well as with the results for the content of dissolved organic carbon, DOC.
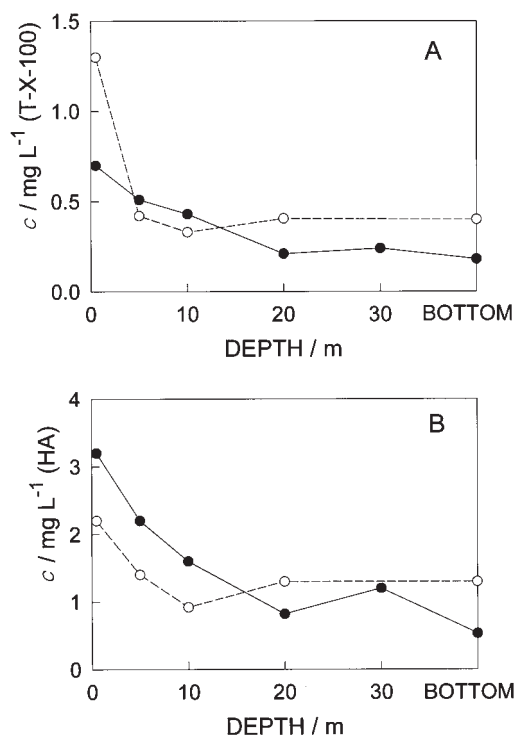
Figure 9. (○) CV and (●) PSACV determination of natural surface active organic molecules in unfiltered sea water samples from a station in northern Adriatic. Sampled in June, 1998. Concentrations are given relative to (A) T-X-100 and (B) HA. Concentrations are read off the calibration curves in Figure 8 using the measured $(I_0–I)/I_0$ values.

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SAŽETAK

Elektrokemijsko određivanje organskih površinski aktivnih tvari u modelnoj i prirodnoj morskoj vodi pomoću Au(111) monokristalne elektrode

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Ispitana je primjenljivost monokristalne Au(111) elektrode za određivanje količine organskih površinski aktivnih tvari uz upotrebu cikličke voltammetrije, CV, i fazno osjetljive voltammetrije izmjenične struje, PSACV. Ponašanje elektrode testirano je u jednostavnom modelu morske vode (0.55 M NaCl ili 0.55 M NaCl + 9.6×10^{-4} M KBr), kao i u uzorcima prirodne morske vode iz sjevernog Jadrana. Korištene modelne površinski aktivne molekule bile su Triton X-100, T-X-100 i humusna kiselina, HA. Razmatrano je njihovo ponašanje u otopini NaCl i uspoređene su tipične krivulje CV i PSACV za otopine koje sadržavaju ione Cl⁻ i Br⁻. Karakteristika površine Au(111) da gubi rekonstrukciju površinskih atoma uslijed adsorpcije aniona Cl⁻ ili Br⁻ iskorištena je u analitičke svrhe, budući da natjecanje u adsorpciji između organskih molekula i anorganskih aniona bitno mijenja rekonstrukcijsko ponašanje Au(111). Dane su kalibracijske krivulje za T-X-100 i HA u modelnoj morskoj vodi, koje su poslužile pri određivanju relativne koncentracije površinski aktivnih tvari u uzorcima prirodne morske vode. PSACV je izabrana kao reproducibilnija i praktičnija metoda, budući da je moguće mjeriti u prisutnosti kisika.