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Interfering Effect of Surfactants on Electrochemistry of Poly(pyrrole) Conducting Polymer Films*

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The effect of anionic, non-ionic and cationic surfactants in solution on electrochemical responses of poly(pyrrole) films were studies. It was found that surfactants present in solution in mmol/dm^3 concentrations practically do not affect voltammetric behavior of cation-exchanging poly(pyrrole) films doped with hexacyanoferrate ions. In contrary, for anion-exchanging poly(pyrrole) films doped with chlorides, PPyCl, charge transfer process observed under conditions of voltammetric experiment was significantly, irreversibly, inhibited by surfactants in solution in μmol/dm^3 concentration; regardless the charge of surfactant molecule. As shown by AC voltammetric experiments the choice of frequency (time) scale can be used to amplify or suppress the conducting polymer sensitivity of the current response of polymer for surfactants. These effect are important from the analytical point of view. For high frequencies or under potentiometric conditions surfactants do not interfere with ions concentration determination. On the other hand, for low frequencies surfactants interactions with PPyCl membrane give rise to analytically useful signal. The linear dependencies of current on logarithm of surfactant concentration were obtained within the concentration range at least from 10^{-7} to 10^{-4} mol/dm^3.

Key words: poly(pyrrole), surfactants, interferences, experiment time scale

Surface-active compounds are nowadays widely used both in household and industry, and are produced in large amounts; the majority of surfactants on the market are the anionic ones. These agents are quite likely to be present in samples, either as analytes [1] or interferents. Due to obvious reasons, determination of surfactants over years has become an important issue. Nowadays, the variety of research techniques can be applied in course of surfactant analysis including two-phase titration, spectrophotometry, chromatography based techniques and biological methods [1]. The further research in the area is stimulated by often not satisfactory detection limits or analysis times of already proposed approaches. The electroanalytical methods are also used in this respect, among others also potentiometry and amperometry (voltammetry) [1].

Potentiometric techniques can be applied both for direct determination of surfactant concentration as well as for indication of titration end point. Potentiometric surfactant sensors mostly utilize the ion-pair formation or complexation reactions occurring between the analyte and membrane components in the liquid [2] or plastic,

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

** Corresponding author, e-mail: agatam@chem.uw.edu.pl solvent polymeric [3,4,5] membrane phase of internal solution containing arrangement. Thus sensors for anionic, non-ionic and cationic surfactants were obtained [1]. All-solid-state electrodes: coated wire construction [6,7,8] and conducting polymer electron-to-ion transducer based potentiometric sensors [9], especially attractive from practical application point of view, were also of interest. In general, calibration graphs obtained after conditioning in surfactant solution are Nernstian reaching low detection limit close [8] to 10^{-7} mol/dm^3; however, the analysis is often time consuming and the relative instability of sensor potential is also a significant drawback in many cases [1].

Amperometric methods of electroinactive surfactants determination are in general based on surfactant concentration dependent inhibition of charge transfer reaction of marker species [1]. In this respect, suppression of polarographic maxima was used [10]; however, narrow accessible concentrations range and lack of specificity limit the interest in this approach. Surfactants present in the solutions affect amperometric and cyclic voltammetric responses of electroactive species giving rise to method of determination of anionic, cationic and non-ionic species [11]. Surfactant present in solution also affects the electrochemistry of self-assembled monolayers [12] on gold electrodes or carbon paste electrodes [13] in presence of redox active compounds in solution. The influence of surfactants on capacity [14] or voltammetric responses of controlled growth mercury electrode or mercury [15], gold and platinum [16] ultramicroelectrodes, respectively, has been also reported. These effects can be of analytical importance [16]. The other electroanalytical alternative are direct or indirect tensammetric methods [1,17].

On the other hand, conducting polymers (CP) are continuously reaching much attentions as attractive materials for electrochemical sensor construction. The most promising application of CP from analytical point of view is construction of common ions potentiometric [18–28] or amperometric [29,30] sensors. Quite often the ion-exchange properties of CP films predestinate these materials to be applied as membrane phase [18–25], taking the advantage of electronic conductivity to transmit the analytical signal to measuring device. This approach is especially promising for these CPs, which can be easily deposited on variety of substrates and are characterized with sufficient environmental stability [18–30]. The most severe drawback in this case seems to be susceptibility of synthetic metal phase for ionic and redox interferences [31–37]. Poly(pyrrole), PPy, remains one of the most studied polymer as it can be easily obtained from watery solutions either in anion- or cation-exchanging form, and moreover, it is characterized with relatively good environmental stability.

However, much research has been done in the area of interfering effects of different species on electrochemistry of conducting polymer films, the influence of surfactants present in solution, to authors best knowledge, was not considered earlier. Thus, the reason of this study was to investigate the surfactants effect on electrochemical responses of conducting polymer poly(pyrrole) films. Both anion- and cation-exchanging conducting polymers, poly(pyrrole) doped with chloride anions or hexacyanoferrate ions, respectively were tested. To study the effect of surfactant charge as model surfactants species: anionic surfactant – sodium salt of dodecylobenzenesulfonic acid (NaDBS), non-ionic surfactant – Triton X 100 and cationic one – cetyltrimethylammonium chloride (RNCl) were applied.

EXPERIMENTAL

Reagents. Distilled pyrrole was stored in a refrigerator and prior to use was purified by passing through a home made alumina gel mini-column. Doubly distilled and freshly deionized water (resistance 18.2 MΩcm, Milli-Qplus, Millipore, Austria) was used throughout this work. Used salts were of analytical grade.

Apparatus and electrodes. In the open circuit potentiometric experiments a multi-channel data acquisition setup and software, Lawson Labs. Inc. (3217 Phoenixville Pike, Malvern, PA 19355, USA) was used. In other electrochemical measurements galvanostat-potentiostat CH-Instruments model 660A (Austin, TX, USA) was applied. The Ag/AgCl in KCl gel (1 M) reference electrode (Detektor, Raszyn, Poland) was used. Platinum sheet of area 2 cm^2 served as counter electrode. Glassy carbon disc electrodes used (area 0.07 cm^2) were polished with Al_2O_3, 0.3 μm, unless otherwise stated. The electrochemical quartz crystal microbalance (EQCM) apparatus applied in the studies is based on electronic design described in [38] and was constructed in Institute of Physical Chemistry (Warsaw) [39]. AT-cut quartz crystals (Phelps Electronics, Goleta, USA) of 5 MHz nominal resonant frequency and 14 mm in diameter were used as mass sensitive oscillators.

Preparation of conducting polymer films. Conducting polymer films were obtained in course of electrochemical deposition from aqueous solution: 0.2 M pyrrole and 0.1 M NaCl to yield poly(pyrrole) doped with chloride anions – PPyCl; 0.1 M pyrrole and 0.5 M $K_4Fe(CN)_6$ to yield poly(pyrrole) doped with hexacyanoferrate anions – PPyFeCN. Poly(pyrrole) layers were electrodeposited potentiostatically at 1.0 V, the polymerization charge was 1.43 C cm^{-2} for PPyCl and 2.15 C cm^{-2} for PPyFeCN (in the latter case 1/3 of the polymerization charge is consumed by doping anion oxidation [40]), with the exception of PPyCl layers used in crystal quartz microbalance studies when polymerization charge was equal to 0.1 C cm^{-2}. Obtained films after polymerization were thoroughly rinsed with deionized water, transferred to 0.1 mol/dm^3 NaCl solution and polarized under conditions of cyclic voltammetry (within the range from –0.5 to 0.5 V, scan rate 50 $mV\cdot s^{-1}$; 5 scans were applied). Thus obtained films were used in amperometric/voltammetric experiments. Films to be used in open circuit experiments were, after above described procedure, conditioned overnight in 0.1 mol/dm^3 NaCl solution. Each film was studied in one surfactant only, the concentration of surfactant was changed from low to high.

RESULTS AND DISCUSSION

Electrochemistry of poly(pyrrole) films in the presence of surfactants in solution. Surfactants species are known to affect the electrochemical responses of redox probes (markers) present in the solution. Electronically conducting polymer film, electrodeposited on substrate electrode is the redox active marker itself. The reduction and oxidation processes of CP are related to ion-exchange occurring at the polymer solution interface. It could be expected that surfactant present in solution would affect the ion exchange, thus leading to alteration of electrochemical responses of conducting polymer films. It was anticipated that the magnitude of effect would be related to (i) ion-exchange properties and (ii) charge of surfactant present in solution. The results of cyclic voltammetric studies are presented in Fig. 1 and Fig. 2.

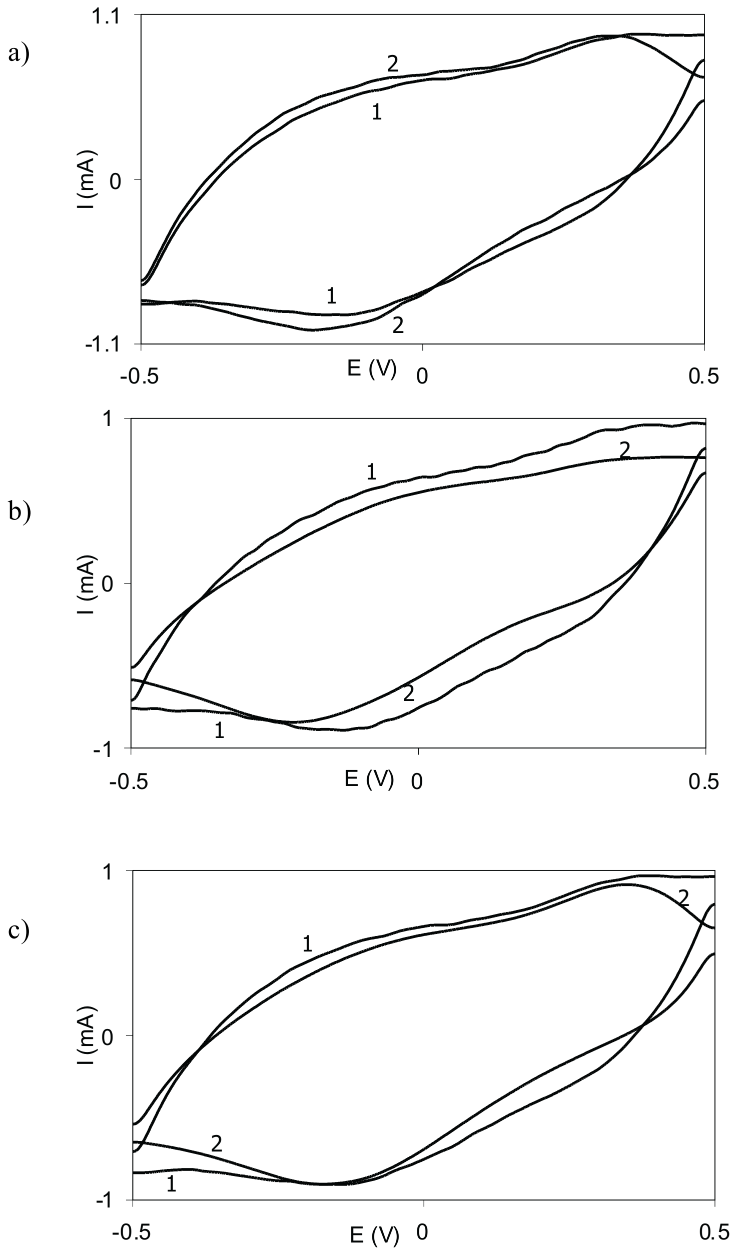

Figure 1. The cyclic voltammograms recorded for PPyFeCN films in 0.1 M NaCl solutions (1) or 0.1 M NaCl spiked with surfactant to concentration 10^{-3} mol/dm^3 (2): a) anionic surfactant – sodium salt of dodecylobenzenesulfonic acid (NaDBS), b) non-ionic surfactant – Triton X 100, c) cationic surfactant – cetyltrimethylammonium chloride (RNCl). Applied scan rate 50 mV/s, stable 5th cycle is presented.

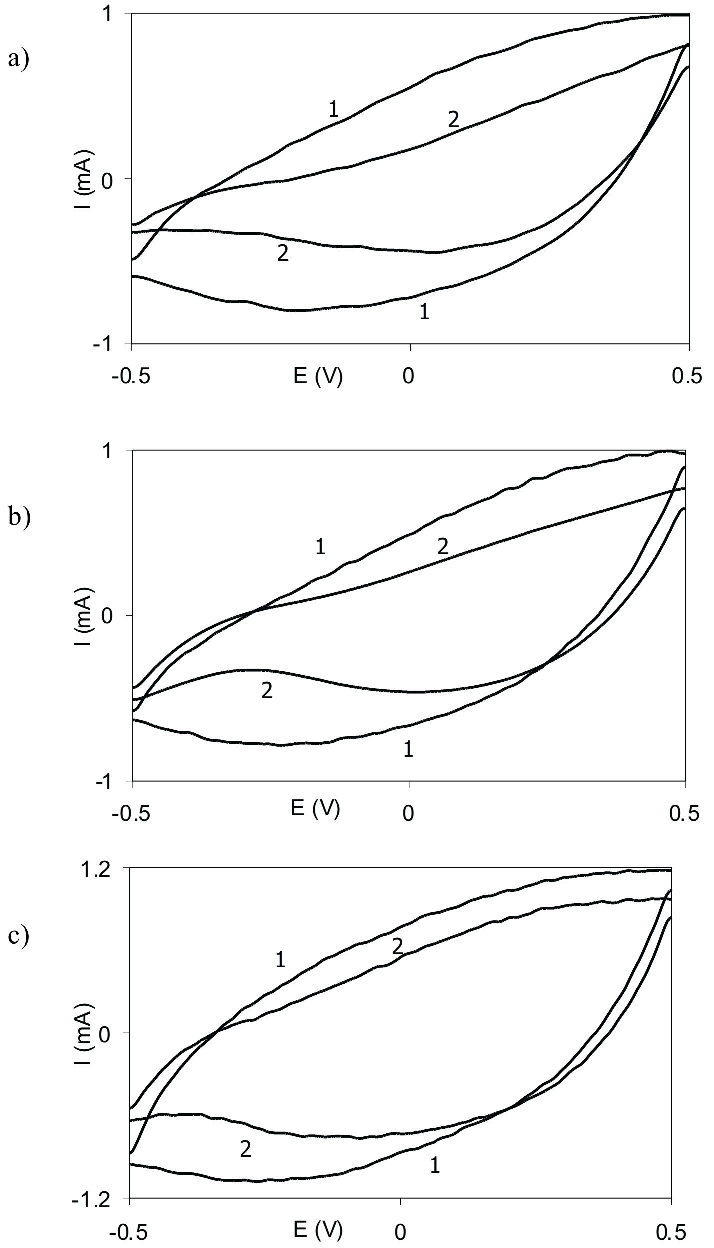

Figure 2. The cyclic voltammograms recorded for PPyCl films in 0.1 M NaCl solutions (1) or 0.1 M NaCl spiked with surfactant to concentration 10^{-6} mol/dm^3 (2): a) anionic surfactant – sodium salt of dodecylobenzenesulfonic acid (NaDBS), b) non-ionic surfactant – Triton X 100, c) cationic surfactant – cetyltrimethylammonium chloride (RNCl). Applied scan rate 50 mV/s, stable 5th cycle is presented.

Fig. 1 presents responses obtained for cation-exchanging PPyFeCN films in presence of 0.1 M NaCl. The obtained voltammograms were typical for this CP film [23,36]. Conducting polymer redox process broad peaks (not well developed, since within tested potential range the polymer is in partially oxidized form) were accompanied with humps attributed to redox process of hexacyanoferrate ions (at –0.2 V and 0.4 V) retained in polymer matrix, these were separated with *c.a.* 0.5 V, gap. When electrolyte solution was spiked with surfactant to concentration 10^{-3} mol/dm^3, recorded curves were practically unaffected. Neither the conducting polymer nor hexacyanoferrate dopant electroactivity was inhibited by presence of any of the tested compounds in solution, regardless charge of surfactant molecule.

Fig. 2 presents voltammograms obtained in parallel experiment conducted for anion-exchanging, PPyCl poly(pyrrole) films. In the absence of surfactants in the solution, *i.e.* in sodium chloride solutions typical voltammograms, characterized with not well developed, broad polymer backbone oxidation and reduction peaks were recorded. Significantly different picture was obtained in NaCl solutions spiked with surfactants, Fig. 2. As it can be seen all tested surfactant presents in solution in the concentration of $1 \cdot 10^{-6}$ mol/dm^3 exert profound effect on recorded voltammograms. For all model compounds tested, regardless charge of surfactant molecule, currents recorded both in anodic and cathodic range were significantly lower compared to those obtained in pure supporting electrolyte. The lower currents obtained point out to hindered ion-exchange occurring at the CP solution interface in the presence of surfactant. In the case of anion-exchanging poly(pyrrole) the inhibition effect was observed not only for anionic surfactant but also for cationic one, and even more surprisingly for non-ionic compound tested. These results were quite unexpected since although in general poly(pyrrole) films are known to be not-permselective, cations present in solution influence both voltammetric and potentiometric responses of anion-exchanging PPyCl film only to limited extent [33,34].

It is interesting to follow the effect of increasing concentration of surfactant present in solution, within range from 10^{-7} to 10^{-2} mol/dm^3, on cyclic voltammograms recorded for both poly(pyrrole) films tested. In Fig. 3a and 3b, exemplary results obtained for anionic surfactant, NaDBS, present in solution are shown. Results obtained for cation-exchanging film, PPyFeCN, as expected, point out that increasing concentration of surfactant in solution, within the range of experimental error, has no significant effect on recorded voltammetric responses of the layer, Fig. 3a. This conclusion was fully supported by experiments with non-ionic and cationic surfactants present in solution.

However, a different picture was obtained for anion exchanging film, PPyCl, Fig. 3b. When the surfactant in concentration as low as 10^{-7} mol/dm^3 was introduced into the background electrolyte, a significant effect on recorded current within the whole range of potential of electrochemical activity of CP is observed. Further increase of surfactant concentration has resulted in even more dramatic change of voltammogram recorded. For 10^{-4} mol/dm^3 NaDBS in solution the recorded voltammogram does not resemble that usually obtained for conducting polymer, further increase of NaDBS concentration to the level of 10^{-2} mol/dm^3 has resulted in practically electrochemically inactive layer of poly(pyrrole).

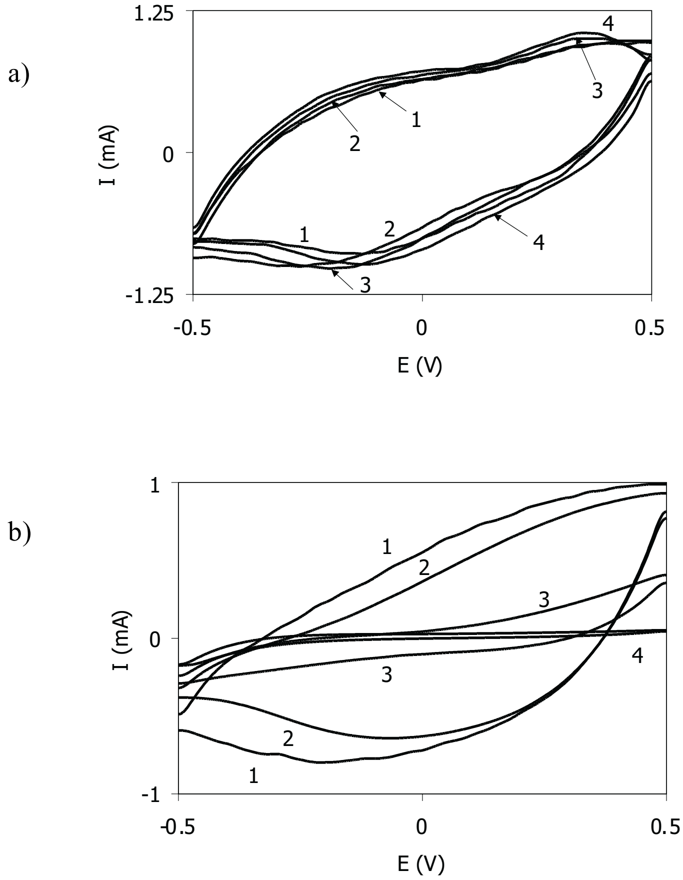

Figure 3. The cyclic voltammograms recorded for a) PPyFeCN and b) PPyCl films in the presence of background electrolyte 0.1 M NaCl and increasing surfactant concentration: 1 – 0.1 mol/dm^3 NaCl, 2 – 0.1 mol/dm^3 NaCl + 10^{-7} mol/dm^3 NaDBS, 3 – 0.1 mol/dm^3 NaCl + 10^{-4} M NaDBS, 4 – 0.1 mol/dm^3 NaCl + 10^{-2} mol/dm^3 NaDBS. Applied scan rate 50 mV/s, stable 5th cycle is presented.

It is worth noting that observed inhibition effect was irreversible, *i.e.* when the polymer film tested in surfactant containing solution was rinsed and transferred to a new portion of NaCl solution, the initial responses, typical for poly(pyrrole) film tested in NaCl solution, were not regained. This observation was common for all tested surfactants.

The above presented effect points out to incorporation (predominantly in the case of ionic surfactant molecule) and/or adsorption (especially in the case of non-ionic one) on the surface or within the structure of electroactive anion-exchanging polymer film. For cation-exchanging CP, despite the fact that concentration of surfactatants tested was 10^3 times higher, the inhibition effect was not observed. It should be stressed that CP films despite different ion-exchange properties are characterized with the same mechanism of susceptibility for redox [37] or divalent ions interferences [36].

To further study the effect of surfactant interactions with PPyCl film, the electrochemical quartz crystal microbalance studies were conducted. Results are presented in Fig. 4. As it can be seen from Fig. 4, in the absence of surfactant both voltammogram and frequency changes recorded were typical for poly(pyrrole) films. The oxidation of the polymer was accompanied with frequency decrease pointing to increase of polymer mass, which can be interpreted as incorporation of solution (Cl^-) anions. Upon reduction scan frequency was gradually increasing, pointing to polymer mass decrease and expulsion of mobile chloride dopants.

When NaCl solution was spiked with anionic surfactant to reach 10^{-4} mol/dm^3 level, Fig. 4b, even the first voltammogram recorded was significantly altered. The following scans show gradual decrease of current attributed to oxidation of conducting polymer backbone. The shape of the part of the curve recorded for positive potentials was also affected: the well-developed peak of polymer oxidation was disappearing. On the part of the curve corresponding to negative potentials the broad peak was observed at *c.a.* –0.65 V; however, the currents were slightly decreasing with cycling progressing. It should be stressed that voltammetric responses of PPyCl films were followed within the potential range from –0.5 V to 0.5 V, *i.e.* in the range where cation-exchange behavior was not exposed. This peak can be attributed to cation exchange occurring between in principle anion-exchanging film and solution, and in the case of responses recorded in NaCl solution (unspiked with surfactant) it was characterized with significantly lower currents than peaks related to anion exchange. The frequency changes response corresponding to above presented voltammogram evolution points out to significant change in conducting polymer mass, Fig. 4c. Upon first scan towards positive potentials a frequency decrease was observed pointing to incorporation of anions to the film structure. It should be stressed that the overall frequency change for the potential change from –0.8 V to 0.5 V recorded in the presence of surfactant was lower than for the experiment conducted in unspiked NaCl solution. This effect points out that in the presence of surfactants in solution changes occur mainly at the CP/solution interface, *i.e.* at the polymer surface, not in the bulk of the CP as for Cl^- exchange in the absence of surfactants in solution. Moreover, in the presence of surfactants the frequency decrease was observed even at potentials more negative than –0.2 V, *i.e.* in the range where in NaCl solution no changes were recorded. Over the reverse scan frequency increase was observed for the potential range from 0.5 V to –0.45 V pointing to decrease of polymer mass possibly due to expulsion of doping anions. For potentials range from –0.5 V to –0.8 V the frequency decrease was recorded pointing to increase in polymer mass. This effect can be attributed to irreversible incorporation of surfactant anions into/on to polymer film, especially since the initial frequencies in the cathodic potential range were not regained. The latter is in good accordance with above described voltammetric response, supporting the conclusion of increased effect of cation exchange upon contact of polymer film with surfactant containing solutions.

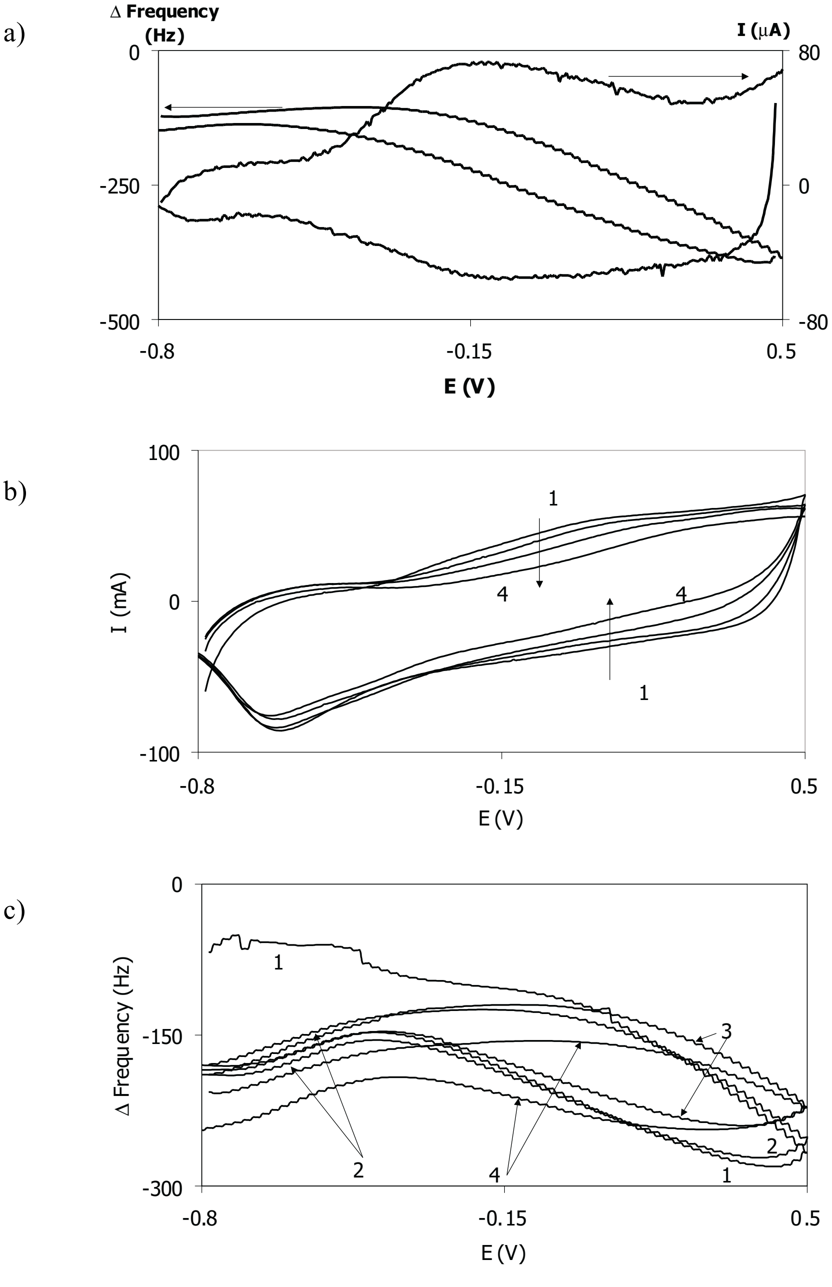

Figure 4. The potential and frequency changes accompanying change of the PPyCl potential within the range from –0.8 V to 0.5 V with scan rate 20 mV/s a) in 0.1 M NaCl solution in absence of surfactant in solution and b) potential and c) frequency changes in 0.1 mol/dm^3 NaCl in the presence of 10^{-4} mol/dm^3 anionic surfactant NaDBS, numbers correspond to the scan number.

Interestingly, the frequencies change corresponding to the second scan, except the negative potentials range on the anodic part of scan, was much resembling that recorded for the first scan. However, frequencies responses accompanying further cycling: third and fourth were pointing to further limitation of ions expulsion from the film upon oxidation and increasing ion incorporation upon reduction. Thus, the gradual transformation from anion-exchanging layer to cation-exchanging one was observed. It should be stressed that overall frequency changes were also significantly smaller, and the frequencies were lower, thus pointing to general inhibition of ion-exchange between polymer and solution coupled with polymer film mass increase due to irreversible binding of surfactant.

It is interesting to speculate on the mechanism of the observed interactions between the PPyCl film and surfactant in solution. In our opinion, it is likely that surfactant molecules are attracted by the polymer surface, even at quite negative potentials where the film is in reduced state. Although the nature of these interactions is obscure, they can be referred to as specific, since occur in the presence of profound excess of Cl^- ions present in solution. This statement is in our opinion justified by the results of frequency changes reported above. It is probable that this effect is independent of surfactant charge but related to polymer film surface morphology or polymer film lipophilicity. These speculations seem to be probable taking into account that hexacyanoferrate doped polymer, characterized with different morphology and being hydrophilic within the whole potential range due to presence of immobilized dopants, was resistant to surfactant interference at 10^3 higher concentration compared to PPyCl film. Upon reduction of PPyCl films in surfactant containing solution expulsion of Cl^- occurs, the polymer film becomes hydrophobic and then possibly more susceptible for surfactant accumulation. However, due to surfactant present at the polymer/solution interface, incorporation of the dopant on the reverse scan is hindered, similarly as it was reported earlier for poly(pyrrole) films doped with dodecylsulphate anions [37]. Incorporation of bulky surfactant molecule, regardless its charge, to the CP structure is rather doubtful. Further scans contribute to continuous increase of polymer mass. If the saturation level with surfactant is reached – upon long enough contact time or high enough surfactant concentration in solution – the ion exchange cannot occur. Thus, the electroactivity of the poly(pyrrole) layer is lost, as pointed out by the results presented in Fig. 3b. It should be stressed that CP-surfactant binding is quite strong, as the initial responses of the film cannot be regained.

From the point of view of practical application of CP it is essential to distinguish experimental conditions of more severe and lowerer interfering effect of surfactant on electrochemistry of CPs. This brings in to experiments question of kinetics of surfactant and poly(pyrrole) film interactions.

The role of kinectics of the surfactant – CP interactions can be exposed by changing the time scale of the experiment. Thus the AC voltammetic studies were undertaken within the wide range of frequencies.

The AC voltammetry experiments (measuring absolute current with no phase selectivity) were conducted for PPyCl film, the exemplary results obtained for NaDBS are presented in Fig. 5. As it can be seen for NaCl solution, the magnitude of AC current was slightly higher for shorter contact times (higher frequencies), which is in good accordance with previous reports [30]. For NaCl solution containing 10^{-6} mol/dm^3 or 10^{-3} mol/dm^3 NaDBS, *i.e.* for concentration resulting in significant alteration of voltammetric curves, the inhibition of the current observed was significantly dependent on frequency applied. This effect was especially pronounced for higher concentration of surfactant. For extremely short contact times (< 10^{-4} s, frequencies near to 10000 Hz) the recorded AC absolute current was practically insensitive to the surfactant concentration. The rate of surfactant adsorption/desorption is low compared to experiment time scale (10^{-4} s for one cycle). On the other hand, for frequencies lower than 100 Hz, especially lower than 1 Hz, the influence of surfactant is profound, resulting in very low AC current recorded.

These results enable choice of appropriate time scale for analytical application of CP films: long time scale (corresponding to low frequencies) is suited for surfactant determination, whereas short experiment times are advisable for amperometric determination of ions in the presence of surfactants interferents.

Analytical applications. The above discussed voltammetric responses of CP in surfactant containing solutions can add value to construction of analytical sensors based on poly(pyrrole) films. Not only the time scale of the measurement but also the kind of doping anion applied affects the responses to surfactants concentration changes. To obtain sensor relatively robust for surfactant interferences cation-exchanging PPyFeCN films are especially suited. On the other hand, strong inhibition of electroactivity of anion-exchanging PPyCl layer, predestinates it to be applied as surfactant sensitive probe.

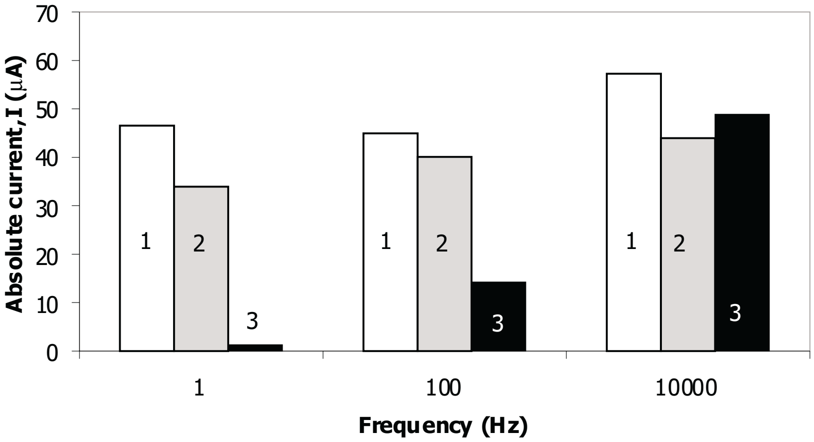

Figure 5. The dependence of current recorded under AC voltammetry conditions at potential equal to –0.5 V on the frequency of potential changes recorded for PPyCl film in: 1) 0.1 mol/dm^3 NaCl, 2) 0.1 mol/dm^3 NaCl + 10^{-6} mol/dm^3 NaDBS, 3) 0.1 mol/dm^3 NaCl + 10^{-3} mol/dm^3 NaDBS.

Figure 6 presents the exemplary amperometric characteristics: current *vs.* log of surfactant concentration obtained under pulse voltammetry conditions for PPyCl films in the presence of model surfactant compounds tested. As it can be seen from Fig. 6, for all surfactants tested, regardless its charge, the inhibition of electrochemical processes has resulted in current decrease recorded for increased surfactant concentration in solution. Interestingly, the highest sensitivity was obtained for NaDBS solutions. Close to linear dependencies were obtained for Triton and RNCl within the concentrations from 10^{-7} to 10^{-4} mol/dm^3, for NaDBS solution the high concentration detection limit was shifted to concentration equal to 10^{-3} mol/dm^3. As expected on the ground of above described experiments for higher concentrations of tested surfactants in solution the electroactivity of PPyCl is lost, resulting in detection limit of the sensors. In this set of experiment the applied pulse duration time was equal to 20 ms, which corresponds – under conditions of AC voltammetry – to frequency close to 50 Hz. Thus in accordance with results presented in Fig. 5, surfactans in solution interfere with CP film.

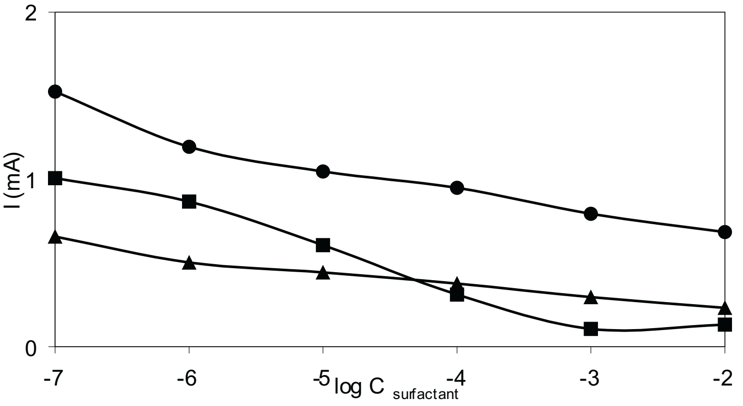

Figure 6. The amperometric dependencies obtained under pulse conditions of pulse voltammetry, pulse time equal to 20 ms, recorded for PPyCl film. Currents were recorded in 0.1 M NaCl and read at 0.5 V: (▲) Triton, (■) NaDBS, (●) RNCl.

Apart from surfactant determination, as pointed by recent reports [30] conducting polymer films can be applied for amperometric sensing of common ions, which are not electroactive within the CP electroactivity potential window. From that application standpoint it is important to study the surfactant interfering effect. To satisfy this need, the effect of model surfactant, NaDBS, presence in solution on current *vs.* concentration dependence was recorded for two arbitrally chosen interferent concentrations: 10^{-6} and 10^{-4} mol/dm^3, for current reading time equal to 5 s. Results obtained for PPyCl are shown in Fig. 7a. In the absence of surfactant in the solution linear dependencies of currents on Cl^- concentration changes were recorded within the concentration changes from 10^{-4} to 10^{-1} mol/dm^3. However, as it can be expected

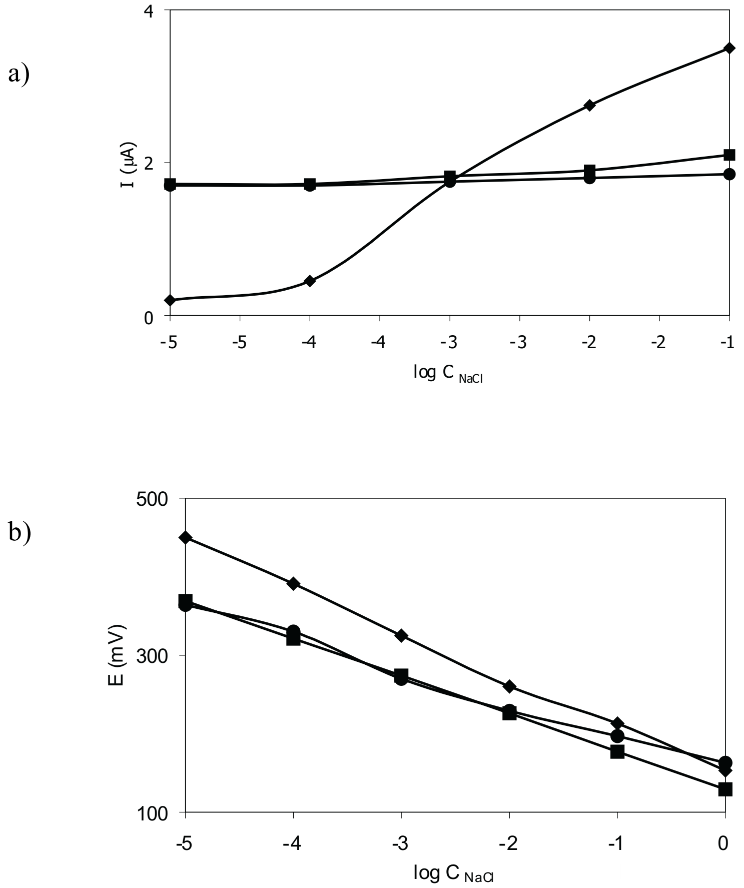

Figure 7. The interfering effect of surfactant present in solution on: a) amperometric (films were initially reduced at –0.5 V for 20 s, then the oxidation at 0.2 V was performed, currents were read at 5 s time) and b) potentiometric dependencies recorded for PPyCl films on changes of NaCl concentrations in absence and in the presence of constant concentration of model anionic surfactant used: (◆) NaCl solutions – in absence of surfactant, (■) NaCl solutions in the presences of 10^{-6} mol/dm^3 NaDBS, (●) NaCl solutions in the presences of 10^{-4} mol/dm^3 NaDBS.

taking into consideration the above presented results of electrochemical studies, presence of surfactant in the concentration 10^{-6} or 10^{-4} mol/dm^3 results in significant interferences. The time scale of this experiment (time 5 s, corresponding to AC frequency below 1 Hz) is sufficiently long to observe surfactant influence.

A different picture was obtained in parallel experiment conducted under open circuit, potentiometric conditions. In the absence of surfactant, a typical anionic potentiometric dependence was obtained, characterized with Nernstian slope equal to -59.9 ± 1.4 mV/dec ($R^2 = 0.998$). In the presence of surfactant in solution, in constant concentration 10^{-6} or 10^{-4} mol/dm^3 the linear responses obtained were characterized with slopes lower than Nernstian equal to –48.0 ± 0.1 mV/dec ($R^2 = 0.999$) and –41.3 ± 2.1 mV/dec ($R^2 = 0.989$), respectively. It should be stressed that although in potentiometric experiment the time scale is relatively long, the effect of surfactant is less pronounced compared to amperometric experiment described above. It seems probable that under conditions of potentiometric experiment an equlibrium at the polymer/solution interface is reached and is reflected by stable membrane potential recorded. Thus, the effect of surfactant is less severe. Moreover, it should be stressed that under potentiometric conditions the polymer film is in semi-oxdized state, *i.e.* it is rather hydrophilic continuously throughout experiment. Therefore, it is less susceptible for surfactant interferences compared to amperometric experiment, where reduction of CP (leading to hydrophobic film) is necessary. The potentiometric anion determination is less affected by presence of surfactant in solution compared to amperometric mode.

CONCLUSIONS

The effects of anionic, non-ionic and cationic surfactants in solution on poly(pyrrole) films using different electrochemical techniques were studied. Anion-exchanging films are good candidates to construct surfactant sensitive probes, using inhibiting effect of surfactant on electrochemical responses of CP films. The 10^{-7} mol/dm^3 concentration of anionic, cationic as well as non-ionic surfactant gives rise to analytically useful signal. The amperometric responses can be obtained within milliseconds to seconds time scale. The sensitivity of poly(pyrrole) membranes for common anion concentration changes in solution is also significantly interfered by presence of surfactant in solution under both amperometric and potentiometric conditions. On the other hand, cation-exchanging poly(pyrrole) films doped with hexacyanoferrate ions are resistive to surfactant present in solution in 10^{-3} mol/dm^3 concentration. Thus, these membranes seem to be good choice for robust for surfactant interferences ionic sensors.

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