Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 44 (2003) 4205–4211

polymer

www.elsevier.com/locate/polymer

Preparation, characterization and taste sensing properties of Langmuir–Blodgett Films from mixtures of polyaniline and a ruthenium complex

M. Ferreira[a,*], C.J.L. Constantino[b], A. Riul Jr[b], K. Wohnrath[a], R.F. Aroca[d], J.A. Giacometti[b], O.N. Oliveira Jr[a], L.H.C. Mattoso[c]

[a]*Instituto de Física de São Carlos, Universidade de São Paulo, Av. Trabalhador São Carlense 400 CP 369, 13566-590 São Carlos, SP, Brazil*
[b]*Faculdade de Ciências e Tecnologia, Universidade Estadual Paulista, CP 467, 19060-900 Presidente Prudente, SP, Brazil*
[c]*EMBRAPA Instrumentação Agropecuária, CP 741, 13560-970 São Carlos, SP, Brazil*
[d]*Materials and Surface Science Group, University of Windsor, N9B 3P4 Windsor, ON, Canada*

Received 16 January 2003; received in revised form 1 May 2003; accepted 5 May 2003

Abstract

Langmuir–Blodgett (LB) films from a ruthenium complex, *mer*-[RuCl$_3$(dppb)(py)] (dppb = PPh$_2$(CH$_2$)$_4$PPh$_2$; py = pyridine) (Rupy), and from mixtures with varied amounts of polyaniline (PANi) were fabricated. Molecular-level interactions between the two components are investigated by surface potential, dc conductivity and Raman spectroscopy measurements, particularly for the mixed film with 10% of Rupy. For the latter, the better miscibility led to an interaction with Rupy inducing a decrease in the conducting state of PANi, as observed in the Raman spectra and conductivity measurement. The interaction causes the final film properties to depend on the concentration of Rupy, and this was exploited to produce a sensor array made up of sensing units consisting of 11-layer LB films from pure PANi, pure Rupy and mixtures with 10 and 30% of Rupy. It is shown that the combination of only four non-specific sensing units allows one to distinguish the basic tastes detected by biological systems, viz. saltiness, sweetness, sourness and bitterness, at the μM level.

Keywords: Polyaniline; Ruthenium complex; Langmuir–Blodgett films

1. Introduction

Langmuir–Blodgett (LB) films of ruthenium complexes have shown remarkable properties that are only observed in organized thin films [1–3]. For the ruthenium complex, *mer*-[RuCl$_3$(dppb)(4-Mepy)] (dppb = PPh$_2$(CH$_2$)$_4$PPh$_2$; 4-Mepy = 4-methylpyridine) (Rupic), for example, electroactivity is observed in LB films whereas these properties are absent in spin-coated (or cast) films [1]. When mixed with other materials, e.g. stearic acid or polyaniline (PANi), molecular-level interaction renders unique properties to the resulting films [2,3]. Advantage has been taken from such interactions to improve the stability of electrical properties of PANi films [4]. LB films from ruthenium complexes are also promising for new materials for electrocatalysis, electroanalysis and photoelectrochemistry. Examples are functionalized polypyrrole films containing transition-metal complexes that have been synthesized and characterized using electrochemical techniques [5–8].

In a previous paper [4], we investigated interactions between Rupy ((mer-[RuCl$_3$(dppb)(py)] (dppb = PPh$_2$(CH$_2$)$_4$PPh$_2$; py = pyridine)) and PANi in both Langmuir monolayers and transferred LB films. Surface pressure and surface potential measurements were employed for the monolayer characterizations, while the deposited LB films were characterized using vibrational spectroscopy, spectro-electrochemical and cyclic voltammetry. The results showed that pure PANi, pure Rupy and mixtures of PANi/Rupy form non-monomolecular structures at the air–water interface [4] while the incorporation of Rupy in mixed LB films could be inducing the oxidation of PANi, resulting in an electroactivity loss. Cyclic voltammetry results could not elucidate PANi oxidation by the ruthenium complex since the oxidation peaks of Rupy are at anodic potentials that could only be reached if PANi was over-oxidized. In this paper, we further investigate the interactions occurring between PANi and Rupy using Raman spectroscopy,

---

* Corresponding author. Tel.: +55-16-273-9825; fax: +55-16-271-5365.
E-mail address: mstela@if.sc.usp.br (M. Ferreira).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00388-4

surface potential and dc conductivity of pure and mixed LB films containing different Rupy percentages. In addition, we exploit the distinct properties for LB films with different amounts of Rupy in establishing a sensor array that is capable of detecting tastants at a level that is considerably lower than the human threshold. The high sensitivity is due to the ultrathin nature of the film, similarly to what has been reported in other works [9–11]. In this context, mention should be made of LB films from metallic complexes with sensing capability based on various physical principles [12]. Included in these are LB films from porphyrin and phthalocyanine-based compounds. Here we employ impedance spectroscopy as it is a powerful tool in the investigation of the interactions between the analytes and the sensor materials [11]. In addition, it has been proven advantageous because it does not require a reference electrode as in other methods, which might be troublesome in miniaturized systems where obtaining a reliable reference is a serious problem.

2. Experimental details

Dedoped PANi (emeraldine base, $y = 0.5$ in Fig. 1) was synthesized as described in Ref. [13], while the complex, Rupy, was synthesized according to the procedures in Ref. [14]. The structures of these compounds are shown in Fig. 1. The Langmuir and LB films were fabricated using PANi in its doped form (emeraldine salt, $y = 0.5$ in Fig. 1). Basically, PANi was dissolved in camphor sulfonic acid (CSA), *m*-cresol and chloroform (under sonication for ca. 2 h). This mixture was then filtrated to remove undissolved PANi, probably the higher molecular weight fractions, while Rupy was dissolved in chloroform. The PANi–Rupy mixed solutions with 10, 30 and 50% in mol of Rupy were prepared immediately prior to being spread onto an acidic subphase, pH = 2.0 (HCl), used to keep the PANi in its doped state. The ultrapure water is supplied by a Milli-RO60 reverse osmosis cartridge feeding a Milli-Q system. Surface pressure–area (π–A) and surface potential–area (ΔV–A) isotherms for Langmuir, as well as LB film deposition, were carried out with a KSV-5000 LB system mounted in a class 10,000 clean room. Surface potential measurements of the monolayers were carried out with a Kelvin probe provided by KSV. LB films were produced by transferring pure PANi, pure Rupy and mixed PANi/Rupy monolayers onto several substrates (glass, gold or ITO (indium–tin-oxide)-coated glass (Asahi Glass Co., Japan)). The typical dipping speed was 3 mm min^{-1}, with 30 min elapsing between the first and the second layer and 5 min for the subsequent layers when the substrate was out of the aqueous subphase. Y-type LB films were produced by transferring the Langmuir films at a fixed surface pressure of 17 mN m^{-1}, for PANi and mixed films, and of 15 mN m^{-1} for Rupy. The presence of the Rupy complex brings the transfer ratio close to one for the LB films, similarly to the effect widely reported for fatty acids.

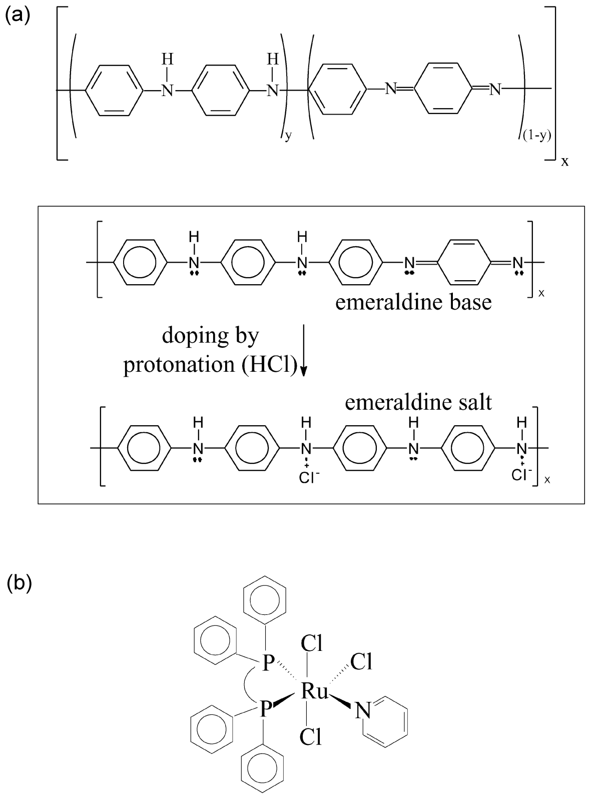

Fig. 1. Structural formulas of the materials used: (a) polyaniline, PANi with y reduced and $(1 - y)$ oxidized units as well as its primary doping by protonation when in the emeraldine form; (b) complex *mer*-[RuCl$_3$-(dppb)(py)], Rupy.

For the surface potential and dc electrical conductivity measurements of LB films, thin (100 nm) gold-evaporated BK7 glass substrates were used. They were washed with ultrapure water prior to deposition. Surface potential measurements were conducted for 41-layer LB films using a Trek 320B electrostatic voltmeter in a homemade set-up in which there is provision to scan the whole surface of the film by moving the sample in the X–Y direction. The dc conductivity of 31-layer LB films was measured with the two-point method (film deposited between two gold fingers), with the current versus voltage, I–V, characteristics being obtained with a current source Keithley 220 coupled to a multimeter HP model 34401A. Electric current was usually varied from −5 to +5 nA, but for less conducting samples the range was extended to −15 up to +15 nA. There is no need to evaporate a metal electrode on top of the LB film with this configuration, avoiding possible pinhole effects.

LB films were deposited onto ITO (Asahi Glass Co.) for Raman measurements. The Raman scattering spectra (Stokes) were recorded with a Renishaw Research Raman Microscope System RM2000 equipped with a Leica microscope (DMLM series). The 50× -microscope objective was used to focus the laser beam onto a spot of ca. 1.0 μm^2. The Raman spectrum was recorded using a Peltier cooled (−70 °C) CCD array detector and a spectrograph equipped with a 1200 g/mm grating, which allows collecting the spectra with ca. 4 cm^{-1} resolution. The high throughput of the instrument permits the use of very low power lasers at the sample such as 2 μW for the 780 nm laser line used here. Raman data acquisition and analysis were carried out using the WiRE software for Windows and Galactic Industries GRAMS/32™ C software including the 3D package. LB films, also 41 layers, onto ITO were characterized by X-ray diffraction using a Rigaku Rotaflex RU 200-B, with a tube voltage of 100 kV and tube current of 50 mA.

Four sensing units were obtained by depositing 11-layer LB films of pure Rupy, pure PANi and a composite 10 and 30% Rupy in PANi, respectively, onto gold interdigitated structures comprising 50 digits [11,10]. The LB films were transferred by the vertical method at a dipping speed of 3 mm min^{-1} during both up and down strokes with a near unity transfer ratio. The ac electrical conductivity measurements of these sensing units immersed in liquid samples were carried out with a Solartron model 1260 impedance/gain phase analyzer at 1 kHz. After each measurement, the electrodes were washed with copious amounts of ultrapure water. Each experiment was repeated at least three times to check reproducibility. The standards for the various tastes were 8 μM aqueous solutions of NaCl (salty), sucrose (sweet), HCl (sour) and quinine (bitter) prepared in ultrapure water.

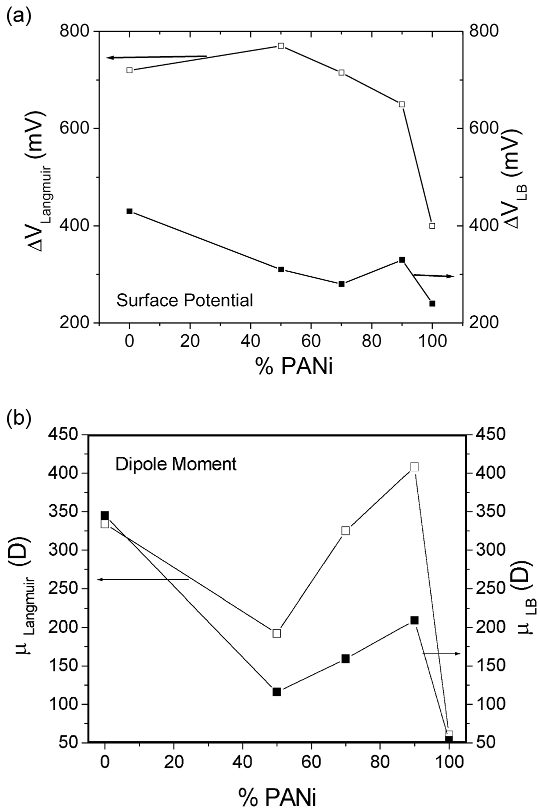

Fig. 2. (a) Surface potential and (b) dipole moment for Langmuir films ($\Delta V_{\text{Langmuir}}$ and μ_{Langmuir}, respectively) and 41-layer LB films (ΔV_{LB} and μ_{LB}, respectively) of neat PANi, neat Rupy and 10, 30 and 50% of Rupy in PANi. The LB films were deposited onto gold/glass substrates.

3. Results and discussion

3.1. Electrical and spectroscopic characterization of LB films from PANi/Rupy mixtures

The properties of Langmuir and LB films from Rupy, PANi and PANi/Rupy mixtures investigated by surface pressure, surface potential, vibrational and UV–vis absorption spectroscopies and cyclic voltammetry have been discussed in a previous paper [4]. Here we shall concentrate on surface potential measurements, Raman spectroscopy and dc conductivity, with particular emphasis on the effects from changing the relative concentration of Rupy and PANi. Fig. 2a shows the surface potential for both pure and mixed Langmuir films at the condensed phase (ΔV_{L}) and 41-layer LB films (ΔV_{LB}). The ΔV_{L} decreases monotonically, but not linearly with PANi concentration. A linear decrease should be expected if there were separate domains of the two components, without any specific interaction, in the mixed films. Because the area per molecule also varies non-linearly with the amount of Rupy, we shall analyze the apparent dipole moment. The Helmholtz equation given by $\mu = \Delta V_{\text{L}} A \epsilon_0$ was used to calculate the apparent dipole moment (μ). For the Langmuir films, ΔV_{L} is the maximum surface potential, A is the area per molecule and ϵ_0 is the vacuum permittivity.[1] The term 'apparent dipole moment' is used because in the calculation the dielectric constant of the film is taken as unity, whereas it is known that higher values must be employed in order to correlate the measured surface potential values to molecular dipole moments. For instance, in fatty acids the effective dielectric constants of the distinct parts of the monolayer are on average 2.8 for the hydrophobic tails and 6.4 for the hydrophilic headgroups, at the film/water interface [15]. For the Rupy or PANi films investigated here one cannot expect such kind of correlation to estimate the dipole moments from theoretical models. For it is not possible to determine individual normal components of the molecular dipoles of these materials at the air/water interface.

Nevertheless, the estimated dipole moment varies non-linearly and non-monotonically with the amount of Rupy in the mixed films, as shown in Fig. 2b. Surprisingly, a very high dipole moment is observed for the PANi matrix with 10% Rupy, which is outstanding from the other relative concentrations. It is clear that a molecular-level interaction takes place, which is particularly remarkable for the 10% Rupy in PANi. Such interaction is also manifested in the deposited LB films. As shown in Fig. 2b, the dipole moment obtained from the measured surface potential, ΔV_{LB}, for 41-layer LB films, behaves similarly to the dipole moment in the Langmuir film. For the LB films, the dipole moments plotted were calculated assuming that the major

---

[1] We use Debye (D) as the unit for dipole moment. $1\ \text{D} = 3.336 \times 10^{-30}\ \text{C m}$.

contribution comes from the dipoles of the molecules, and also that the area per molecule was not altered during the transfer of the Langmuir film onto the substrate. Lower surface potentials are normally measured for LB films, in comparison to the corresponding Langmuir monolayers, due to the negative contribution from the film/substrate interface [16]. Again, the most striking feature is the value for the 10% Rupy composite film, which is also found in Raman and dc conductivity measurements discussed below.

Fig. 3 shows the Raman spectra for 41-layer LB films obtained from doped PANi and from the mixtures with 10, 30 and 50% of Rupy in PANi obtained with the 780 nm laser line. The spectra are dominated by that of PANi since Rupy has almost negligible Raman activity (results not shown). According to Ref. [17], the two electronic absorption bands located at ca. 463 and 833 nm for PANi are assigned to the radical cation segments. Therefore, for the 780 nm excitation laser line semiquinoid bands are prominent. Here, two factors should be analyzed: (i) the presence of *m*-cresol in LB films and (ii) the effect from Rupy on PANi in LB films. The effect of *m*-cresol on PANi has been well documented by Pereira-da-Silva et al.. [18] and by Cochet et al.. [19] using the Raman spectroscopy as the analysis tool. Pereira-da-Silva et al.. [18] observed that *m*-cresol causes structural and conformational alterations in the PANi polymeric chain, referred to here as secondary doping of PANi. They observed a change from quinoid to semi-quinone structures, with the bands at 1486 (C=N stretching quinoid) and 1580 (C=C stretching quinoid) cm^{-1} becoming weaker due to *m*-cresol treatment while the bands at 1596 (C–C stretching benzenoid) and 1221 (C–N benzene di-amine) only appeared after *m*-cresol treatment. There was also a small shift in the quinoid C–H bending band from 1166 to 1170 cm^{-1} (benzenoid C–H bending) after exposing the film to *m*-cresol, and the coalescence of the bands at 1317 and 1338 cm^{-1} (radical cation $C{-}N^+$ stretching) into a broad band at 1336 cm^{-1} and a shoulder at 1381 cm^{-1}. The bands at 574, 1381 and 1643 cm^{-1} appear weak after exposing the polymer to *m*-cresol, but they become stronger by annealing a primarily doped (by protonation) PANi/CSA sample. The intensity of these bands is not altered significantly in the case of annealing a secondarily doped PANi/CSA/*m*-cresol sample. Pereira-da-Silva et al. [18] attributed this difference to both reticulation (cyclized structures containing tertiary nitrogen) and oxidation (imine segments reacting with oxygen) that should occur especially in annealed PANi/CSA samples. Cochet et al.. [19] observed that exposing cast films to *m*-cresol causes the bands at 1488 and 1520 cm^{-1} to collapse into a wide band around 1500 cm^{-1}. In addition, the bands at 1584 (quinoid C=C stretching [18]) and 1620 cm^{-1} (quinoid C–C stretching [18]) decrease in intensity while the band around 1592 cm^{-1} (benzenoid C–C stretching) increases. It must be mentioned that the band at 1377 cm^{-1} reaches a prominent intensity for an intermediate level of primary doping of PANi using HCl but becomes a shoulder for longer exposition time to HCl [19].

In the results reported here, PANi was processed with *m*-cresol and the monolayers were transferred from an acidic subphase. Previous works showed that *m*-cresol is usually dissolved in the water and that upon transferring the PANi Langmuir film onto a solid substrate *m*-cresol is not transferred [20]. Its presence is nevertheless felt, as a memory effect because the conformation of the PANi molecules in Langmuir films is affected [21]. It is not surprising, therefore, that the spectra in Fig. 3 display bands due to primary doping (PANi doped with CSA), but are dominated by bands associated with secondary doping (with CSA and *m*-cresol), analogously to what was observed in Refs. [18,19,22,23]. With regard to the effect from Rupy on PANi in LB films, it can be inferred from Fig. 3 that 30 and 50% of Rupy in PANi do not seem to affect significantly the doping level of the polymer. However, the incorporation of 10% of Rupy induces important changes in the doping level. For instance, the intensity of the 1482 cm^{-1} band, related to the dedoped PANi (insulating form), increases while bands

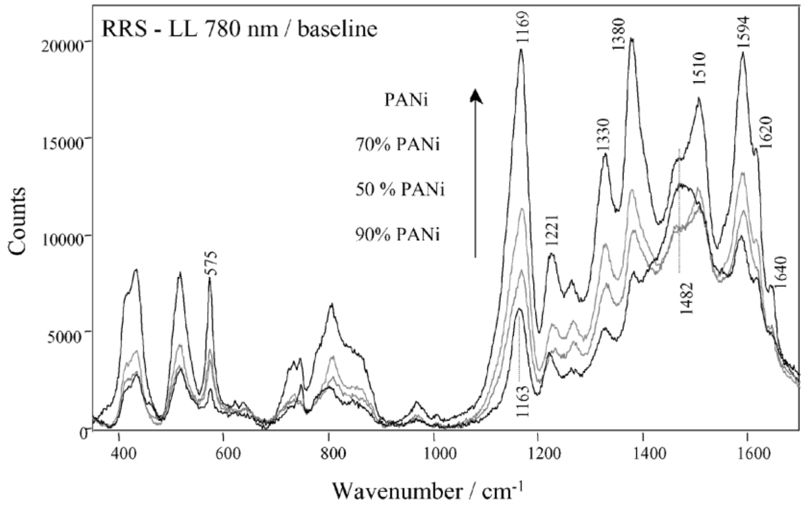

Fig. 3. Resonance Raman spectra ($\lambda_0 = 780$ nm) for 41-layer LB films of neat PANi and 10, 30 and 50% of Rupy in PANi, with baseline correction.

associated with the doped PANi (conducting form) have their intensity decreased.

The dc conductivity measurements are consistent with partial dedoping of PANi promoted by the addition of 10% of Rupy. Fig. 4 shows the dc conductivity of 31-layer LB films from pure Rupy, pure PANi and mixtures of PANi and Rupy at different concentrations. The highest conductivity (10^{-2} S cm^{-1}) is obtained for pure doped PANi. Pure Rupy has a conductivity of ca. 10^{-3} S cm^{-1}. The conductivity decreases sharply for the 10% of Rupy and then increases with the amount of Rupy, approaching the value of pure Rupy. Considering from the Raman spectra results that with 10% of Rupy there are more quinoid species than in the other composite films, a less conducting state should be expected in this film, as observed experimentally. The increase in conductivity for higher % of Rupy seems to indicate that the maximum dedoping of PANi due to the presence of Rupy occurs for 10% of Rupy within the range of concentrations studied. It should be mentioned that the cyclic voltammetry results from Ref. [4] did not indicate a distinctive behavior for 10% Rupy in PANi. The most likely reason for the latter is that the PANi dedoping process that should take place at 10% Rupy is hindered by the acidic electrolyte used (HCl 1 M) during cyclic voltammetry.

The distinctive behavior of the 10% Rupy mixture for both Langmuir and LB films was reported in Ref. [4], but no explanation was put forward. Considering the results presented here we believe that the incorporation of 10% Rupy may allow a better miscibility of Rupy in the PANi matrix, while aggregates are probably formed with the addition of higher % of Rupy in the composite films [3,4], thus leading to phase separation. Indeed, the formation of aggregates was confirmed in subsidiary experiments. For example, after 4 h of preparation of fresh solutions, a greenish precipitate was formed for the 30:70 and 50:50 mol% relative concentrations of Rupy and PANi. However, no precipitate was seen for the mixture with 10% of Rupy. Furthermore, cast films were fabricated using fresh solutions of the three mixtures and only that containing 10% of Rupy in PANi showed a homogeneous aspect (macroscopically). The interaction may consist of dedoping of PANi by 'deprotonation' or oxidation induced by the coordination of the imine nitrogen of PANi to the Rupy metallic center. Both mechanisms could produce more quinoid units in the PANi structure leading to a more insulating form, as suggested by the results reported here and cyclic voltammetry data from a previous work [4]. For low contents of Rupy, deprotonation appears to be predominant since no drastic changes were observed in the spectrum for the films with 10% Rupy when compared with those reported by Pereira-da-Silva [24] for secondarily doped PANi submitted to different potentials. We have also attempted to investigate the structure of PANi/Rupy films. X-ray diffraction data in the 2θ range up to 50° for mixed LB films of PANi/Rupy showed no Bragg peaks. Diffractograms of LB films from pure Rupy did not exhibit Bragg peaks either, which indicates that these films do not display any long-range order [2].

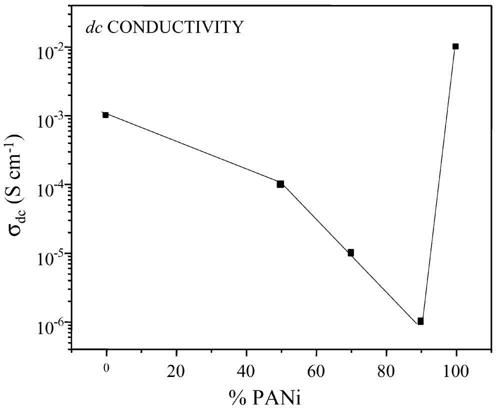

Fig. 4. Conductivity measurements for 31-layer LB films of doped PANi, Rupy and 10, 30 and 50% composite PANi/Rupy films deposited onto gold tracks made on glass substrates.

3.2. Using LB films from PANi/Rupy mixtures as taste sensors

The rationale behind a taste sensor for evaluating tastants and beverages is to achieve a set of combined non-specific sensing units that are able to discriminate the tastes detected by the human tongue [11] (sweetness, saltiness, sourness, and bitterness). Therefore, using LB films from various PANi/Rupy percentages might be handful to build up a simple, cheaper sensor employing only modest amounts of two different materials. Impedance spectroscopy has been chosen as the sensing principle for artificial sensors owing to its advantages compared with other methods reported in the literature [11]. The sensors are modeled with an equivalent circuit [11,10] representing a metal coated by a thin film immersed in an electrolytic solution. The figure of merit employed is the film capacitance at 1 kHz because it reflects better any possible interaction between the LB film and tastants in solution [25].

Fig. 5 shows the data for 11-layer LB films of pure dedoped PANi and Rupy and 11-layer composite films containing 10% Rupy and 30% Rupy. The film from PANi is referred to as dedoped or undoped PANi because in contact with the aqueous solutions analyzed, pH ~ 5.8, PANi becomes dedoped, in spite of being originally doped during the transfer onto the solid substrates. Each film responds differently when in contact with a solution, and such a difference in the electrical signal among the sensing units can be used as a fingerprint to identify the liquid samples [10]. Hence, the phase separation of materials is not a problem in this sort of application as it can be used to combine different electrical responses of the sensing units to form the 'fingerprints'. The capacitance data from Fig. 5 were treated with a mathematical tool, referred to as principal component analysis (PCA), which statistically correlates the samples and reduces the dimensionality of the

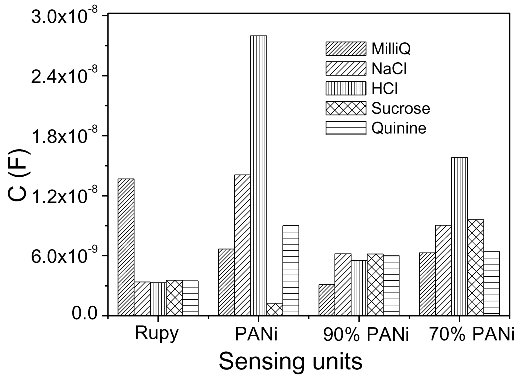

Fig. 5. Capacitance measurements at 1 kHz for different tastants using electrodes coated with 11-layer LB films from pure Rupy, pure dedoped PANi and the mixture with 10% Rupy and 30% Rupy: Milli-Q water and 8 μM of NaCl, sucrose, quinine and HCl.

data set. For the PCA analysis, the experimental results are transformed in a data matrix whose rows correspond to the number of experiments (samples analyzed = objects), while the columns consist of a number of variables, i.e. the sensing units used. A loading plot for the data in Fig. 5 is shown in Fig. 6, which indicates that Rupy is the variable that contributes most for distinguishing the samples along the first principal component, while the mixed film containing 10% Rupy has the major loading on the second principal component.

A score plot in Fig. 7 demonstrates that the sensor array is capable of distinguishing all the tastants. Note that the concentration at 8 μM is considerably below the human limit of detection for saltiness, sweetness and sourness as the threshold values in humans are 10 mM for sucrose and NaCl, 0.9 mM for HCl and 8 μM for quinine [26]. Regarding to selectivity, it should be stressed that a single sensor unit may be unable to distinguish all tastes [27]. For example, the capacitance for the Rupy film is almost the same for sucrose, quinine, HCl and NaCl in Fig. 5. On the other hand, PANi is selective for the substances analyzed, but the inclusion of less-selective sensing units does not hamper the sensor ability to distinguish samples. On the contrary, the combination of LB films with various relative concentrations of Rupy and PANi has been proven promising.

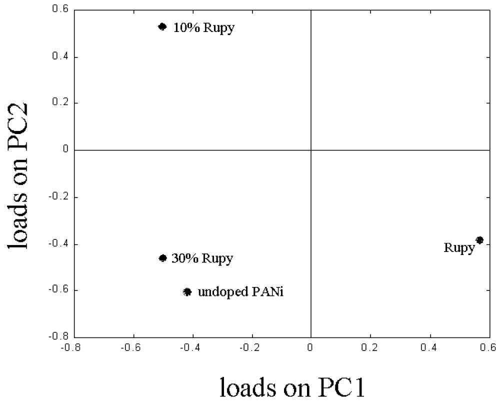

Fig. 6. Loading plot of the sensor immersed in the liquid systems described in Fig. 5.

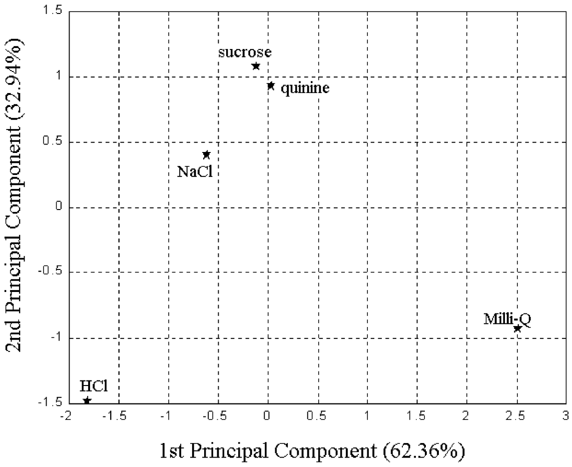

Fig. 7. Principal component analysis (PCA) using the sensing units composed by pure dedoped PANi, pure Rupy, 10 and 30% Rupy composite films, and the bare interdigitated immersed into the different solutions (Milli-Q water and 8 μM of NaCl, sucrose, quinine and HCl) whose capacitance values were collected at 1 kHz.

It is clear that the distinguishing ability of sensor arrays such as the one reported here is not associated with specific interactions of a given material and the analytes. This explains why films from diverse materials may be employed in taste sensors using impedance spectroscopy as the physical principle [10,11]. The only requirements are that the materials in the sensing units should respond differently among each other to the analytes and that the films must be ultrathin to yield high sensitivity. Conducting polymers, for example, are suitable not only because they are affected differently by electrolytes with distinct pHs and ionic strengths but also because their response may vary substantially depending on the preparation procedures for the thin films [10,11]. Here we took advantage of the molecular-level interaction between Rupy and PANi to produce sensing units with electrical responses varying considerably with the amount of Rupy in the film.

4. Conclusions

Characterization by Raman spectroscopy, surface potential and dc conductivity of pure and mixed LB films containing Rupy and PANi has suggested a strong interaction at the molecular level, particularly for 10% of Rupy in PANi. LB films with 10% of Rupy are less conducting because Rupy induces an increase in the number of quinoid units in the PANi structures, which are associated with the insulating form of PANi. Mixed LB films containing 30 and 50% of Rupy seem to possess phase separation with aggregates of Rupy in the PANi matrix, thus indicating a low level of miscibility. We have shown how the molecular-level interaction between PANi and Rupy leads to distinct film properties from those observed in the pure components. The electrical response, in particular, may be significantly varied by changing the amount of Rupy incorporated into the PANi matrix. This was exploited to achieve a set of non-selective sensors to form an electronic tongue. The principle has been demonstrated with LB films from pure PANi (emeraldine form), pure Rupy and a mixture with 10 and 30% Rupy, in which the combination of the four sensing units made it possible to distinguish the basic tastes detected by the biological system, in some cases considerably below the human threshold.

Acknowledgements

This work was supported by FAPESP and CNPq (Brazil) and NSERC (Canada).

References

[1] Wohnrath K, Garcia JR, Nart FC, Batista AA, Oliveira Jr. ON. Thin Solid Films 2002;402:272–9.

[2] Ferreira M, Wohnrath K, Giacometti JA, Riul Jr. A, Oliveira Jr. ON. J Phys Chem B 2002;106:7272–7.

[3] Ferreira M, Wohnrath K, Oliveira Jr. ON. Synth Met 2003;135–136: 455–6.

[4] Ferreira M, Wohnrath K, Torresi RM, Constantino CJL, Aroca RF, Oliveira Jr. ON, Giacometti JA. Langmuir 2002;18:540–6.

[5] Bettega HCY, Hissler M, Moutet JC, Ziessel R. Chem Mater 1997;9:3–5.

[6] Cosnier S, Deronzier A, Moutet JC. J Electroanal Chem 1986;207: 315–21.

[7] De Giovani WF, Deronzier A. J Chem Soc Chem Commun 1992;19: 1461–3.

[8] De Giovani WF, Deronzier A. J Electroanal Chem 1992;337:285–98.

[9] Stussi E, Stella E, De Rossi D. Sensors Actuators B 1997;43:180–5.

[10] Riul Jr. A, Gallardo Soto AM, Mello SV, Bone S, Taylor DM, Mattoso LHC. Synth Met 2003;132:109–16.

[11] Riul Jr. A, Dos Santos Jr. DS, Wohnrath K, Di Tommazo R, Carvalho AACPLF, Fonseca FJ, Oliveira Jr. ON, Taylor DM, Mattoso LHC. Langmuir 2002;18:239–45.

[12] Petty MC. Biosens Bioelectron 1995;10:129–34.

[13] Mattoso LHC, MacDiarmid AG, Epstein AJ. Synth Met 1994;68: 1–11.

[14] Wohnrath K, Araújo MP, Batista AA, Dinelli LR, Oliva G, Castellano EE, Ellena JJ. Chem Soc Dalton Transitions 2000;19:3383–6.

[15] Oliveira Jr. ON, Taylor DM, Lewis TJ, Salvagno S, Stirling CJM. J Chem Soc Faraday Trans 1989;85:1009–18.

[16] Constantino CJL, Dhanabalan A, Riul Jr. A, Oliveira Jr. ON. Synth Met 1999;101:688–9.

[17] Huang WS, MacDiarmid AG. Polymer 1993;34:1833–45.

[18] Pereira-da-Silva JE, Faria DLA, Córdoba-de-Torresi SI, Temperini MLA. Macromolecules 2000;33:3077–83.

[19] Cochet M, Louarn G, Quillard S, Buisson JP, Lefrant S. J Raman Spectrosc 2000;31:1041–9.

[20] Dhanabalan A, Riul Jr. A, Gonçalves D, Oliveira Jr. ON. Thin Solid Films 1998;327–329:60–4.

[21] Dhanabalan A, Riul Jr. A, Constantino CJL, Oliveira Jr. ON. Synth Met 1999;101:690–0.

[22] Furukawa Y, Ueda F, Hyodo Y, Harada I, Nakajima T, Kawagoe T. Macromolecules 1998;21:1297–305.

[23] Louarn G, Lapkowski M, Quillard S, Pron A, Buisson JP, Lefrant S. J Phys Chem 1996;100:6998–7006.

[24] Pereira-da-Silva JE, Cordoba-de-Torresi SI, Temperini MLA. J Braz Chem Soc 2000;11:91–4.

[25] Taylor DM, MacDonald AG. J Phys D: Appl Phys 1987;20:1277–83.

[26] Pfaffman C. Handbook of Physiology. J.Field (ed) vol. American Physiology Society; 1959. Washington, DC.

[27] Legin A, Rudnitskaya A, Vlasov Y, Di Natale C, D'Amico A. Sensors Actuators B 1999;58:464–8.