



Functionalized polyanilines made by nucleophilic addition reaction, applied in gas sensors field



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ABSTRACT

Resistive sensors for organic volatile compounds are built using functionalized polyanilines. The functionalization of polyaniline (PANI) is achieved by nucleophilic addition with thiols and is confirmed by X-ray Photoelectron Spectroscopy. The modified polymers tested as resistive sensors change the polymer sensitivity to volatile compounds. PANI shows a signal that increases when the chain length increases, however, functionalized polyanilines show a completely different behaviour. The sensitivity to long chain alcohols increases when PANI is modified with long alkyl chains, the opposite behaviour occurs when more hydrophilic groups are bonding to the polymer. We conclude that the different sensitivity of the functionalized polyanilines to the same volatile molecule allows identifying the analyte. In that way, multisensor arrays based on these materials could be used as an electronic nose. To explain this behaviour measurements of contact angle were performed. The data reveal that all modified polyanilines are more hydrophobic than PANI, this is likely to be due to the presence of the sulphur atoms. Therefore, we conclude that the hydrophobic/hydrophilic nature of the surface plays an important role but is not decisive in the sensor response. Also, Van der Waals interactions between the alkyl chains bound to de PANI and present in the sensed alcohols play an important role. Accordingly, the sensitivity for a plain alkane (heptane) increases strongly when PANI is modified with long alkyl chains.

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1. Introduction

Gas sensing is important in environmental control, explosives detection, aroma identification and health diagnostics [1]. Specifically, volatile organic contaminants should be detected to control the concentration and the exposure of humans [2]. Conductivity sensors are based on a change of conductance (or resistance) due to a physical interaction of the sensing material with the volatile compounds [3]. Semiconducting oxides (e.g. SnO₂) are usually used for such purpose but they have to be heated above 200 °C to have a measurable conductance [4]. Other conducting materials, such as conducting polymers [5],

carbon nanotubes [6] and graphene show measurable conductivity at room temperatures (e.g. 25 °C) [7]. Therefore, they have been widely used to build sensors for volatile organics [8,9]. Sorption (surface adsorption and bulk absorption) of a volatile organic compound on a conducting polymer could induce different processes, which change the conductivity [10,11]. The resistance changes (ΔR), results from sorption of an analyte can be divided into three components: $\Delta R = (\Delta R_{\text{ele}} + \Delta R_{\text{hop}} + \Delta R_{\text{ion}})$; ΔR_{ele} is the change intrinsic resistivity of conducting polymer chains. The analyte interaction could change the polarons and bipolarons density of these materials, affecting the total resistivity. ΔR_{hop} is the resistivity change in electron hopping between polymer chains, which could be modulated by the presence of the analyte. The analyte could cause physical swelling of the film and therefore increase the interchain distance, making the hopping more difficult [7]. The polarity of the analyte could screen the charge carriers, decreasing the resistivity. ΔR_{ion} is the change in ionic resistivity across the polymer layer. Since the conducting polymer

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has mobile counterions balancing the charge, the ions could transport charge between the electrodes. If charged groups (e.g. $-\text{COO}^-$) are present, the ionic contribution could be more important. Again, polar analytes could screen the ion charges and affect the resistivity. The effect of the analyte on the electronic properties of the polymer is usually negligible when it is compared with the effect on the hopping [12]. However, the swelling could be very small due to the relative rigidity of the polymer chains.

For sensor applications, it is important to be able to produce sensing materials, which have a large sensitivity to a specific analyte. In single sensor applications, the material should show a high sensitivity for one analyte while it should show low sensitivity for the others present in the same sample. In multiple sensor applications (electronic noses) different sensitivity for different analytes is required. In that sense, the exposure of various sensors to a given analyte generates a defined signal pattern, which is different from the patterns produced by other analytes. In any case, the ability to tailor the sensitivity to the analyte is very relevant. As it was pointed before, the arrays of conducting polymers show relatively low diversity in affinity toward a very diverse set of analytes, thereby producing less than an optimal separation of many analytes in the sensor array data space [13]. It is reasonable to assume that the functional groups incorporated into the conducting materials affect its sensitivity to different volatile organic compounds. Indeed, it has been shown that different copolymers of pyrrole show different response than the homopolymer [14]. Moreover, different schemes can be used to produce conducting polymers bearing different functional groups. Among them, the different monomers polymerization [14,15], and the homopolymer formation in the presence of different counterions (e.g. polypyrrole) have been employed [16,17]. Both methods present a serious disadvantage; they need a precise polymerization condition, making the method difficult and hard to reproduce. The functionalization of a preformed conductive polymer film only requires setting the conditions for the reaction, since the base film is the same. In this field several researchers and our research group have been worked extensively in the development of methods for post-functionalization of conductive polymer films [18–24].

In the present work, we describe the use of different functionalized polyanilines as sensing materials for model volatile compounds (alcohols and alkanes). It is shown that the response is affected by the hydrophobic/hydrophilic properties of the material surface and the polarity of the volatile molecules. When different alcohols are sensed, PANI shows a signal that increases as the chain length increases. Moreover, the results suggest that hydrophilic or hydrophobic groups incorporated on the PANI backbone change the sensitivity to different alcohols. At the same time, it is shown that the sensitivity for heptane is larger when a polyaniline is modified with long alkyl chains. The data prove that the hydrophobic/hydrophilic nature of the sensor surface and its sensitivity to volatile molecules cannot be directly predicted taking into account only the nature of the added functional group. Further, the use of functionalized polyanilines as sensors allows identifying one analyte from a mixture, due to these sensors show different sensitivity to each one of them. In that way, multisensor arrays based on these materials could be used as an electronic nose.

2. Materials and methods

Aniline (Merck) was distilled under reduced pressure before polymerization. Ammonium persulphate (Aldrich) was used as received from the manufacturer. All aqueous solutions were prepared using twice-distilled water. All the other reagents were of analytical quality.

2.1. Polyaniline films synthesised onto woven cloth of Polyethylene-terephthalate (PET)

PANI (emeraldine form) was prepared by oxidation of aniline (0.1 M) in 1 M HCl with ammonium persulphate (equimolar to aniline) following the procedure published elsewhere [25,26]. The reactor was immersed in an ice-water bath to keep the temperatures below 5 °C. In order to produce PANI woven cloth of PET [27], 4 × 4 cm² pieces were immersed in the polymerization solution. The woven cloth of PET was used to increase the total surface area for a given geometric area. Thin films (200–600 nm) of PANI were formed on these substrates [28]. After the polymerization finished, the PANI films on the woven cloth of PET were washed for 15 min in pure water to ensure that no reactant was retained in the film. The bulk PANI synthesised in the same conditions was washed several times with bidistilled water.

2.2. Polyaniline bulk and film functionalization


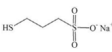


A solution (50 mL) 0.5 molar of the each nucleophile agent was prepared, the polyaniline films and 0.5 g of PANI bulk were dispersed in the nucleophile solution and refluxed during 2 h at 60 °C. The reaction mixture was cooled; the films were extracted and washed with successive portions (250 mL) of deionized water. The PANI bulk were filtered and washed with successive portions (500 mL) of deionized water. Then, the films were dried under dynamic vacuum for 24 h. The modified PANI bulk was dried under dynamic vacuum at 50 °C for 48 h. The nucleophiles used to modify the polymer are described in Table 1 and in Scheme 1 the reaction of functionalization are depicted.

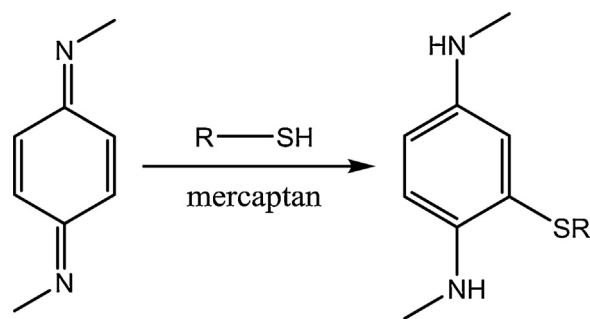
The characterization of the modified PANI was performed using X-ray photoelectron spectroscopy (XPS) using the modified PANI bulk, and the surface modification was investigate using contact angle measurement of the PANI films.

2.3. Measurement set-up

The electrical resistance of sensor materials stripes were measured along the specimen length (the materials were cuts out in pieces of 15 mm of length and 5 mm of width) by the two-point technique using a multimeter Sefram 7338. The stripe was placed on a planar holder with copper electrodes fixed on both sides of the specimen. Time-dependent electrical resistance measurements were performed during adsorption and desorption cycles. In the former case the holder with the specimen was quickly transferred into an airtight erlenmeyer flask (0.500 L) saturated with vapors of the respective analyte due to the presence of a 0.050 L of the analyte at the flask bottom. The measurements were conducted in saturated vapours at atmospheric pressure and temperature 25 °C. After 6 min of measurement, the holder was promptly removed from the flask and for the next 6 min the sample was measured in the desorption mode. These cycles were repeated

Table 1
Nucleophiles used for modification of polyaniline.

| Molecule | Shorthand | Chemical structure |
|--------------------------------|-----------|---|
| Thioglycolic acid | TIO |  |
| Sodium mercaptopropansulfonate | MPS |  |
| Dodecanothiol | DOT |  |
| Cysteamine | CIA |  |



Scheme 1. Schematic representation of the PANI modification reaction with nucleophiles.

5 times. The temperature of the experiment was maintained by a thermostated chamber (ET619-4, Lovibond, Germany).

2.4. Contact angle measurement

A computer controlled microscope (Intel QX3) was set-up with a horizontal view (60 X) to photograph the shape of water drops (3 μ L) deposited on the surface of the material pieces standing on a manually controlled tilt table. The drops were illuminated from behind with an LED white light source. The drop photographs pictures were analysed using “drop analysis” software [29], to acquire the static contact angle.

2.5. Materials characterization

The samples were analysed by X-ray photoelectron spectroscopy (XPS) on TFA XPS Physical Electronics instrument at the base pressure in the chamber of about 6×10^{-8} Pa. The samples were excited with X-rays over a 400 μ m spot area with a monochromatic Al $K_{\alpha 1,2}$ radiation at 1486.6 eV. Photoelectrons were detected with a hemispherical analyser positioned at an angle of 45° with respect to the normal to the sample surface. Survey-scan spectra were made at the pass energy of 187.85 eV, and the energy step was 0.4 eV.

3. Results and discussion

The functionalization of PANI thin films was carried out as described in the experimental part. The sensing materials are conducting polymer films supported on a woven cloth of PET, in this way polyaniline films present a c.a. 400 nm of thin and it is quite compact. The XPS Spectroscopy results (Table 2) show that all the materials incorporate new functional groups. Quantitative peak analysis of the sample is shown in Table 2.

As it can be seen in Table 2 the ratio S/N of the all modified PANIs is larger than in PANI. The small amount of sulphur in plain PANI results from retained sulphate from the polymerization reaction (which uses persulphate ion as oxidant). PANI-DOT shows a ratio S/N c.a. 1, that indicating that there is one modifying group per aniline unit in the backbone for PANI-DOT, and the other modified polyanilines (The PANI-TIO, PANI-CIA and PANI-MPS)

present a ratio S/N ratio c.a. 0.4 indicating that there is c.a. 2 group per 5 aniline units. From the analysis of these results, we can guarantee that all the modified materials present sulphur in its structure. Since the nucleophilic addition to the polyaniline backbone produces a C-S bond, the XPS confirm that the samples have been successfully modified [17].

The films are placed in a two point resistance measuring set-up, in a temperature controlled box and the sensor is sequentially exposed to air and air saturated with the volatile compound. The mean humidity is setting in the order of 50%, using this setup and conditions, typical resistance-time responses for repetitive exposures to methanol are shown in Fig. 1. All the polymers were exposed to the same concentration of methanol in the air since the temperature, the humidity and air pressure was the same for all the experiments. As it can be seen, PANI and PANI-MPS presents a different response to the same compound, the other modified polymers show the same behaviour (not shown). The different response could arise from a different degree of interaction between methanol and the film. The data shown in Fig. 1 suggest that the sensitivity of the resistive sensors to methanol depends mainly on the molecule used for functionalization.

In the case of PANI, the hydrophilic/hydrophobic properties can be easily changed by incorporation of functional groups to the polymer chain. In order to modify the polymer, the nucleophilic addition of thiols bearing different functional groups was made. In Fig. 2a–c, it is shown the comparison of PANI and modified PANI films response to different alcohols. From the greatest signal value of the plots, the sensitivity to a specific analyte can be calculated. Taking into account that the analyte concentration in the air depends on its vapour pressure at a given temperature, the greatest signal value of the plots represents the saturation value for different systems. To calculate the specific response of a sensor material to different volatile liquids, the signal is rationed by the vapour pressure of each volatile liquid at the measurement temperature Fig. 2d.

As it can be seen, all the materials are sensitive to the presence of the organic molecules and the sensitivity depends on both the material and the molecule to sense. The signal of PANI and PANI-DOT sensor (Fig. 2a and c) increases when the length of the alcohol chain increases until the propanol, however for alcohols with more than 4 carbons the signal decreases. The response of a PANI-CIA bearing hydrophilic groups ($-\text{NH}_2$) obtained by reaction of the polymer with cysteamine is shown in Fig. 2b. In the case of PANI-CIA, the signal increases when the alcohol chain length increases. As it can be seen, the behaviour of this sensor is quite different to the PANI and PANI-DOT. The signal for all the analytes increased when the length of the alcohol chain increases. Indeed, plotting the normalized signal as a function of the logarithm of the partition coefficient ($\log P$ of octanol/water) of the volatile molecule, a well-known measure of hydrophobicity, renders a

Table 2
Surface composition of samples (in atomic%), determined by survey XPS spectra.

| Sample | C | N | S | S/N | C/S |
|----------|-------|------|------|------|-------|
| PANI | 75.18 | 7.58 | 0.83 | 0.11 | 90.58 |
| PANI DOT | 80.28 | 4.34 | 3.98 | 0.92 | 20.17 |
| PANI MPS | 70.39 | 5.79 | 4.56 | 0.39 | 15.43 |
| PANI TIO | 67.33 | 5.13 | 1.95 | 0.38 | 34.53 |
| PANI CIA | 68.14 | 8.82 | 3.18 | 0.36 | 21.43 |

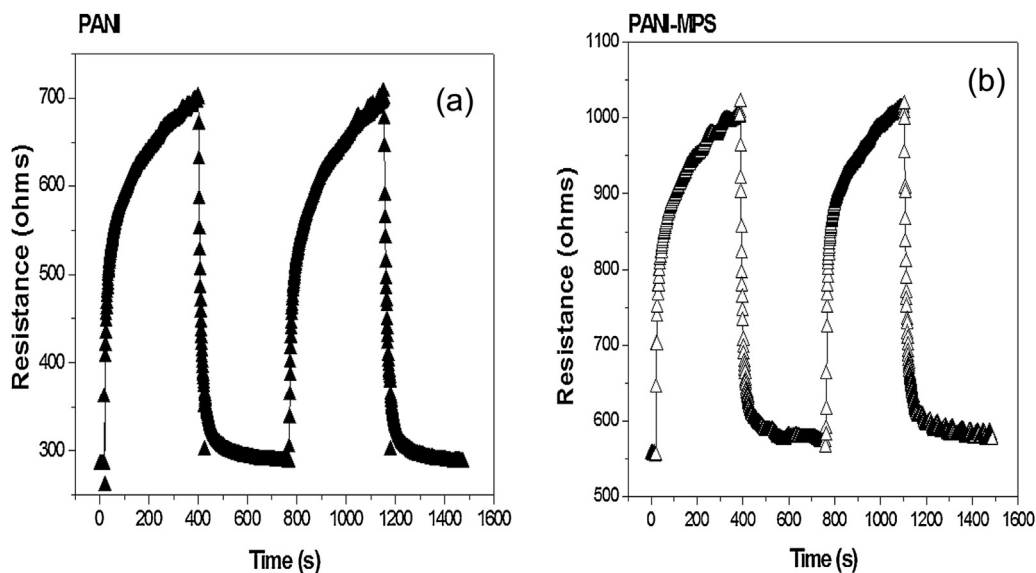


Fig. 1. Resistance-time response of different films exposed to methanol. (a) Polyaniline; (b) functionalized polyaniline: PANI reacted with mercaptopropansulfonic acid.

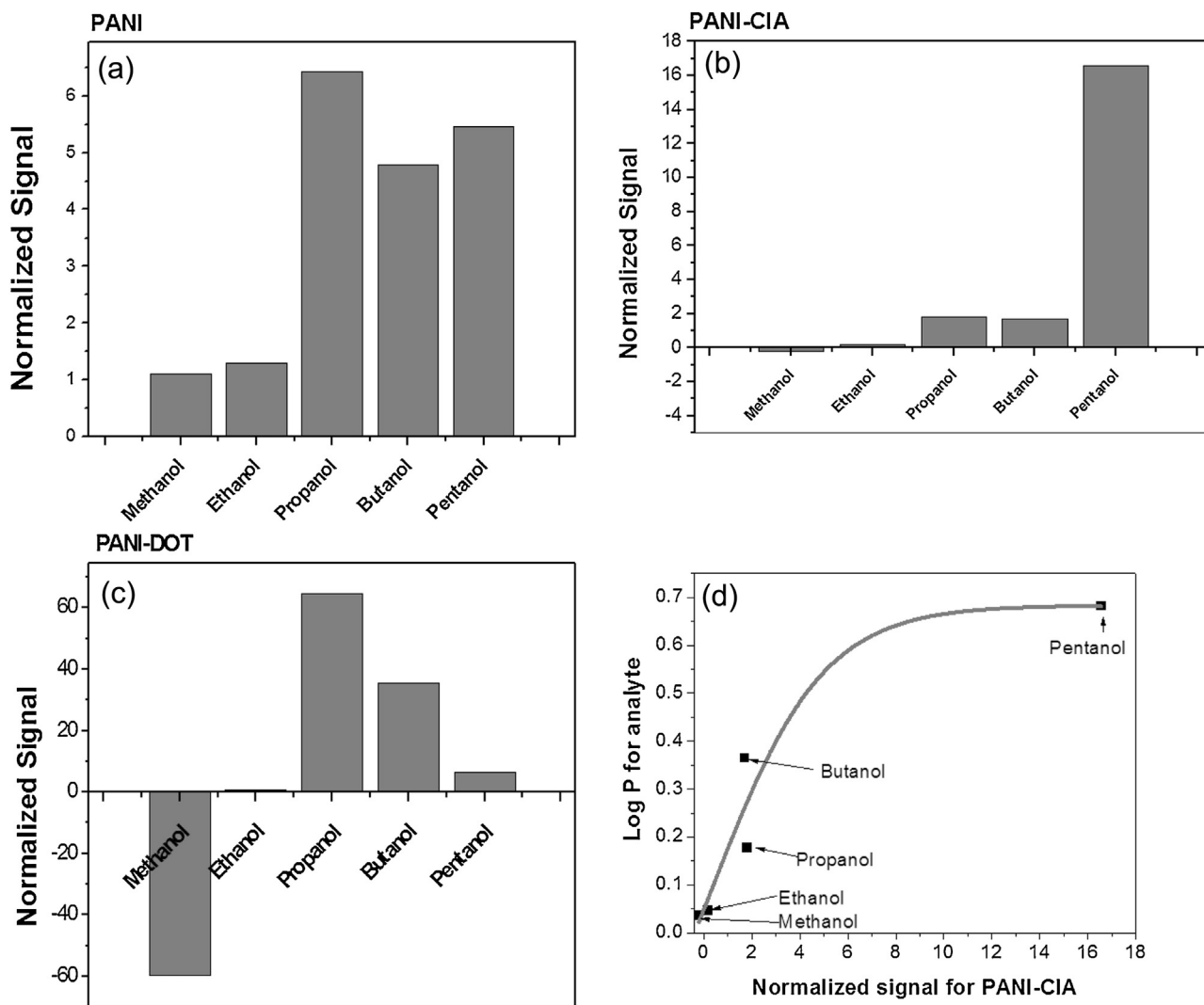


Fig. 2. Comparative resistance signal (at saturation) of (a) polyaniline, (b) polyaniline modified with cysteamine (c) polyaniline modified with dodecanthiol when are exposed to different alcohols and (d) the relationship between the normalized signal and log P of the volatile molecules when PANI-CIA is used as a sensing material.

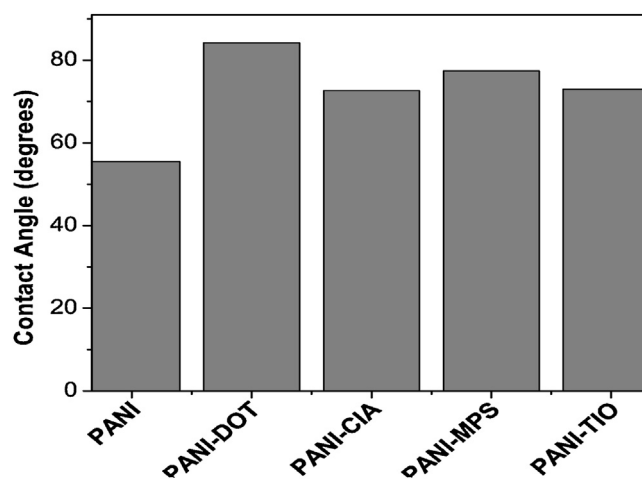


Fig. 3. Contact angle measurements for surfaces of different functionalized polyanilines.

clear tendency (Fig. 2d). Hydrophobic polyaniline was produced by incorporation of and hydrophobic group ($-S-C_{12}H_{23}$), after the pristine PANI reaction with dodecanthiol. The response of this sensor is similar to the unmodified PANI. As it can be seen in Fig. 2c, the signal begins in a negative value (methanol), increases with the chain length of the alcohol until propanol and then decreases for alcohols with more than four carbons in its molecule. It seems likely that better solvation of the film having alkyl a chain is achieved by the alcohols with intermediate alkyl chains. Nevertheless, it should be expected for alcohols with longer chains to interact better the PANI-DOT. It common to assume that the incorporation of polar or no polar groups leads to changes of surface hydrophilic/hydrophobic properties, However, we demonstrate that sensor response depends not only depends on to the hydrophobicity but also depends on the dispersion forces between alkyl chains in the added groups and the alkyl chain of the alcohols. A direct assessment of the surface nature can be made by measuring the water contact angle (Fig. 3). As it can be seen, there is a direct relationship between the nature of the length of the alkyl chain of the modifying group present and the contact angle. The bonding of long alkyl chains to PANI (PANI-DOT) increases the water contact angle, as expected. However, even addition of polar groups (PANI-CIA, PANI-MPS or PANI-TIO) with short chains generates a more hydrophobic surface than the pristine PANI. Taking into the results account, it is possible to conclude that all

modifications produce more hydrophobic surface than the unmodified polyaniline. This behaviour suggests that the functionalization with thiols already incorporate $-S-(CH_2)_n-$ groups. However, the hydrophobicity/hydrophobicity strongly depends on the length of the chain and the conformation of the modified molecule take place when is bound to the polymer. Comparing the behaviour of the different sensor to the alcohols, the results show that the response is not directly correlated to the hydrophobicity but is related to dispersion forces between alkyl chains in the added groups and the alkyl chain of the alcohols.

To assess directly the interaction with alkyl chains, the response of different functionalized polyanilines was tested when the sensors were exposed to ethanol and heptane, Fig. 4a and b respectively. Those molecules have an almost equal vapour pressure at 25 °C, therefore the signals can be directly compared. As it can be seen, the resistive signal of different sensors exposed to ethanol shows larger signals with less hydrophobic polyanilines. When ethanol is used as analyte the smallest signal for the most hydrophobic material (PANI-DOT) is observed (Fig. 4a). It seems that weak wetting of hydrophobic materials by the polar ethanol induces a small resistance signal.

The resistive signals of the sensors exposed to heptane are quite small for all the materials. However, the one observed for PANI-DOT is larger than those observed by other functionalized polyanilines. It seems likely that strong Van der Waals interactions

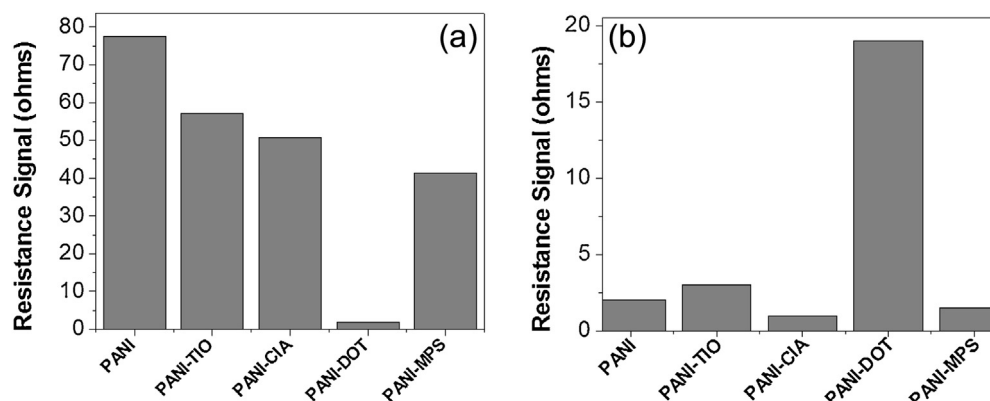


Fig. 4. Comparative resistance signals (at saturation) of different functionalized polyanilines when they are exposed to ethanol (a) and heptane (b).

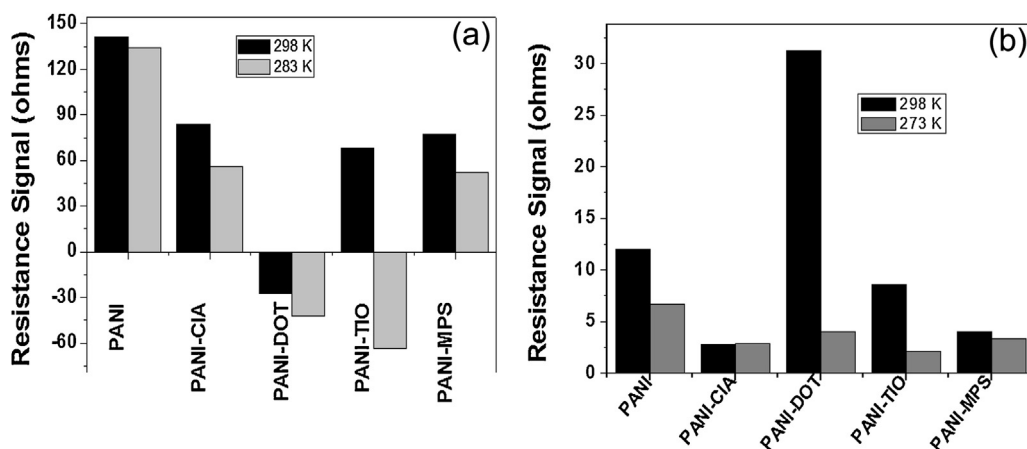


Fig. 5. Effect of temperature on the comparative resistance signal (at saturation) of different functionalized polyanilines when they are exposed to ethanol (a) and pentanol (b).

between the alkyl chains in PANI-DOT and alkanes induces a large change in the conductivity. In that way, a specific detector of toxic alkanes (e.g. hexane) could be built using functionalized polyanilines.

Besides, the temperature has a significant effect on conducting polymers conductivity since the materials behave as amorphous semiconductors. That is, the conductivity increases with temperature due to an increased mobility of the charge carriers.

Another important parameter to taking into account when polymers are used as sensors is the temperature. It is very known that the resistance changes due to the interaction of the polymer with organic compounds could show a different trend. This behaviour depends on the adsorption of the organic molecule on the polymer, which has an entropic component (due to the fact that an entropy loss occurs upon adsorption of gas molecules on the solid) which contribution to the free energy is scaled by the temperature (Eq. (1)):

$$\Delta G_i = \Delta H_i - T\Delta S_i \quad (1)$$

Therefore, the effect of temperature on changes in the resistance, of different polyanilines was studied for two analytes: ethanol and pentanol (Fig. 5).

As it can be seen, the signal of the resistance increases with temperature for all the sensing materials studied, this is the typical behaviour of semiconductors. In the case of PANI-DOT sensing ethanol the negative signal decreases in magnitude, and in the case of PANI-TIO, the increase of the signal involves a change of sign when the temperature increase.

When the sensors are exposed to pentanol, a clear signal increment of resistance is observed for all the sensing materials as the temperature increases, except for PANI-CIA. Moreover, the increase of signal for PANI-DOT is the largest (c.a. 7.8 times) suggesting a strong effect of temperature on the interaction between long chain alcohols and the polymer modified by long alkyl chains.

On one side, the results suggest that a careful temperature control should be exerted when the materials are used as sensors.

4. Conclusions

The sensitivity of conducting polymers to alcohols and heptane is strongly affected by the chemical functionalization of the materials. Polyaniline shows an increasing signal when the chain length of different alcohols uses as an analyte increases. Also, the

incorporation of hydrophilic or hydrophobic groups on the PANI backbone increases the sensitivity of the sensor to the alcohols. At the same time, the sensitivity for heptane is larger when a polyaniline modified with long alkyl chains is used. Besides both the hydrophobic/hydrophilic nature of the surface and the kind of volatile molecules sensed cannot be directly predicted by the nature of the added functional group.

The different sensitivity of the functionalized polyanilines to the same volatile molecule allows identifying the analyte. In that way, multisensor arrays based on these materials could be used as an electronic nose.

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