Relation between ambient humidity and ionic conductivity of poly(thionaphtheneindole): behaviour as an amperometric humidity sensor

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The electrical characteristics of oxidized poly(thionaphtheneindole) were investigated as a function of ambient relative humidity (r.h.). The current flowing through a pressed pellet of material between two massive gold electrodes plotted against voltage gives a wave-shaped curve with a halfwave potential at $V = {\sim}3$ V. The current recorded at 4 V (plateau of the wave) is a sigmoidal function of r.h. with the inflexion point at ${\sim}60\%$. An interpretation of these findings is given, based on the influence of water on the dielectric constant of the material and on acid–base equilibrium between poly(thionaphtheneindole) and water, from which protons are produced. The behaviour of poly (thionaphtheneindole) as the active component of an amperometric humidity sensor is also reported.

1. Introduction

Polymer proton conductors are interesting candidates for a wide range of technological applications, mainly for the realization of sensors [1–3], fuel cells, thermoelectrochromic and electrochromic devices [1] and batteries [4]. These materials can be obtained either by doping polymers [2, 5–9] with acids or by electrochemical polymerization of organic monomers, as in the case of polyanilines [10].

Because polymer proton conductors are essentially used in technological applications in which humidity must be avoided, their electrical conductivity has been mainly studied in dry conditions [6]. Proton motion can follow a Grotthus mechanism [7] in the presence of acid–base pairs. It has also been demonstrated that the electrical conductivity of the above mentioned compounds is often a function of humidity, but a mechanism which explains the motion of the protons in these conditions has not yet been well defined; a hypothesis was put forward, according to which the ion transport is a surface process, which can be affected by the water content [1].

Poly(thionaphtheneindole), (pTNI, Fig. 1(a)), an oligomer showing prevailing proton conductivity, was obtained, in the form of a black powder, by potentiostatic oxidation of TNI [11]; it was utilized as electrolyte in solid state batteries [4] and investigated as an active element for a resistive water vapour partial pressure sensor [12]. In the presence of humidity, the following equilibrium, inside the pTNI powder, was hypothesized [13]:

$$NH^+ \cdots ClO_4^- + H_2O \longleftrightarrow N + H_3O^+ + ClO_4^- \quad (1)$$
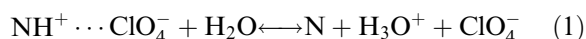
where $NH^+ \cdots ClO_4^-$ stands for the oxidized protonated polymer (Fig. 1(a)) and N for its deprotonated form (Fig. 1(b)). The protons liberated by the water, according to Reaction 1, act as charge carriers inside the polymer under the effect of the applied electric field. However the mechanism of ion conduction inside pTNI is not completely understood.

In the present work the electrical properties of pTNI, as a function of humidity, are investigated and
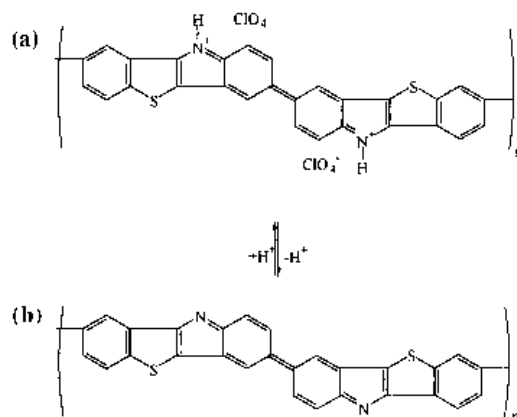

Fig. 1. Protonated (a) and deprotonated (b) form of pTNI.

compared with those shown by other organic proton conductors. The characteristics of this polymer as a material for amperometric humidity sensors are illustrated.

2. Experimental details

pTNI was obtained as fine black powder by electrochemical oxidation, at constant potential, of TNI [11], whose preparation is reported in a previous paper [13]. The polymer powder was pressed, at 2 tons, in pellets of 0.5 cm diameter and 0.2 cm thickness. The electrical characteristics of the doped polymer as a function of per cent relative humidity (r.h.%) were tested, at room temperature, in a home-made cell equipped with a commercial humidity sensor. To obtain different r.h.% values, dry argon was bubbled through water at different rates and then passed through the cell. The chronoamperometric and voltammetric experiments were carried out with an AMEL system 5000 multifunction instrument driven by home-made software. The impedance measurements were made by a Solartron 1255 FRA apparatus, over a frequency range of 0.1–500000 Hz.

3. Results and discussion

It was found that the electrical characteristics of pTNI depend on the ambient humidity [12]. Chrono-amperometric measurements, at different constant values of r.h.%, were carried out on pTNI pressed pellets, sandwiched between two massive gold electrodes; typical behaviour is reported in Fig. 2. At each applied potential, ranging between 0.1 and 4.0 V, the current decreases with time, reaching a quasi constant value (Fig. 2). It is controlled by a diffusion process – as can be observed by plotting i against $t^{-1/2}$ (see inset, Fig. 2) – suggesting that charge is transported across the material by ions. At each r.h.% value, the current/voltage plot is similar to a voltammetric wave. A half-wave potential of ~3.05 V is generally observed (Fig. 3).

Under dry conditions (i.e., with a flow of dry argon) the system behaves as an electronic conductor, the current/voltage curves being straight lines (Fig. 4). The electron conductivity at room temperature of pTNI was found to be very low (~10^{-8} Ω^{-1} cm^{-1}), as reported previously [14], and is noncomparable with the much higher ionic conductivity only observed in the presence of water. In any case, the low value of the electronic component, the activation energy of which is ~0.8 eV [14], can be explained by the fact that pTNI is not a long-chain polymer, but an oligomer with a small conjugated double-bond system.

Plotting the current measured at 4 V (i.e., the value corresponding to the plateau of the voltammetric waves) as a function of r.h.%, a sigmoidal curve (Fig. 5) is obtained. A similar sigma-shaped plot was previously [12] observed by plotting the conductivity of oxidized pTNI pellets against r.h.%. The likeness of these curves suggests that the limiting current should be related to the conductivity of the material.

By assuming that the material is a proton conductor ($t_H^+ = 1$) which, in the presence of water, is involved in equilibrium 1, the charge transfer across the electrodes in the system Au/pTNI(water)/Au can be schematized as below:

$$\text{anode}: \quad H_2O - 2e^- \longrightarrow 2H^+ + 1/2O_2 \qquad (2)$$

$$\text{cathode}: \quad 2H^+ + 2e^- \longrightarrow H_2 \qquad (3)$$
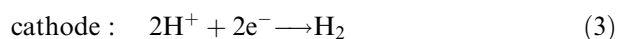
At the electrodes the current flow is controlled by the diffusion of electrode active species, while in the bulk of the pellet the current is driven by the migration of protons under the influence of the electric field.

The anodic oxidation of water can lead to the formation of Au_2O_3 films of molecular scale thickness; this reaction is reversible [10] but corrosion of the gold electrode can occur. This process; the effects of which are clearly detectable when the pellet is removed, could explain the irregular, sometimes observed, rise in the current/voltage waves at constant r.h.%.

When, at constant r.h.%, the equilibrium for Reaction 1 is attained, the H^+ concentration is given by
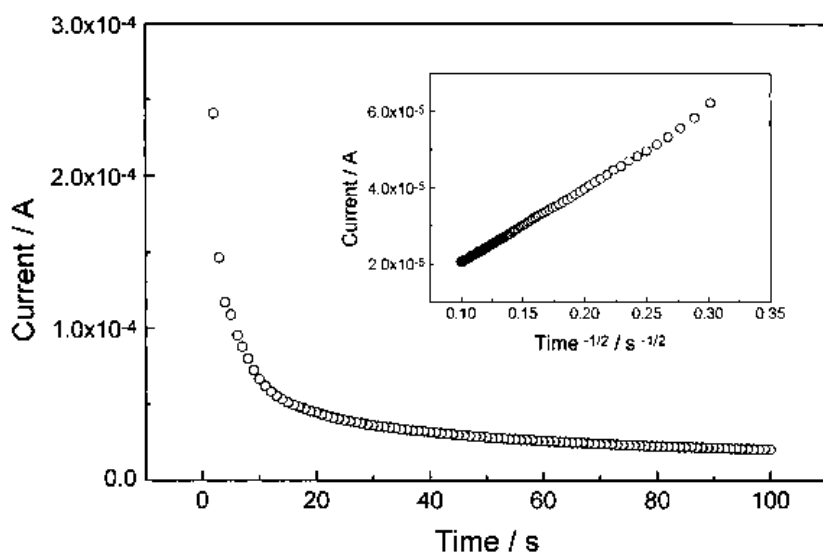

Fig. 2. Chronoamperometric measurements for a pressed pellet of pTNI between two massive gold electrodes. Voltage between the electrodes = 1.5 V, r.h. = 51%. Inset: I vs $t^{-1/2}$ for the same experiment.
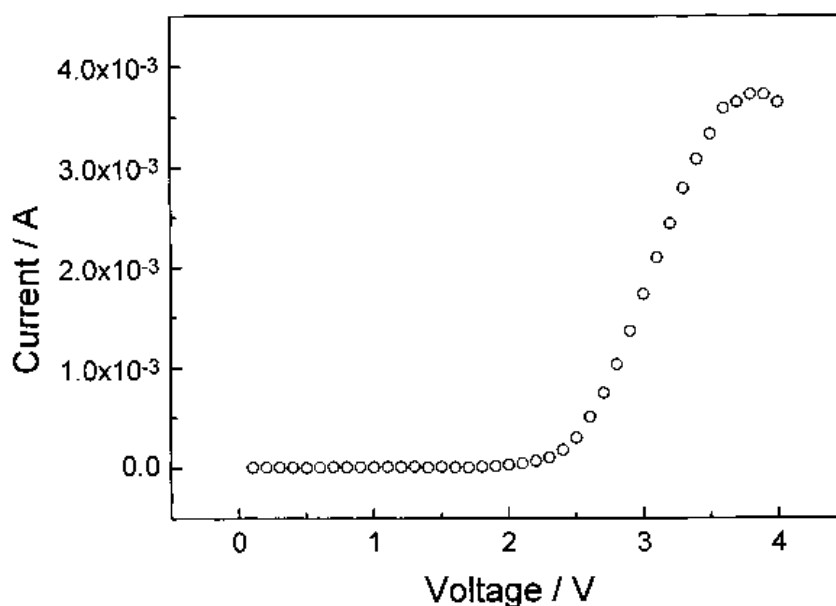
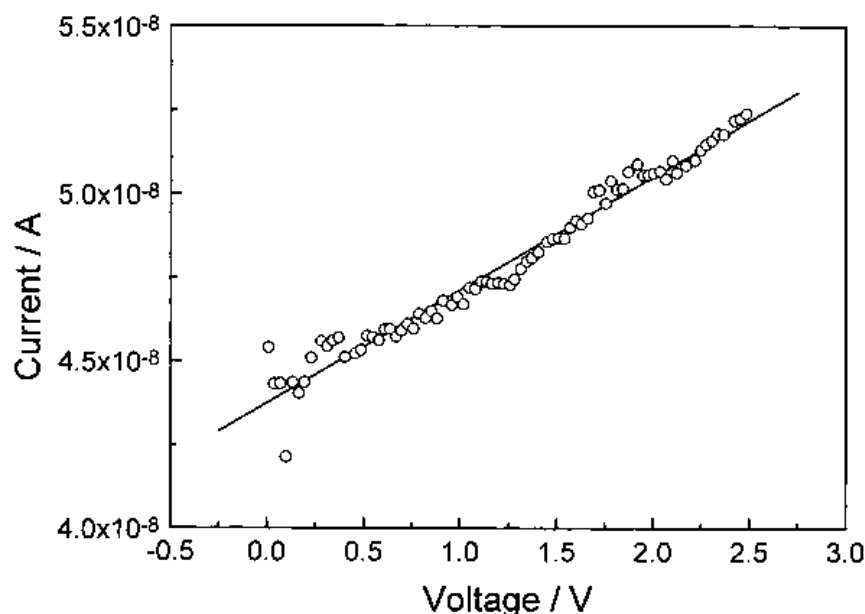Fig. 3. Current/voltage plot for a pressed pellet of pTNI between two massive gold electrodes. r.h. = 70%.

Fig. 4. Current/voltage plot for a pressed pellet of pTNI between two massive gold electrodes for low humidity values (r.h. < 8%).

$$[H_3O^+] = \frac{[H_2O][NH^+]K}{[N]} \quad (4)$$

where K is the equilibrium constant of Reaction 1.

Plots of the H_3O^+ concentration as a function of r.h.% were obtained for different K (Fig. 6) by substituting in Equation 4 the values of the concentrations in moles per cm^3, as specified in the following equation:

$$[H_3O^+] = \frac{k(\text{r.h.\%})\{[NH^+] - [H_3O^+]\}K}{[H_3O^+]} \quad (5)$$

In this equation, the total concentration of NH^+ (2.63×10^{-3} mol cm^{-3}; density of the pellet = 1 g cm^{-3}) was calculated by dividing the pellet weight by the weight of the monomer unit, taking into account

that, as previously found [14], one positive charge per monomer unit is present in the oligomer chain; the water amount in the pellet was considered proportional to the ambient r.h.%; the proportionality factor ($k = 1.37 \times 10^{-4}$ mol cm^{-3}) was obtained with some approximation from the amount of water contained in the polymer at r.h. = 40% [14]. Unfortunately, the curve obtained by plotting i_l (limiting current) and $[H_3O^+]$ against r.h.% does not show a similar trend.

An alternative explanation of the sigmoidal shape of the i_l/r.h.% plots can be given by taking into account, as in a previous paper [8], the effects of water on the dielectric constant of the material and, consequently, on the mobility of the charged species, in particular the protons, and considering the polymer as a solid phase in contact with an aqueous solution
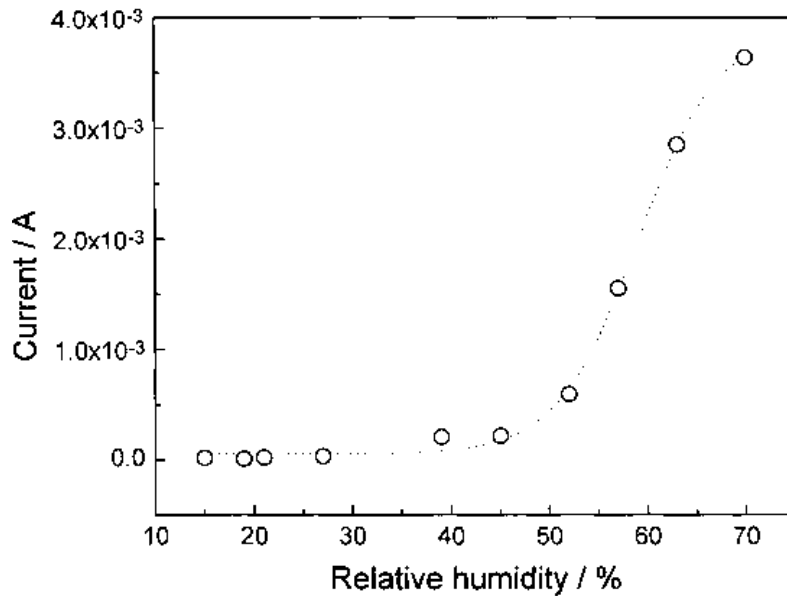
Fig. 5. Limiting current ($V = 4.0$ V) flowing through a pressed pellet of pTNI between two massive gold electrodes as a function of r.h.%.

of perchloric acid (Fig. 7). This model agrees with the above mentioned hypothesis that, in the presence of water, the resistivity decreases owing to changes in surface conductivity [1]. Equilibrium 1 has been

Fig. 6. Proton concentration in a pressed pellet of pTNI, calculated by Equation 5 as a function of r.h.%, using three different equilibrium constants.

treated as it would occur in aqueous solution; in reality, this equilibrium is heterogeneous and depends on the total surface of the pTNI grains; therefore, the surface concentrations $[NH^+]_s$ and $[N]_s$ could be used in Equilibrium 1.

As in the previous case [8], the following assumptions were made:

(a) The transport number of protons can be taken as 1. This is probably true, though not proved. In fact, it is known that the mobility of protons is much higher than those of the anions in aqueous solutions. On the other hand, by considering the material as an acid solution filling the voids among the solid polymer grains, the anion could also contribute to the charge transfer. Nevertheless, because charge transport occurs through very small channels, the size of the ions might be an important factor affecting their mobility. In any case, an eventual contribution on the anion to the charge transfer must be taken into account.

(b) The viscosity of the aqueous solution in contact with the polymer grains remains unaffected by changing r.h.%.

(c) Diffusion layers, through which protons diffuse to the cathode and from the anode and through which water molecules diffuse to the anode, form at both electrodes. Under steady current conditions an equilibrium is established between the migration and diffusion currents:

$$i = i_d = AnFC_x \frac{D_x}{\delta_x} = i_\mu = AE \sum C_x \lambda_x \cong A C_{H^+} \lambda_{H^+} E \tag{6}$$

where i is the current, i_d the diffusion current, i_μ the migration current (amperes), A is the surface of the electrodes (0.2 cm^2), n the charge of species x, F the Faraday constant. C_x (mol or g-ion cm^{-3}), D_x, δ_x and λ_x (S cm^2 mol^{-1}) are concentration, diffusion coeffi-
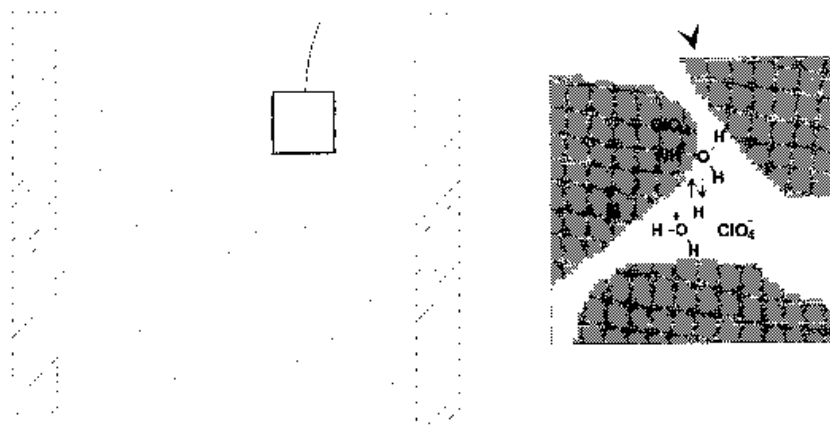
Fig. 7. Model of a pressed powder of pTNI in presence of water, showing the acid–base equilibrium involving the hydrogen atom, bonded to nitrogen in protonated pTNI, and water molecules. The dark spots are solid pTNI grains and the light dark zone is a water solution adherent to the solid polymer.

cient, diffusion layer, and equivalent conductivity, respectively, of the species x, C_{H^+} and λ_{H^+} have the same meaning for the protons and E is the electric field (V cm^{-1}).

The actual value of the voltage across the pellet is given by the difference between the applied voltage and the potential difference between the electrodes, which arises as the result of the change in the electroactive species concentration due to Reactions 2 and 3. A buildup of a voltage of about 50–100 mV, which vanishes after a few seconds, was detected between the electrodes after chronoamperometric measurements; it was assumed that this voltage does not meaningfully affect the value of E in Equation 6.

When, during the chronoamperometric experiments, Equilibrium 6 is established the current must reach a constant value; in these conditions, the ratio D_x/δ_x for the species H$^+$ and H$_2$O has a value which depends on the respective diffusion coefficients and concentrations in the bulk of the material. The current does not reach constant values only if the water consumption at the anode is very high and is not counterbalanced by water absorption; in such a case, the dielectric constant change induces a progressive decrease of current until a balance between the water consumption at the anode and its absorption by the material, is attained.

The Onsager equation can be applied to the hypothesized model:

$$\lambda = \lambda_0 - \left\{ \frac{A}{(\varepsilon T)^{3/2}} \lambda_0 + \frac{B}{(\varepsilon T)^{1/2}} \right\} \sqrt{c_{ClO_4^-} + c_{H_3O^+}} \quad (7)$$

where λ is the equivalent conductivity (S cm^2 mol^{-1}), λ_0 is the limiting value of the equivalent conductivity, ε is the relative dielectric constant, $c_{ClO_4^-}$ and c_{H^+} are the ion concentrations (g-ions cm^{-3}), A and B are constants which depend on viscosity and temperature. According to this equation, at constant tem-

perature, the conductivity of the material depends on the dielectric constant and on the electrolyte concentration in contact with the polymer grains.

As in the case of poly(propargyl-alcohol) doped with sulfuric acid [8], the capacity of the material was determined from impedance spectroscopy. As an example, the results of one of these measurements are shown as a Nyquist plot in Fig. 8. The interpretation of the impedance spectra of such a system was given in a previous paper [12]; the electrical characteristics of the polymer pellet can be obtained by the semicircle at the higher frequencies.

By defining the cell constant from the geometric size of the pellet, the relative dielectric constants (very high, ranging from 10^3 to 10^4) were calculated; the
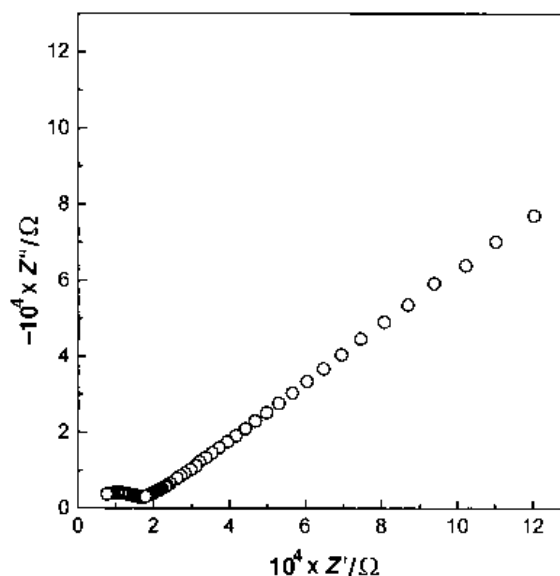

Fig. 8. Nyquist plot inherent to a pressed pellet of pTNI between two massive gold electrodes at r.h. = 12%. Alternating voltage: 10 mV, frequency range: 1–500000 Hz.

pellet of pTNI, as many other similar compounds, behaves as a double-layer capacitor [15]. A sigmoidal function, $\varepsilon = f_1(\text{r.h.\%})$, relating the dielectric constant to relative humidity, was derived as the best fit for the experimental values.

By using Equation 5, the analytical expression for the function $f_2(\text{r.h.\%})$, which describes the relationship between the proton concentration in pTNI and r.h.%, was found. The above Onsager equation can then be rewritten in the form:

$$\lambda = \lambda_0 \left\{ \frac{A}{(f_1(\text{r.h.\%})T)^{3/2}} \lambda_0 + \frac{B}{(f_1(\text{r.h.\%})T)^{1/2}} \right\}$$
$$\times \sqrt{c_{\text{ClO}_4^-} + f_2(\text{r.h.\%})} \tag{8}$$

and the correlated equation for the current is

$$i = \alpha f_2(\text{r.h.\%})\lambda = \alpha f_2(\text{r.h.\%})$$
$$\times [\lambda_0 - \left\{ \frac{A}{(f_1(\text{r.h.\%})T)^{3/2}} \lambda_0 + \frac{B}{(f_1(\text{r.h.\%})T)^{1/2}} \right\}$$
$$\times \sqrt{c_{\text{ClO}_4^-} + f_2(\text{r.h.\%})} \tag{9}$$

with

$$\alpha = A\rho V / l\beta = 4\rho/\beta \tag{10}$$

where V is the supplied voltage (4 V), l the distance (0.2 cm) between the electrodes of area A (0.2 cm^2), ρ the roughening factor of the electrodes and β the tortuosity coefficient. The tortuosity coefficient is the ratio between the actual average path the ions have to cover between the electrodes and their geometrical distance (thickness of the pellet). The meaning of this parameter, which depends on the characteristics of the pellet, becomes clear by taking into account the model reported in Fig. 7.

The fitting of Equation 9, calculated for three different K values (10^{-3}, 1, 10^3), with the experimental current values, is shown in Fig. 9; it is quite satisfactory for all the K values and the best results are obtained for $K = 10^{-3}$.

From the fit (using $K = 10^{-3}$) optimized values of α (1.2 V cm) and λ_0 (32.8 S cm^2 mol^{-1}) were obtained. The former parameter is quite consistent with that expected for a cell having the size of the pellet, under a voltage of 4 V, considering the same value for the roughening factor and the tortuosity coefficient; the latter is not far from that expected in the case of an acidic aqueous solution.

The same fitting was also carried out for the equation:

$$i = \alpha[f_2(\text{r.h.\%}) + C_{\text{ClO}_4^-}]\lambda \tag{11}$$

which takes into account the contribution of ClO_4^-. The fit for $k = 10^{-3}$ is, also in this case, very satisfactory, but the values of α and λ_0 are now ~0.1 V cm and ~30 S cm^2 mol^{-1}, respectively, acceptable, but not so good as in the case where protons are assumed to be the only species involved in the charge transport.

In any case, even if it is impossible to evaluate all the quantities contained in Equation 9, the very good
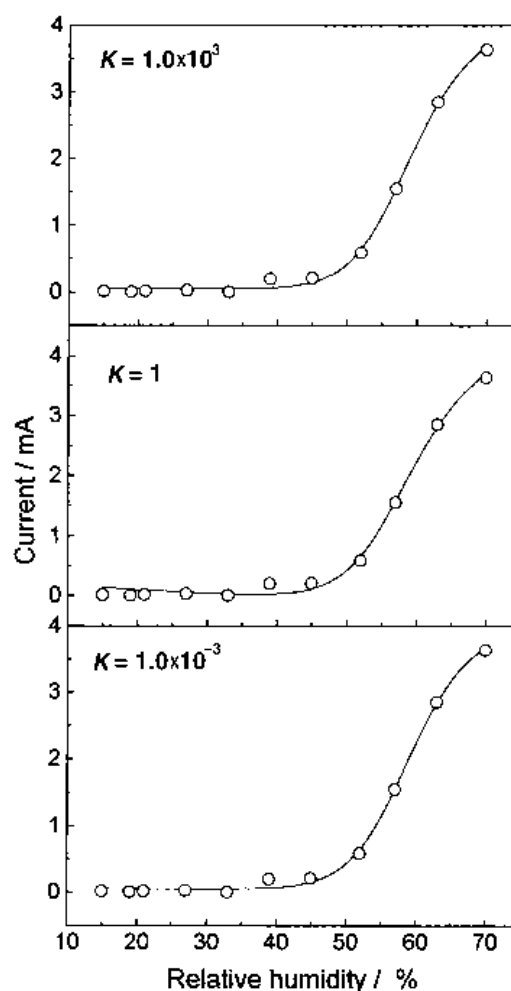

Fig. 9. Fitting of the experimental limiting current flowing through a pressed pellet of pTNI between two massive gold electrodes (open points) with Equation 9 for three different values of the equilibrium constant of Equation 6; full line: best fitting. The parameters optimized by the fitting are reported in the Figure as well as the chi-square values. For $K = 1.0 \times 10^3$: $\lambda_0 = 2729$ S cm^2 mol^{-1}, $\alpha = 5.9 \times 10^{-4}$ V cm and $\chi^2 = 2.5 \times 10^{-10}$; for $K = 1$: $\lambda_0 = 2520$ S cm^2 mol^{-1}, $\alpha = 8.1 \times 10^{-4}$ V cm and $\chi^2 = 2.2 \times 10^{-9}$; for $K = 1.0 \times 10^{-3}$: $\lambda_0 = 32.7$ S cm^2 mol^{-1}, $\alpha = 1.2$ V cm and $\chi^2 = 1.3 \times 10^{-10}$.

agreement of this equation with the experimental data supports the proposed model for the ionic charge transport in pTNI.

What has been reported above might suggest that polymers containing nitrogen heteroatoms, in the presence of water, behave as proton conductors, like polymers doped with acids. Nevertheless a great difference exists between the two families of polymers: in the former the H_3O^+ ion derives from the reaction between the water and the oxidized form of the polymer, while in the latter it derives from the dissociation of the doping acid. In heterocyclic compounds, obtained by electrochemical polymerization, the binding energy for the proton is expected to be higher than that acting in the acid-doped polymers and, consequently, a higher activation energy for the conduction mechanism in the heterocyclic compounds as well as a greater thermodynamic stability can be expected. In fact, pTNI was found to be very stable, even over a period of years.
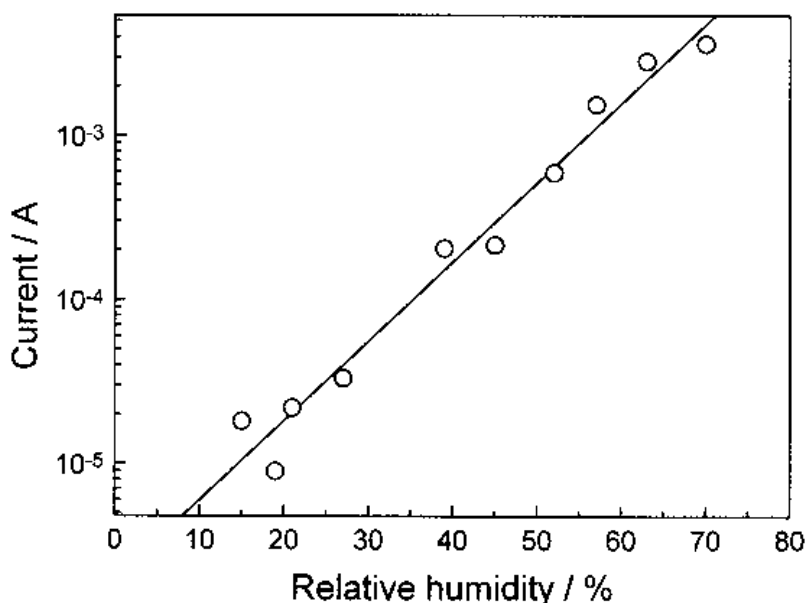
Fig. 10. Limiting current against r.h.% for a pressed pellet of pTNI between two massive gold electrodes.

Conducting polymers which are essentially proton conductors can be tested as materials for either resistive or electrochemical humidity sensors . In the present case, the compound was tested as the electrolyte in an amperometric device. By plotting the current – which flows through the system (pTNI pellet between two massive gold electrodes) under a bias of 4 V – on a logarithmic scale, as a function of r.h.%, a straight line is obtained up to r.h. = 70% (Fig. 10). Such behaviour was observed, without any deviation, for months. Preliminary experiments showed a relatively long response time; nevertheless a more appropriate design of the sensor may significantly improve this parameter.

4. Conclusions

Poly(TNI), a conducting oligomer prepared by electrochemical oxidation of TNI at controlled potential, reversibly absorbs environmental humidity. The electrical characteristics of pTNI pressed pellets were investigated in detail as a function of relative humidity.

In order to understand the conduction process in the process in the polymer, the mechanism already proposed for an acid-doped polymer, poly(propargyl-alcohol) doped with sulfuric acid [8], was utilized. This model is drawn from chronoamperometric and voltammetric measurements and studies of complex impedance performed on a pTNI pressed pellet between two massive gold electrodes. The system is seen as a very thin layer of perchloric acid aqueous solution adherent to the polymer grains; the equivalent conductivity of this solution depends on its dielectric constant, which is a function of the water content in the polymer pellet. In pTNI, differently from the case of the acid-doped poly(propargyl-alcohol), Equilibrium(1), due to H_2O and responsible for the production of free protons inside the material, must be

considered. The Onsager equation was applied to this model and very good fit with the experimental data was observed. This result supports the hypothesis that the decrease in resistivity occurring in a polymer proton conductor in the presence of humidity should be due to a change in its surface conductivity.

Pressed pTNI pellets included between massive gold electrodes give rise, under a bias of 4 V, to a current which is a sigmoidal function of the r.h.%. As these characteristics remain constant with time, pTNI can be proposed as active material for the construction of amperometric humidity sensors.

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