ADSORPTION OF GASEOUS PROPYLAMINE ON FILMS OF POLYPYRROLE IN DIFFERENT OXIDATION STATES

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Quartz crystal microbalance and Kelvin probe were used to investigate the interaction between propylamine ($PrNH_2$) vapour and polypyrrole (PPy) films. The films were prepared by oxidative electropolymerization of pyrrole on a platinum electrode in acetonitrile solution. The nature of interaction is strongly influenced by the oxidation state of the film and co-adsorption of water. On the surface of the oxidized PPy, water adsorbs to form a multilayer. The work function increase of the Pt/PPy electrode exposed to both water and $PrNH_2$ vapoures was attributed to the $PrNH_2$ dissolution and dissociation within the water layer followed by the formatted $PrNH_3^+$ cation adsorption on the liquid surface with the alkyl group facing the gas phase. On the contrary, the water adsorption on the reduced PPy is rather weak and the work function decrease observed at the $PrNH_2$ exposure might be connected with the neutral molecules adsorption directly on the polymer surface. The water co-adsorption is documented by a drop in the adsorption of $PrNH_2$ upon lowering the water vapour pressure in the gas phase.
Key words: Propylamine detection; Polypyrrole-based sensors; Quartz crystal microbalance; Kelvin probe; Electropolymerization.

The nature of interactions between organic vapours and conducting polymers underlying the sensing mechanism of polymer-based gas sensors has been a matter of growing interest[1–6]. On the basis of the results obtained by UV/VIS spectroscopy and the Kelvin probe technique, the mechanism has been suggested comprising adsorption of vapour molecules on the polymer, partial charge transfer to or from a mid-gap state and lateral dispersion of the charge between the adsorbed molecules[4]. Changes in the optical and electric properties of a polymer film upon its exposure to an organic vapour apparently reflect the donor–acceptor properties of the gaseous molecule,

the nature of the solvent which the film is grown from, and the nature of the dopping ion in the film[4,7].

In order to increase the selectivity of the polymer-based sensors, attempts have been made to modify properties of the polymer film either inserting active additives into the polymer structure[5], or by preparing multilayer composite films[8,9]. Physicochemical properties of the electrochemically prepared films depend also on the electropolymerization potential[10]. In this case, the conducting polymer can be prepared in a defined oxidation state, which is likely to influence interactions of the polymer with molecules of different donor–acceptor properties[7]. Such possibility has been indicated by the linear correlation between the vapour-induced shifts in the polymer work function and the initial value their potential[4].

The aim of this work is to clarify the effect of the oxidation state of a polypyrrole film on the adsorption of gaseous propylamine, which is chosen as a model substance with electron-donor properties. Of the other alkylamines, $PrNH_2$ has the least marked odour and its detection possibilities in gaseous phase are also of practical importance[9]. This paper shows that the behaviour of films exposed to propylamine in air containing water vapour is significantly influenced by the co-adsorption of water molecules.

EXPERIMENTAL

Acetonitrile, ACN, 99.99%; propylamine, $PrNH_2$, 98%; acetone, reagent grade; pyrrole, purum; $LiClO_4$, 99%; KCl, reagent grade from Fluka or Aldrich were used as received.

Mass changes during the exposure of the polymer film to propylamine vapour were followed by using a home-made quartz crystal microbalance (QCM) apparatus[11]. The AT cut 4 MHz (Krystaly, Hradec Králové, Czech Republic) or 5 MHz (Kristall-Verarbeitung, Neckarbischofsheim, Germany) quartz crystal plates were 14 mm in diameter. The Au electrodes with the electrochemically active area of 0.38 cm^2 were sputtered on both sides of the plate. The mass sensitivity of the QCM was determined by a galvanostatic deposition of silver from a silver cyanide bath; it was 20.8 ng cm^{-2} Hz^{-1} and 15.8 ng cm^{-2} Hz^{-1} for 4 MHz and 5 MHz quartz plate, respectively.

The work function of the film was measured with the Kelvin probe (Delta-Phi-Elektronik Kelvin Probe 07, Besocke, Jülich, Germany) in the automatic compensation mode. The sample and the reference electrode (the vibrating gold gauze) were placed in a stainless steel chamber equipped with the gas inlet and outlet. Air with the relative humidity ranging from 4.6 to 94% served as the carrier gas for propylamine vapour of a known concentration. The latter was produced from liquid propylamine in a capillary diffusion tube thermostatted at 30 °C (ref.[9]). The gas flow rate was regulated in the range 50–500 cm^3 min^{-1}.

The data from the QCM and Kelvin probe measurements were collected *via* the A/D input of the PC-LabCard (PCL 718).

All measurements were performed at the ambient temperature, 25 ± 2 °C.

RESULTS

Calibration of the Kelvin Probe

A suitable procedure for the calibration of the Kelvin probe in a water-saturated gas phase (G) can be based on the measurement of the potential *V* of the voltaic cell[12],

$$Ag \mid AgCl \mid KCl(sat.), water \mid G \mid Au \tag{1}$$

under the conditions that the difference between the outer (Volta) potentials of the saturated KCl solution (S) and the reference electrode (Au) is zero, *i.e.*, $\Psi^S = \Psi^{Au}$. The construction of the Kelvin probe and the stainless chamber did not allow to use the arrangement with the solution phase flowing continuously over the surface of the Ag/AgCl electrode[12]. Instead of this, a drop of the solution phase (0.2 ml) was placed into a small silver dish with the inner surface covered by AgCl, which was fixed under the reference electrode. In order to maintain the same conditions as in measurements of polymer films, the gas phase was the air with the 50% relative humidity. The potential *V* of the cell (*1*) can be expressed as the difference of the absolute potential (work function) of the Ag/AgCl electrode, E_{abs}^{im} (Ag/AgCl), and the work function of the reference electrode, Φ^{Au},

$$V = E_{abs}^{im} \left(Ag / AgCl\right) - \Phi^{Au} / e_0 , \tag{2}$$

where e_0 is the elementary charge, and E_{abs}^{im} (Ag/AgCl) or Φ^{Au} is the difference in the electron energy between the Fermi level in Ag or in the metal contact to the reference Au electrode and the gas phase just outside S or Au, respectively. The value E_{abs}^{im} (Ag/AgCl) = 4.637 eV was calculated from the potential of the Ag/AgCl electrode relative to the standard hydrogen electrode (SHE), *E*(Ag/AgCl) = 0.197 V, and the absolute electrode potential of SHE, E_{abs}^{im} (SHE) = 4.44 V (ref.[13]). Although the latter value has been the matter of the continuing debate[14], it can serve as a tentative reference. On this basis, the work function of the reference Au electrode exposed to the carrier gas without propylamine was found to very only slightly between 4.89 eV and 4.97 eV, *i.e*, Φ^{Au} = 4.93 ± 0.04 eV.

Work Function Measurments of the Polymer Film

Films of polypyrrole (PPy) grown from ACN solution or ACN and water mixtures are known to exhibit most convenient mechanical and electrical properties[15]. Therefore, PPy was deposited from ACN solutions of pyrrole on a platinum electrode by oxidative polymerization in a galvanic cell

$$Pt \mid 0.01 \text{ M pyrrole, } 0.5 \text{ M LiClO}_4, \text{ ACN} \mid 0.1 \text{ M AgNO}_3, \text{ ACN} \mid Ag \quad . \quad (3)$$

The polymerization was carried out at a constant potential of 0.6 V with the charge consumption of 300 mC cm^{-2}. The platinum electrode covered by the polymer film was washed with ACN and polarized in the cell (*3*) in the absence of monomer at the potentials E_i = 600, 300, 0 or –300 mV for 10 min. The electrode was then washed again, dried and transferred into the stainless chamber for the work function measurements in the voltaic cell

$$Pt \mid PPy \mid G \mid Au \quad . \quad (4)$$

The potential *V* of the cell (*4*), which is measured under the conditions that the difference between the outer (Volta) potentials of PPy film and Au is zero, can be expressed by the equation

$$V = \left(\Phi_a^{PPy} - \Phi^{Au} \right) / e_0 \quad , \quad (5)$$

where Φ_a^{PPy} is the apparent work function of the PPy film, which can be considered as the absolute potential of the emersed Pt/PPy electrode, *i.e.*, $\Phi_a^{PPy}/e_0 = E_{abs}^{em}$ (Pt/PPy) (ref.[16]).

Figure 1 shows the effect of water vapour on the work function of the PPy film in the oxidized state (E_i = 600 mV). The value of Φ_a^{PPy} in the water-saturated air was about 80 meV more positive than in the dry air. Changes in the work function are much smaller when PPy is in the reduced state (E_i = –300 mV).

In the presence of water vapour, PrNH$_2$ induces the positive or negative shifts of Φ_a^{PPy} depending on the oxidation state of the polymer film, as displayed in Fig. 2. The initial values of Φ_a^{PPy} in the absence of PrNH$_2$ and the values of Φ_a^{PPy} after introducing PrNH$_2$ are summarized in Table I, column A

and B, respectively. Owing to a drift in the measured potential, the data in column B were obtained by adding the potential change upon introducing propylamine indicated by the arrows in Fig. 2 to the initial value. At the water vapour pressure as low as 4.5% of relative humidity, the changes in the work function upon introducing $PrNH_2$ are negligible.

After finishing the Kelvin probe measurements, the open circuit potential E_{OCP} of the Pt/PPy electrode was measured in the galvanic cell (3) in the absence of pyrrole (Table I).

TABLE I
Initial potential E_i and the open circuit potential E_{OCP} of the Pt/PPy electrode in the cell (3), and its apparent work function Φ_a^{PPy} upon the exposition to air with the relative humidity of 33% in the absence (A) or the presence (B) of propylamine (260 ppm)

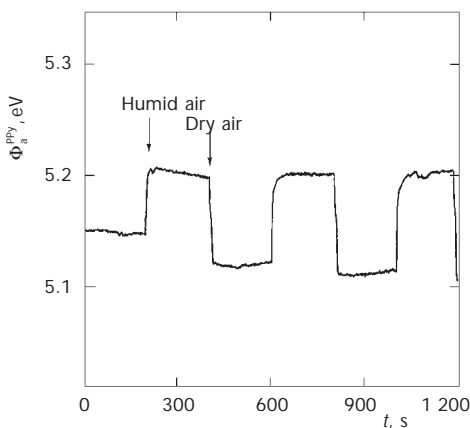| E_i, mV	E_{OCP}, mV	Φ_a^{PPy}, eV	
		A	B
600	200	5.13 (5.03)[a]	5.20
300	80	5.01	5.07
0	−20	4.91	4.93
−300	−150	4.86 (4.84)[a]	4.83

[a] Dry air (7% relative humidity).

FIG. 1
Apparent work function Φ_a^{PPy} of the Pt/PPy electrode with the oxidized (E_i = 600 mV) PPy exposed to humid (94% relative humidity) or dry air (7% relative humidity)

QCM Measurements

Figure 3 shows the mass changes of the oxidized PPy film upon its exposition to the humid or dry air (Fig. 3a), and to PrNH$_2$ in the dry or humid air. It is seen that the adsorption of water on the PPy surface is reversible and reaches approximately 0.7 µg cm^{-2}, *i.e.*, $3.9 \cdot 10^{-8}$ mol cm^{-2}. Provided that the maximum area occupied by one water molecule is 0.066 nm^2, the adsorbed amount corresponds to about 15 monolayers. In contrast, the adsorption of PrNH$_2$ from the dry air is rather weak (Fig. 3b), and significant
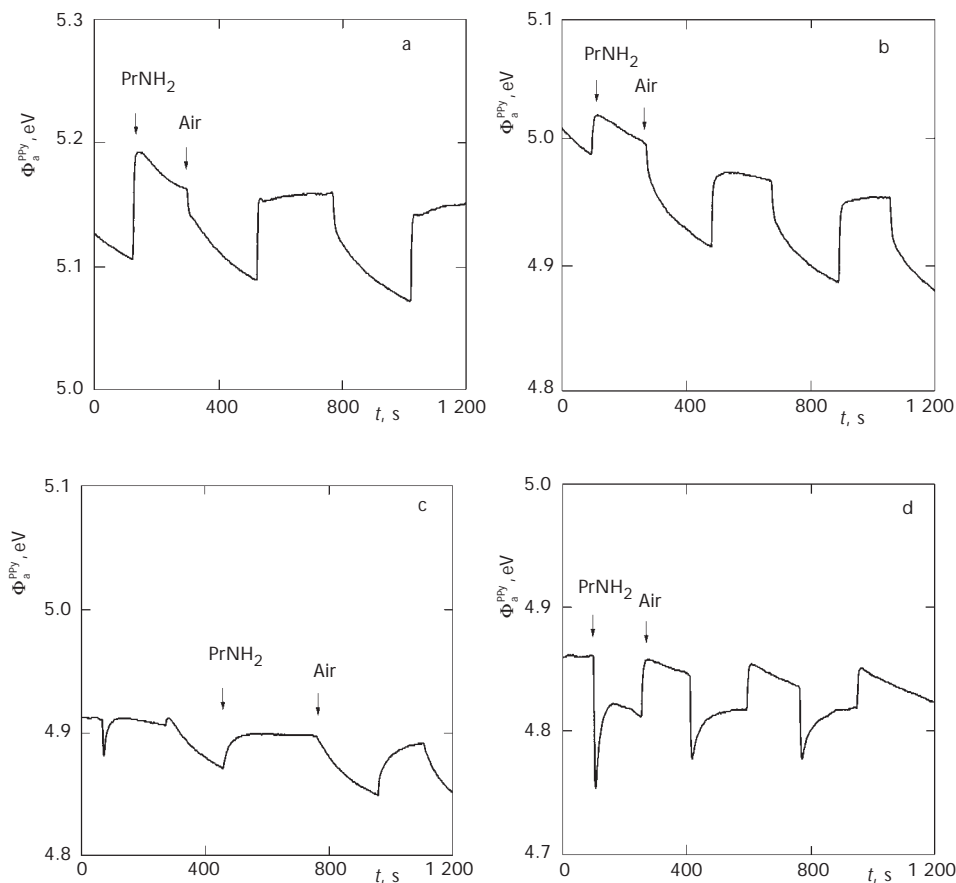
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Apparent work function Φ_a^{PPy} of the Pt/PPy electrode exposed to propylamine vapour (260 ppm, 33% relative humidity) with PPy in different oxidation states, E_i (in mV) = 600 (a), 300 (b), 0 (c) and −300 (d)

amounts of $PrNH_2$ are adsorbed only in the presence of water vapour (Fig. 3c). Besides, the adsorption of $PrNH_2$ is not quite reversible. In the first exposition, about 0.8 µg cm^{-2} of $PrNH_2$ is adsorbed, while this amount drops to 0.3 µg cm^{-2} in repeated expositions, *cf.* Fig. 3c. The latter number corresponds to $5.1 \cdot 10^{-9}$ mol cm^{-2} or, if the area occupied by one molecule of propylamine is taken as 0.15 nm^2, to about 12 monolayers of $PrNH_2$.

Mass changes of the oxidized PPy film in the presence of water vapour are proportional to the concentration of $PrNH_2$ (Fig. 4).

DISCUSSION

The sequence of states of the Pt/PPy electrode corresponding to the experiments performed can be described as the electrode immersed in the ACN
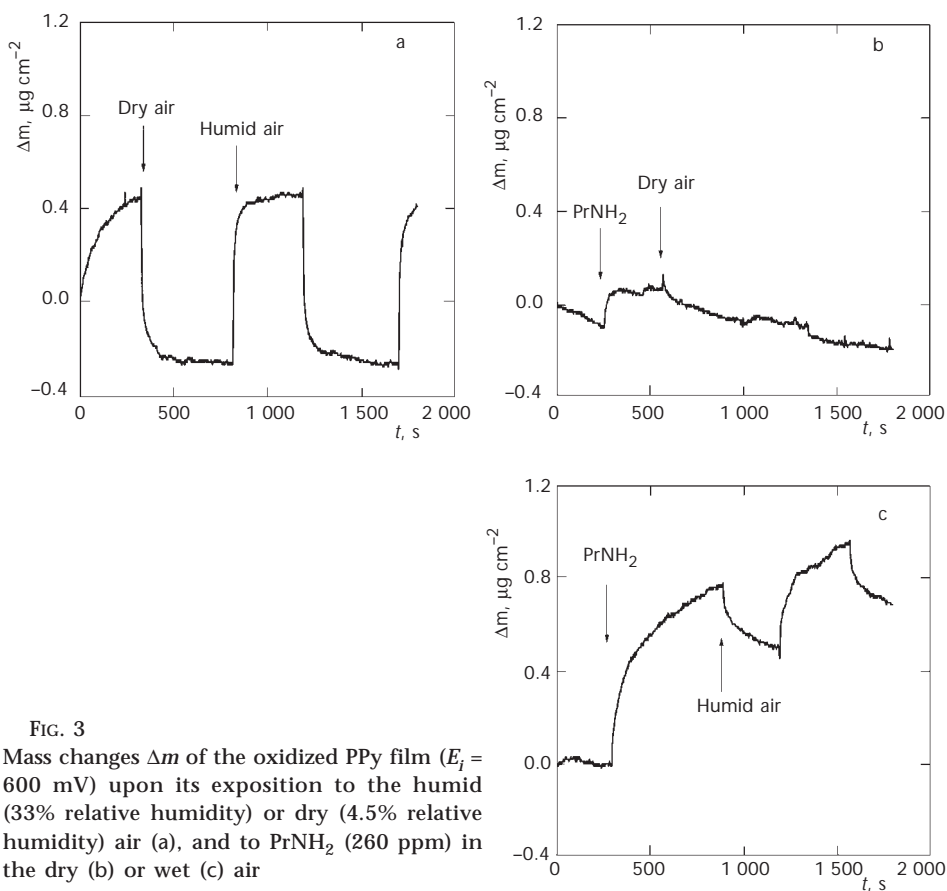

FIG. 3
Mass changes Δm of the oxidized PPy film (E_i = 600 mV) upon its exposition to the humid (33% relative humidity) or dry (4.5% relative humidity) air (a), and to $PrNH_2$ (260 ppm) in the dry (b) or wet (c) air

solution in the cell (*3*) and polarized to the potential E_i = 600, 300, 0 or –300 mV; the electrode emersed from this solution, washed and dried; the electrode exposed to the air containing water vapour; the electrode exposed to the air containing water vapour with propylamine and the electrode re-immersed into the solution in the cell (*3*) for the measurements of the open-circuit potential E_{OCP}.

A convenient reference potential, which is common to both immersed and emersed states, is the outer (Volta) potential of the Pt/PPy electrode, *i.e.* the electrical potential in the gas phase just outside the solution or the polymer layer of the immersed and emersed electrode, respectively, relative to the potential at infinity in vacuum[16]. The potential E of the cell (*3*) can be then expressed as the difference of the absolute electrode potentials of the Pt/PPy and reference electrodes,

$$E = E_{abs}^{im}\left(Pt/PPy\right) - E_{abs}^{im}\left(ref\right). \tag{6}$$

If the boundary between Pt and the PPy film represents an electrochemically polarizable interface, the former absolute potential can be written as[17]

$$E_{abs}^{im}\left(Pt/PPy\right) = \Phi^M/e_0 - \delta\chi^M + g_{ion}^P - g_{dip}^P + \Delta_S^P\varphi + \chi^S , \tag{7}$$

where Φ^M is the electronic work function of the metal in vacuum, $\delta\chi^M$ is the change in the surface potential of the metal caused by the polymer,
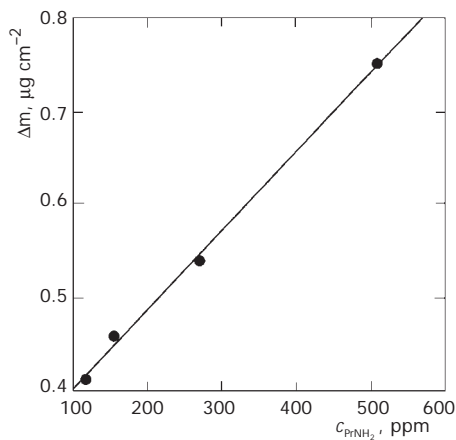

FIG. 4

Mass changes Δm of the oxidized PPy film (E_i = 600 mV) as a function of concentration of propylamine c_{PrNH_2} in humid air (50% relative humidity)

g_{ion}^P and g_{dip}^P are the respective ion and dipolar contribution of the polymer phase to the electrical potential difference across the metal/polymer interface, χ^S is the surface dipole potential of the solution and $\Delta_s^P\varphi$ is the electrical potential difference across the polymer/solution interface[18]. However, evidence has been provided that the contact between a high-work function metal, such as Au and Pt, and the PPy film is ohmic[19]. In such a case, the electron Fermi levels in Pt and the PPy (or the electrochemical potentials of electrons) are equal, the contributions g_{ion}^P and g_{dip}^P vanish, and the term $\Phi^M/e_0 - \delta\chi^M$ is to be replaced by the corresponding term for the PPy phase, $\Phi^{PPy}/e_0 - \delta\chi^{PPy}$. The potential difference $\Delta_s^P\varphi$ arises from the equilibrium partition of the anion or cation, which compensates for the polymer charge. The corresponding Donnan potential depends on the ratio of the concentration of the charges fixed in the polymer phase, c^x, and of the electrolyte in the solution, c^S. For univalent ions[20],

$$\Delta_s^P\varphi = \pm\,(RT/F)\,\ln\{(c^x/2c^S) + [1 + (c^x/2c^S)^2]^{1/2}\}\,,\qquad(8)$$

where the upper or lower sign applies to the anion- or cation-exchange polymer, *i.e.* the potential difference $\Delta_s^P\varphi$ is always positive or negative, respectively. The oxidized PPy film behaves as an anion-exchange membrane with $\Delta_s^P\varphi > 0$. With decreasing potential, the concentration of positive charges in the polymer phase decreases and $\Delta_s^P\varphi$ vanishes.

Obviously, if the electrode were emersed from the galvanic cell at a given potential E_i without any change in the structure of the PPy film or the PPy/solution and solution/air interfaces, the difference between the absolute potentials of the immersed and emersed electrodes, $\delta_P = \Phi_a^{PPy}/e_0 - E_{abs}^{im}$ (Pt/PPy), would be zero, and the potential V or the work function Φ_a^{PPy} would correlate with the potential E_i. Indeed, such a correlation was observed for polymer-coated metal electrodes emersed from an aqueous electrolyte into the water-saturated nitrogen gas or air[21,22]. However, the difference δ_P was found to be negative or positive for the anion (*e.g.*, polyvinylpyridinium)[21] and cation (*e.g.*, Nafion)[22] exchange membrane, respectively. These changes were ascribed to the collapse of the electrical double layer at the polymer/solution interface during which $\Delta_s^P\varphi$ vanishes[21,22]. Another explanation refers to the reorientation of the water molecules at the solution/gas interface resulting in a change of the surface potential χ^S (ref.[23]). The latter potential is small and positive (about 0.1 V, ref.[17]) for an electrode immersed in an aqueous solution. On the other hand, the pre-

ferred orientation of water molecules adsorbed on the polymer surface and their long-range order may give rise to the negative or positive value of χ^S for the positively or negatively charged polymer surfaces, respectively[23]. In the latter case, the double layer at the polymer/solution interface would be preserved upon emersion.

A similar analysis of the present data is less straightforward, inasmuch the potential of the Pt/PPy electrode emersed from the ACN solution is to be correlated with the potential of the electrode exposed to the gas phase containing water vapour. As indicated by data in Table I, the apparent work function Φ_a^{PPy} increases with increasing E_i for the Pt/PPy electrode exposed to both the water vapour and water vapour containing propylamine, though the plot of Φ_a^{PPy} *vs* E_i is not linear and its slope is much less than unity. Somewhat lower values of the open circuit potential E_{OCP} in Table I point to a drop in the Pt/PPy electrode charge during washing and drying the electrode after its emersion and, as the case may be, during the QCM and work function measurements that followed. Hence, the correlation of measured V or Φ_a^{PPy} with E_{OCP} appears to be more meaningful. Indeed, an almost $1 : 1$ correlation is found in both the absence or presence of propylamine (Fig. 5). As explained above, the linear correlation of the potentials of the Pt/PPy electrode in the cells (*3*) and (*4*) implies that the differences between the values of various contributions to E_{abs}^{im} and Φ_a^{PPy} are constant. However, after washing and drying the polymer surface, the electrical double layer with the corresponding Donnan potential can hardly be established at the polymer/gas interface. The $1 : 1$ correlation apparently reflects the dominant contribution of the work function term $\Phi_0^{PPy}/e_0 - \delta\chi^{PPy}$
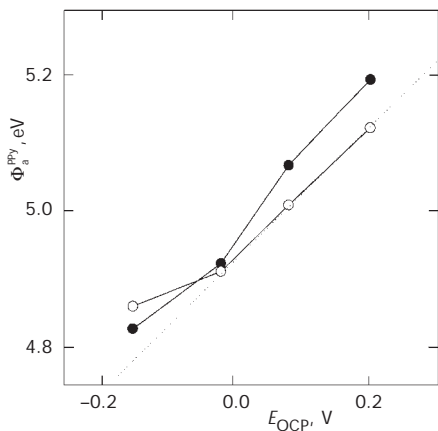

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Apparent work function Φ_a^{PPy} *vs* the open circuit potential E_{OCP} for the Pt/PPy electrode exposed to water vapour ($\bigcirc$) or propylamine vapour, 260 ppm, 33% relative humidity ($\bullet$). The unity slope is shown by the dotted line

to E_{abs}^{im} (Pt/PPy), which can be maintained during immersion. A deviation from this correlation can be ascribed to changes in this term or in the surface potential of the aqueous film on the PPy surface.

Thus, the deposition of a relatively thick aqueous film on the oxidized PPy surface exposed to the gas phase containing water vapour (*cf.* Fig. 3a) is accompanied by an increase in Φ_a^{PPy} (Fig. 1, Table I) corresponding to the orientation of water dipoles with their negative ends facing the gas phase, like on the surface of water. The change in Φ_a^{PPy} is much less pronounced for reduced PPy (Table I), where only weak adsorption of water was observed in the QCM measurements. The presence of the aqueous film appears to be a necessary condition for the adsorption of $PrNH_2$ (*cf.* the negligible mass changes observed at oxidized PPy in the absence of water, Fig. 3b).

The introduction of $PrNH_2$ causes an increase or decrease in Φ_a^{PPy} for the oxidized and reduced PPy film, respectively, *cf.* Table I and Fig. 5. In the former case, the propylamine adsorption can be viewed as the dissolution of the gas molecule in the liquid film, which is corroborated by the linear dependence of the amount of the gas adsorbed on its concentration in the gas phase (Fig. 4). The increase in Φ_a^{PPy} can be linked to the dissociation of $PrNH_2$ in the liquid film and to the adsorption of $PrNH_3^+$ ions on its surface.

Indeed, alkylammonium ions are known to be adsorbed at the water/gas interface with the alkyl group facing the gas phase, *i.e.*, with the orientation increasing the surface potential χ^S of water. On the other hand, water is unlikely to form an aqueous film on the reduced PPy surface. Here, the decrease in Φ_a^{PPy} is probably due to the direct adsorption of the neutral $PrNH_2$ molecule possesing strong electron-donor properties on the PPy surface.

CONCLUSIONS

The nature of interaction between propylamine vapour and polypyrrole film is strongly influenced by the oxidation state of the film and co-adsorption of water. On the surface of the oxidized PPy, water adsorbs to form a multi-layer. An increase in the work function of the Pt/PPy electrode exposed to both water and $PrNH_2$ was ascribed to the dissolution and dissociation of $PrNH_2$ in the water layer followed by the adsorption of $PrNH_3^+$ ions on the liquid surface with the alkyl oriented towards the gas phase. On the other hand, adsorption of water on the surface of the reduced PPy is rather weak. The observed decrease in work function is likely to be associated with the adsorption of neutral $PrNH_2$ molecules possessing strong electron-donor properties directly on the polymer surface. The significant

role of the water co-adsorption is evidenced by a drop in the adsorption of PrNH$_2$ upon lowering the water vapour pressure in the gas phase.

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