Characterisation of the Carbon Paste Electrode / Carmine Indigo Aqueous Solution Interface for Electrochemical Sensor Application

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Abstract: *Electrochemical sensors are used for regular monitoring of water, environmental and food matrices for trace metal elements (TMEs). These devices have on their surface a layer of active substances that complex ETMS such as mercury (II). Their effectiveness lies in the control of chemical reactions, the effect of the solvent and processes at the interface. The electrochemical behaviour of the indigo carmine dye was determined using cyclic voltametry at pH = 3 and pH = 10 on the carbon paste electrode (CPE). The acidic medium shows four current peaks giving two oxidising/reducing pairs: Indigo carmine (IC)/Leuco-indigo (LIC) Carmine and Dehydroindigo Carmine (DHIC)/Indigo Carmine (IC). In a basic medium, the voltamogram shows the existence of a single peak, that of dehydroindigo carmine. The mercury (II) sensor is optimal in a basic medium at pH = 10. Dehydroindigo carmine is a positive bipolaron which adsorbs to the surface of the working electrode by the internal sphere mode. Its structure contains groups enabling it to form 1:2 and 1:1 stoichiometric complexes. The sensor interface is influenced by current and mass transport phenomena. Their electrical parameters enable the equivalent electrical circuit of the interface to be constructed.*

Keywords: electrochemical sensor, indigo carmine, interface, Mercury, Cyclic voltammetry

1. Introduction

A chemical reaction has a utilitarian purpose. Producing a chemical reaction must have a purpose. The purpose of the chemical reaction derives from the interest and current use that can be made of it. The electrochemical reactions used to design sensors depend on all the parameters that govern chemical reactions (T, pH, concentration of ligands, etc.) but also on parameters linked to the nature of the electrode material, its surface condition and, in particular, the presence of adsorbed species [1]. The reaction of the forced oxidation of indigo carmine, a textile [2] and cosmetic [3] dye, using voltametry therefore has a dual aspect. It enables kinetics to be studied and reaction parameters to be deduced. By controlling these parameters and the processes on a working electrode, it is possible to optimise the electrochemical sensors developed. These sensors enable precise in situ measurements. They consist of a bioreceptor linked to a transducer that transforms the biochemical signal into a physical electrical signal that can be used directly. This signal translates the properties of the sensitive layer. The sensitive layer is the most important part of an electrochemical sensor [1].

It is partly made up of active substances adsorbed on the surface of the working electrode and having complexation sites. To carry out the redox reaction, a potential difference is supplied to the electrochemical cell by means of a potentiostat. When the energy supplied is greater than the minimum energy required, the reaction occurs easily, causing electrolysis of the species in solution. The aim of this work is to analyse the phenomena that influence the interface of the electrochemical sensor we have developed and, ultimately, to design the electrical circuit at the interface.

2. Experimental

2.1 Equipment

The electrochemical experiments were carried out using a PalmSens1 potentiostat (PalmSens BV) controlled by the pstrace software and driven by computer. The analytical method is cyclic voltammetry. The carbon paste electrode is used as the working electrode (W). The Ag/AgCl/KClsat electrode is used as the reference electrode (R) and platinum as the counter electrode (C). The pH of the indigo carmine solutions was measured with a Hanna pH meter. The curves were plotted using Origin pro 8 software. The body of the working electrode is made of a glass tube with a surface area of 0.07 cm^{-2} open on both sides into which a metal rod is inserted to act as a contact; the tube is filled each time with carbon paste. It is cleaned whenever necessary by manual polishing on clean, smooth paper. The electrodes are immersed in indigo carmine solutions from Aldrich company inc. At pH = 3 and pH = 10 prepared with distilled water. The mercury (II) solution is from Merck. The method of analysis is voltametry. All reagents are of analytical purity. The room temperature is $25° \pm 1$.

2.2 Study of the indigo carmine reaction

Voltammetry techniques are based on the study of the relationship that is established between the electrode potential E and the current I that flows through an electrochemical cell when this potential is imposed. The current measured reflects the mechanism and rate of the various reactions associated with an electrode process, and enables a qualitative or quantitative determination of the associated characteristic parameters (thermodynamic and kinetic) when a theoretical model of the process is available

In cyclic voltammetry (CV), the imposed potential is a linear function of time at a constant rate (sweep rate) and is varied first in one direction (generally towards negative potentials) and then in the opposite direction in the same experiment. Scanning makes it easy to observe the behaviour of the system at different potentials and thus to identify the different electroactive species. Reversing the direction of potential variation allows us to observe the electrochemical behaviour of both reactants and products, and therefore the reversibility of reactions. In addition, the sweep rate provides a direct means of controlling the kinetic regime of the reactions (reversible, quasi-reversible, irreversible) and its variation makes it possible to observe the reactions under different regimes and to diagnose their mechanism. The characteristics I = f (E) are called voltamograms, in which I is the current intensity of the redox reaction. It represents the rate of consumption of the reactants or formation of the products at the surface of the electrode. The potential E is the voltage at which the redox species appears. It also represents the energy of formation of the redox species. The overall current is influenced by the faradic current and the capacitive current. In voltametry, the voltamograms obtained show peaks that obey the Randles-Sevcik equation [4], [5].

$$I_p = (2,687.10^5) \; n^{3/2}.A.D^{1/2}v^{1/2}.C \qquad (1)$$

where n is the number of electrons involved in the redox reaction; A is the area of the electrode in cm^2, v is the sweep rate in V/s; C is the concentration of the active species in mol/cm^3, D is the diffusion coefficient in cm^2/s. The Randles-Sevcik peak current is a faradic current linked to the diffusion of redox species. This creates the diffusion layer. The thickness (δ) of the diffusion layer is expressed in equation 2 [6], [7].

$$\delta = \sqrt{\pi.D.t} \qquad (2)$$

where D is the diffusion coefficient and t (s) is the electrolysis time. The duration of the reaction in a basic medium is 141 s. The duration of the reaction in an acid medium is 212 s.

The resistance of the solution obtained from the current is given by Ohms' law (3).

$$E = R_e.I_0 \qquad (3)$$

A cyclic voltamogram is used to study reversibility or the reaction mechanism. The kinetic parameters of the reaction can also be deduced from the plots. The charge transfer resistance due to the faradaic process [8], [9] is given by relationship (4).

$$Rct = \frac{RT}{nFI_0} \qquad (4)$$

where: R is the perfect gas constant; T is the absolute temperature (K); n is the number of electrons transferred; F is Faraday's constant and I0 is the exchange current density at equilibrium potential. This current density is linked directly to the kinetic constant k0 of electron transfer [9] by the following relationship (5):

$$I_0 = nFSC_0k^0 \qquad (5)$$

S is the active surface of the electrode and C_0 the concentration of the redox couple in solution. For the reaction at the electrode, the active species diffuse from the solution to the electrode surface [9]. This diffusion phenomenon is characterised by the Warburg(6) impedance:

$$W^*(\omega) = \frac{R_t \times y}{\sqrt{j\,\omega}} \qquad (6)$$

where $y = \dfrac{K_{red}}{\sqrt{D_{ox}}} + \dfrac{K_{ox}}{\sqrt{D_{red}}}$

During a redox reaction involving a solid electrode and a redox species, the reaction structures the solution into a layer: this is the electrochemical double layer. The double layer capacity is obtained using the relationship (7) [10].

$$2\pi.f.R.C_{dl} = 1 \qquad (7)$$

where f is the potentiostat setting frequency, i.e. 50 Hz, R is the electrolyte resistance and C_{dl} is the double layer capacitance.

3. Results and Discussion

3.1 Study of the electrochemical behaviour of indigo carmine using cyclic voltametry

Indigo carmine is a dye used in cosmetics, pharmaceuticals, medicine, etc. Several studies have already been carried out by numerous authors [11]-[17] in cyclic voltametry with different working electrodes. A comparative study of the electrochemical behaviour of indigo carmine on carbon paste and silicon paste electrodes was carried out by N'dri et al. 2016 [17]. The various studies show that in an acid medium at pH = 3, indigo carmine exhibits two anodic peaks and two cathodic peaks showing the existence of two oxidising/reducing pairs: the indigo carmine/Leucoindigo carmine pair and the dehydroindigo carmine/indigo carmine pair. Redox reactions are virtually reversible and influenced by transport phenomena by diffusion and adsorption. In a basic medium, there is a single anodic peak, the oxidation of indigo carmine to dehydroindigocarmine. The reactions of indigo carmine on the different electrodes are influenced by the pH of the solution and by competing reactions. The different redox reactions of the dye indigo carmine identified by Fanjul-Bolado et al [11] are shown in Figure 1.
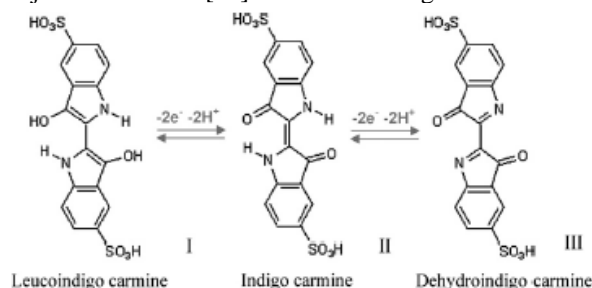

Figure 1: Redox reaction process of indigo carmine in an acid medium [11].

The aim of this study is to investigate the phenomena that influence the solid electrode/aqueous solution interface in order to create the electrical circuit that best explains the redox reactions. To achieve the objectives of this study,

indigo carmine was once again studied on the carbon paste electrode (CPE) at pH = 3 and pH = 10 using cyclic voltammetry. This electrochemical technique is often used to study reaction mechanisms. Two successive potential sweeps in the forward and reverse directions trigger the redox reaction. The deposition potential determines the direction of the reactions. A positive deposition potential allows an oxidation reaction to take place before reduction. A negative deposition potential allows a reduction reaction before an oxidation reaction. In cyclic voltametry, the fixed sweep rate is equivalent to fixing the activation energy. Figure 2 shows the potential sweep and voltamogram of indigo carmine obtained in an acid medium at pH = 3.
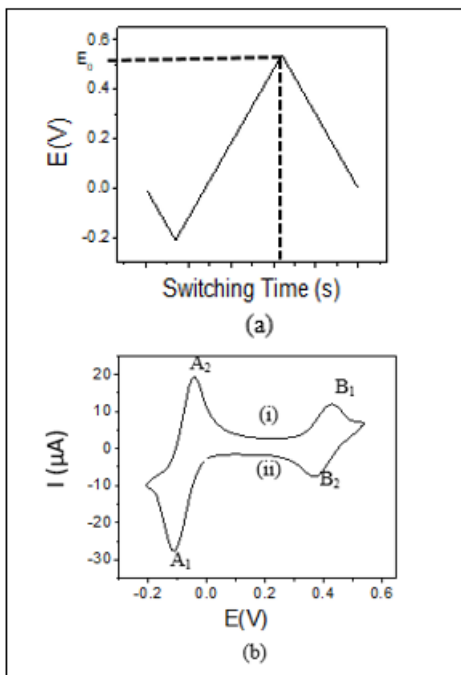

Figure 2: (a) Shape of the electrode potential; (b) Shape of the voltammogram of the electrochemical behaviour of indigo carmine on the carbon paste electrode in an acid medium pH = 3, concentration 0.65 M; sweep rate 70 mV/s.

Figure 2 (a) shows the potential sweep that induces the electrochemical reaction. This curve shows three potential variations:
- an initial drop in potential from 0V to -0.2V ;
- an increase in potential from -0.3 V to 0.50 V;
- a second drop in potential from 0.50 V to 0 V.

The maximum potential $E_0 = 0.5$ V of this scan represents the inversion potential which allows the reactions that could not take place during the forward scan to occur during the reverse scan. Figure 2 (b) is the voltamogram obtained when the species is subjected to the cyclic potential sweep 2 (a). The presence of redox peaks shows that the electrode material is active. The voltamogram shows the four redox peaks mentioned in the literature. These four peaks reflect the existence of two redox couples A_2/A_1 (Indigo carmine (IC)/Leucoindigo carmine (IC)) and B1/B2 (dehydroindigo carmine (DHIC) to indigo carmine (IC)). The reactions are almost reversible ($\Delta Ep > 0.057/2$) [18]. Between the redox peaks, there is a gap representing two almost linear curves (i) and (ii) with equations I = 2.5 µA and I = - 5 µA respectively. These curves represent current lines. Each redox peak is

therefore characterised by its electrochemical impedance, Z. The impedance of peak A1 is noted Z_{A1}, that of A_2, Z_{A2}; that of B_1, Z_{B1} and finally that of B_2, Z_{B2}. The current lines (i) and (ii) have different intensity values. This suggests that the series impedances Z_{A2} and Z_{B1} are in parallel with the series impedances Z_{A1} and Z_{B2}. The simplistic approach gives a representation of the equivalent electrical circuit of the sensor interface in the acid medium in Figure 2.
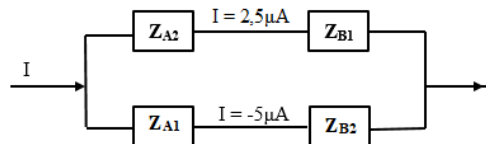

Figure 3: First approach to the equivalent circuit of the CPE/indigo carmine interface (pH =3)

Equivalent electrochemical impedance (Z) of the circuit shown in Figure 3 containing the partial impedances of the circuit is determined using relationship (8):

$$Z = \frac{Z_{A2}.Z_{A1} + Z_{A2}.Z_{B2} + Z_{B1}.Z_{B2}}{Z_{A1} + Z_{B2} + Z_{A2} + Z_{B1}} \qquad (8)$$

The parameters of the partial electrochemical impedance for a redox reaction are the constituents of the Randles-Sevcik circuit [4], [5]. They are the electrolyte resistance (Re), the charge transfer resistance (R_{tc}), the Warburg impedance (W) and the double layer capacitance (C_{dl}). They are determined using the voltamogram and the relationships (1) to (7) given. The parameters obtained are listed in Table 1. The electrical quantities current and potential taken from the voltamograms are taken as absolute values indistinctly according to their nature.

Table 1: Electrical quantities and parameters at the EPC/indigo carmine interface in an acid medium.

Electrical parameters	A₂	A₁	B₁	B₂
I (µA)	19,2	27,8	11,8	7,6
E (V)	0,004	0,112	0,04V	0,37
D (cm² s⁻¹)*10⁻⁶	4,40	9,23	1,66	0,69
δ (cm)	0,054	0.0783	0 ,0332	0.0214
Re (kΩ)	0,208	4,03	3,64	48,69
K⁰(10⁻⁵cm s⁻¹)	3,12	4,52	1,98	1,24
$Rct(\Omega/cm^2)$	47,44	32,73	71,12	119,74
Warburg impédance (j⁻⁰,⁵ Ωcm2)	0,043	0.0305	0,0665	0,109
C_dl(µF)	15,71	0,790	0,875	0,065

The electrical parameters listed in the table characterise the nature of the current flowing through the system under study. These currents are linked to the faradic current and the capacitive current. The faradic current is the current generated by the redox reaction. Capacitive current, on the other hand, is a current that opposes the reaction. Each type of current is therefore defined by its own electrical quantities. The electrical quantities of the faradic current are the coefficient, the charge transfer kinetic constant, the charge transfer resistance and the Warburg impedance

- The diffusion coefficient gives information about the movement of the redox species from the solution boundary to the electrode surface. It is influenced by the viscosity of the solution and by the solvation of the species being electrolysed. All the diffusion coefficients obtained for the

redox species are of the order of 10^{-6} cm^2.s^{-1}. These values are consistent with those reported for aqueous solutions in the literature. They range from 10^{-5} to 10^{-7} cm^2.s^{-1}[6]. Indigo carmine therefore activates the surface of the carbon paste electrode in an acid medium.

- The diffusion layer is a thin layer of the solution in contact with the electrode. Its concentration is different from that of the rest of the solution. Its value in relation to the electrode radius gives information about the nature of the diffusion. The values obtained are greater than the radius of the electrode used (r = 0.15 cm). The values found are smaller than the radius of the cylindrical electrode; the diffusion process is planar at the interface [6], [7].

- The charge transfer resistance represents the response of the interface to a frequency high enough to avoid relaxation. The charge transfer resistances of the redox species obtained range from 30-120 Ω/cm2. These values can be considered low compared with those obtained in the case of a fibrinogen-modified carbon paste electrode [19]. This result suggests that the electrons involved in the production of redox species are weakly bound. These are the π electrons of the conjugated aromatic system. The parent poly film formed is not solid

- The charge transfer kinetic constant k0 is a parameter that measures the rate at which electrons are transferred across the electrode/electrolyte interface. Fast charge transfer processes are characterised by low values. Slow processes are characterised by higher values [19].

- Warburg impedance is characteristic of ionic movement at the interface. The values obtained are all less than unity. The electrolysis of indigo carmine does not produce a large quantity of ions [9].

- The electrical quantities of the capacitive current are: the resistance of the electrolyte or solution and the capacitance of the electrochemical double layer:

- The resistance of the solution is a parameter that affects the flow of current at the interface. The resistances of the electrolyte are influenced by the pH, the solvent and the concentrations of the species. The resistances obtained are of the order of kiloOhm (kΩ). The anodic peaks (A$_2$ and B$_1$) have low electrolyte resistance values compared with the cathodic peaks. This observation suggests that the anodic reactions of indigo carmine are favoured by the acidic pH in the aqueous medium [19].

- The presence of a solid phase in contact with an electrolyte disturbs the charge distribution in the solution, and the forces generated impose a particular distribution of ions in the vicinity of the electrode. This charge distribution causes an excess of charge at the electrode/electrolyte interface and a redistribution of charge in the electrolyte in order to achieve thermodynamic equilibrium. This phenomenon of charge separation at the interface is known as an electrochemical double layer. By applying a cyclic potential difference between the voltammetric analyser's working and reference electrodes. These become polarised. An excess of ions of opposite charge and similar size to those present in the electrode is created at each interface. All these phenomena are represented by the electrochemical double layer capacitance C$_{dl}$. The electronic double-layer capacitances obtained during the production of the redox species of indigo carmine are less than one microfarad for peaks A$_1$, B1 and B$_2$, and more than one microfarad for A$_2$. The low value would indicate

that there is no opposition to these reactions taking place. On the other hand, a high value indicates strong opposition to this reaction. Applying the potential allows all these reactions to occur. The redox reactions of indigo carmine are forced reactions.

Using the parameters electrolyte resistance (Re), charge transfer resistance (R$_{tc}$), Warburg impedance (W) and double layer capacitance (C$_{dl}$), the equivalent circuit is constructed. Figure 4 shows the partial electrochemical impedance (Zi) and the corresponding electrical circuit.
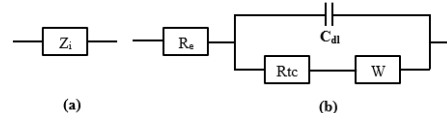

Figure 4: (a) Partial electrochemical impedance; (b) Equivalent electrical circuit

The construction of the equivalent electrical circuit of the CPE/carmine indigo solution interface at pH = 3 is obtained by simply replacing the partial impedance by the Randles-Sevcik equivalent electrical circuit.

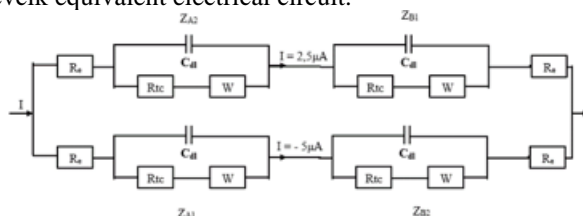**Figure 5:** Equivalent electrical circuit of the CPE/IC interface at pH = 3.

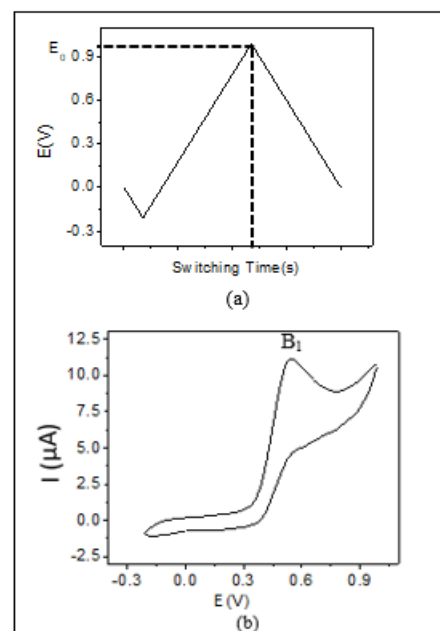The electrochemical behaviour was studied in a basic medium on the carbon paste electrode (CPE).

Figure 6: Cyclic voltammetry: (a) shape of the electrode potential (b) shape of the voltam-mogram of the electrochemical behaviour of indigo carmine on the carbon paste electrode in a basic medium pH = 10, concentration 0.65 M, sweep rate 60 mV/s.

Figure 6 shows the evolution of the current as a function of time and the cyclic voltammogram of the redox reaction of indigo carmine obtained. Figure 6 shows a single redox peak. This peak is characteristic of an irreversible chemical reaction. The intensity of the peak Ip = 11.5µA at a sweep speed of 60 mV/s.

This peak reflects the oxidation of indigo carmine to dehydroindigo carmine (DHIC). The oxidation product is a positive bipolaron. It appears at a potential of Eappl = 0.45V. The existence of a single peak shows that the reaction takes place in one direction only. The reaction is therefore unidirectional. The basic medium does not favour the reverse reaction, which is the reduction of dehydroindigo carmine (DHIC) to indigo carmine (IC), nor the redox reaction of the indigo carmine (IC)/leucoindingo carmine (LIC) pair. The pH of the medium affects the reactions and the direction of the redox reactions of indigo carmine [11]-[16]. During this reaction, indigo carmine loses two H+ protons and two electrons (e-) at the solid/liquid interface. This results in the creation of imine groups on the carbon chain. The presence of imine and carbonyl groups on the dehydroindigo carmine molecule gives it its complexing property. The existence of a single peak shows that the reaction takes place in one direction only. The reaction is therefore unidirectional. The reaction equation (9) is:
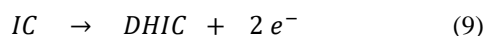
$$IC \rightarrow DHIC + 2\,e^- \qquad (9)$$

The basic medium does not favour the reverse reaction, which is the reduction of dehy-droindigo carmine (DHIC) to indigo carmine (IC), nor the redox reaction of the indigo carmine (IC)/leucoindingo carmine (LIC) pair. The pH of the medium affects the reactions and the direction of the redox reactions of indigo carmine [17]. During this reaction, indigo carmine loses two H^+ protons and two electrons (e^-) at the solid/liquid interface. This results in the creation of imine groups on the carbon chain. The presence of imine and carbonyl groups on the dehydroindigo carmine molecule gives it its complexing property. The electrical parameters of the only peak obtained in a basic medium are given in Table 2.

Table 2: Electrical values deduced from voltamograms of indigo carmine in alkaline medium

Electrical parameters	Valeurs
I(µA)	11 ,5
E(V)	0.45
Re (kΩ)	39,13
D (cm^{2}s^{-1}) *10^{-6}	1,84
δ (cm)	0;0285
K^0 (.10^{-5}cms^{-1})	1,87
Rct(Ω/cm^2)	79,13
Warburg impédance (j$^{-0,5}$ Ωcm^2)	0,0317
C$_{dl}$ (µF)	0,081

Table 2, obtained in a basic medium, groups together the electrical values of the faradic current and the electrical values of the capacitive current.
- The value of the current peak obtained is almost identical to that of B$_1$ in an acid medium.
- The value of the diffusion coefficient 1.84.10^{-6} cm^{2}s^{-1} obtained is in line with the values given in the literature for aqueous solutions. This value compared with that of the B$_1$ peak in the acid medium is almost identical. The

diffusion coefficient of the redox species does not seem to be influenced by the pH of the medium. The same applies to the electrolyte resistance and the charge transfer resistance.
- All the other parameter values, such as charge transfer kinetic constant, double layer capacitance and diffusion layer thickness, are similar to the values for the acidic medium, with the exception of the electrolyte resistance. The basic medium is more resistive than the acid medium. The aqueous medium has a high resistivity.

The indigo carmine reaction alone will be represented by the electrochemical impedance Z$_{B1}$ and by the equivalent Randles-Sevick electrical circuit [4, 5] in Figure 6.
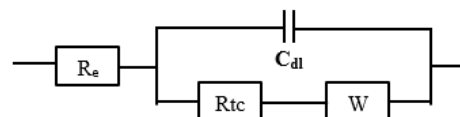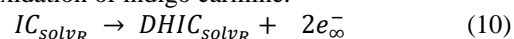

Figure 6: Equivalent electrical circuit for the electrochemical impedance of Z$_{B1}$ in a basic medium.

3.2 Influence of solvation

The cyclic voltammetry study showed that the electrochemical activity of indigo carmine is influenced by the pH of the aqueous solution. The reaction takes place in an aqueous medium and is influenced by solvation. The adsorbed molecules surrounded by their solvation shells on the working electrode will give rise to the electrochemical double layer, the zone located just after the surface of the carbon paste electrode. The electronic transfer of indigo carmine to the electrode takes place according to the "inner sphere" system because of the double layer [20], [21]. According to Franck Condon [22], electron transfer is accompanied by a reorganisation of the solvation shell around the reacting entities. There are two possible stages in this irreversible oxidation of indigo carmine.

$$IC_{solv_R} \rightarrow DHIC_{solv_R} + 2e_\infty^- \qquad (10)$$

$$DHIC_{solv_R} \rightarrow DHIC_{solv_O} \; (-2\lambda r) \qquad (11)$$

$$e_{solv_R}^- \rightarrow e_\infty^- \qquad \text{Ionisation (I) (12)}$$

$$e_\infty^- \rightarrow e_{solv_O}^- \qquad Affinity \qquad (13)$$

The energy balance of the redox equation is established by equation (14)

$$I - A - 2.\lambda r = 0 \qquad (14)$$

The energies of this system of equations are determined from the energy levels of the HOMO and LUMO atomic orbitals, already discussed in another publication [17]. The dissipation energy λr for an electron equal to 0.075 eV is therefore estimated from the calculation of the electrochemical gaps on the B1/B2 pair and from relation (15).

3.3. Complex formation

When the electrochemical cell is subjected to potential scanning, a non-equilibrium reaction occurs. This reaction

takes place at the surface of the working electrode. Under the effect of the electric field, at alkaline pH, the dehydroindigo carmine molecules migrate to the surface of the working electrode where they encounter the insulating paraffin layer. They are thus adsorbed: this is the electrochemical double layer. The sensor developed in this way has cationic affinity groups on its surface. A complex is formed.

Mercury (II) has two complexation sites, as shown in the figure. The complex formed by the indigo carmine adsorbed on the working electrode is either of stoichiometric configuration 1:1 or 1: 2. The authors agree that the stable complex is of stoichiometric configuration 1:1.
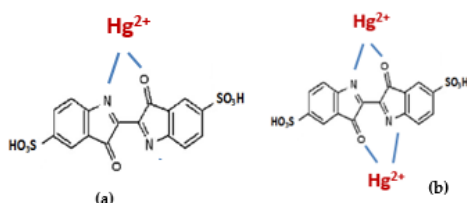

Figure 8: Stoichiometry of the complexes formed by indigo carmine:(a) HgIC (b) Hg₂IC

4. Conclusions

The dye indigo carmine (IC) is used in the medical, pharmaceutical and textile fields. A study of the electrochemical behaviour using cyclic voltametry showed that various reactions take place at the interface as a function of pH. The reactivity of this molecule is linked to the delocalised π electrons of the aromatic ring. Electron transfer occurs via the internal sphere mode. In an acid medium, the reaction gives rise to bipolaron couples: dehydroindigo carmine/indigocarmine and indigocarmine/ leucohindigocarmine. The electrical circuit at the interface shows the impedance of the anodic peaks in shunt with the impedance of the cathodic peaks. The acidic medium is a complex medium for optimising the sensor made with indigo carmine. In a basic medium, on the other hand, the reaction on the carbon paste electrode shows a single peak, that of the positive bipolaron of dehydroindigo carmine. During the formation of dehydroindigo carmine, two protons and two electrons are transferred. Their departure from indigo carmine allows the molecule to be reorganised. The new molecule has attack sites for the mercury (II) ion on its structure. The baisic medium is a favourable environment for optimising the sensor. Finally, the study showed that the electrical magnitudes of the B1 peak (dehydroingicarmine) are almost similar. The pH does not significantly influence the faradic current and capacitive current parmeters of dehydroindigo carmine.

Authors' contributions
This work was carried out in collaboration among all authors. All authors read and approved the final manuscript

Competing Interests
Authors have declared that no competing interests exist.

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