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A Water-Insoluble β-Cyclodextrin Derivative for Hydroquinone Sensor Applications

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ABSTRACT

A water-insoluble β-cyclodextrin derivative (β-CDMeAl) was synthesized and characterized. An impedimetric water-stable sensor based on β-CDMeAl-modified gold electrode was described for detection of hydroquinone. The wettability of the sensitive membrane was evaluated using contact angle measurements and the electrochemical impedance spectroscopy was used to study its response to hydroquinone in aqueous medium. The diverse processes taking place at the different interfaces were studied according to an equivalent circuit fitting of the experimental data. The results reveal an enhancement of the membrane resistance by increasing the hydroquinone concentration, indicating the good sensitivity of the β-CDMeAl membrane to this toxic molecule.

Keywords: Cyclodextrin, Bio-based materials, Hydroquinone, Sensor, Impedance spectroscopy.

INTRODUCTION

The β-cyclodextrin (β-CD) is a bio-sourced macromolecule produced from the starch via enzymatic conversion. It is a cyclic oligosaccharide formed by the association of seven glucose units (Figure 1); its outer surface is connected with hydroxyl groups that allow it to be water-soluble. It has a shape of a truncated cone and shows a relatively hydrophobic cavity. Hence, it can form inclusion complexes with a wide variety of organic molecules in aqueous solution [1-4]. The complexing properties of β-CD support its use in chemical and biological sensors [5-10]. Hydroquinone (HQ) is a phenolic compound which presents high toxicity to the human organism and a harmful effect to the ecosystems and especially to water [11].

At present many methods have been established to detect HQ, such as chromatography, [12] capillary electrophoresis, [13] spectrophotometry [14] and electrochemical techniques [15-22]. In this work, we investigate a β-CD-based sensor for HQ, using the electrochemical impedance spectroscopy. In fact, this method is the most favorable to determine HQ due to its low cost, high sensitivity and easy operation. Though, the immobilization of cyclodextrin on the work electrode usually presents a real problem due to their solubility in aqueous media. Several approaches have been tried to obtain water-stable sensors, such as the incorporation of CD in polymer matrices (e.g. polypyrrole [23,24] and polyaniline [25,26]), the development of sensor from a mixture of carbon powder and CD [27,28] or the chemical modification of

CD [29]. In this study, we chose to proceed by allylation of the methylated cyclodextrin (β-CDMe) to obtain the allylated-methylated hydrophobic derivative (β-CDMeAl) which is soluble in common volatile organic solvents.

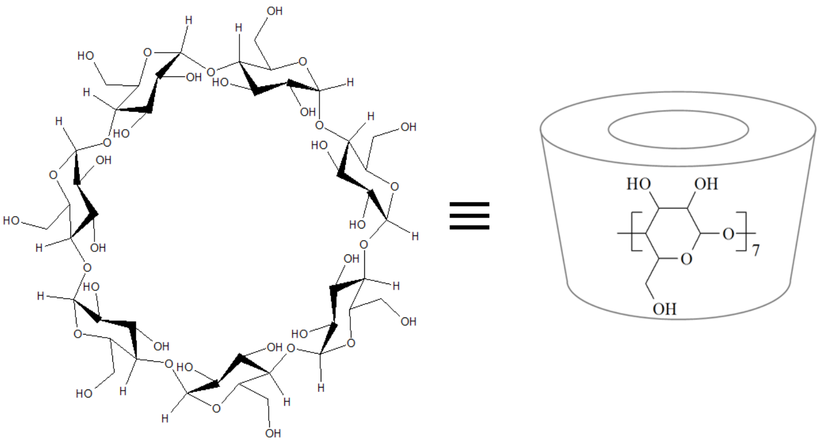


Figure 1: The molecular structure of β-cyclodextrin.

MATERIALS AND METHODS

Methyl-β-cyclodextrin (β-CDMe; average methylation degree of 12 and M_n =1305 g.mol^{-1}, as determined by MALDI-TOF), sodium hydride (60%), hydoquinone (HQ, certified reference material), allyl bromide (99%) were purchased from Sigma-Aldrich. Deionized water was purified with a MilliQ plus system. The ^{1}H NMR spectral data were obtained on a Bruker AV200 spectrometer and the chemical shifts were referenced to the $CHCl_3$ signal at 7.26 ppm. The MALDI-TOF mass spectrum was recorded with a Perseptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument is equipped with a nitrogen laser (337 nm), a delayed extraction and a reflector; it was operated at an accelerating potential of 20 kV. The sample was prepared in 2,5-dihydroxybenzoic acid (2,5-DHB) matrix and sodium iodide was added in to induce cationization.

Synthesis of the allyl-methyl-β-cyclodextrin (β-CDMeAl): The β-CDMe (34 mmol of OH groups, 5.25 g) and sodium hydride (102 mmol, 4.08g) were dissolved in DMF (50 mL) and stirred at room temperature for 40 min. A solution consisting of allyl bromide (102 mmol, 9 mL) in DMF (20 mL) was added dropwise at 0 °C. After 24 h at room temperature, the mixture was poured into an excess of distilled water and extracted with chloroform. The organic phase was washed with water; then, the solvent and the excess of allyl bromide were removed under reduced pressure. The resultant crude was dissolved in acetone and precipitated in distilled water to obtain β-CDMeAl as a white powder. The precipitate was washed with distilled water overnight, filtered and dried under vacuum. Thus, 5.4 g of dry product was obtained with a reaction yield of 82%.

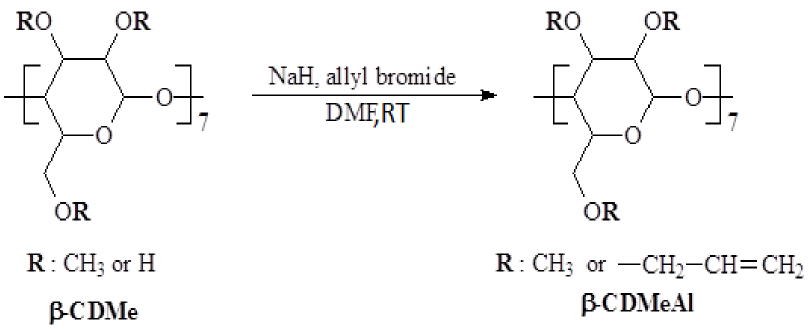
Elaboration of the β-CDMeAl membrane: The Gold substrates are purchased from the "Centre de Recherche LAAS" (France) and cut into 1cm ×1 cm square solids; the gold layer thickness is about 50 nm. These surfaces were first degreased with acetone for 10 min, then immersed in piranha solution (1/3 H_2O_2 + 2/3 H_2SO_4) during 1min and finally rinsed with ultra-pure water. The electrode was dried with nitrogen flow after each step. Following cleaning, the sensitive membrane based on the new β-CD derivative was deposited on the gold surface by the spin-coating technique. 30 μL of β-CDMeAl/chloroform solution (10^{-3} M) was spread out on the gold electrode surface; the spinning rate was of 2700 rpm. The obtained uniform membrane was dried at room temperature for 30 min.

Contact angle measurements: The contact angle measurements were performed with Digidrop GBX applying a sessile drop method. The measurements were carried out by applying 4 μL of the liquid on the β-CDMeAl membrane surface. The drop image on the surface was acquired and analyzed with a digital camera. Every reported contact angle measurement represents an average value of at least three separated drops on different areas of the membrane.

Impedance spectroscopy measurements: The electrochemical impedance spectroscopy (EIS) measurements were carried out by using impedance analyzer Autolab747 supported by Frequency Response Analysis system software (FRA2) controlled by computer. A conventional three-electrode cell was used, with saturated calomel electrode (SCE) as reference, a platinum wire as counter electrode and the modified gold as working electrode. A sinusoidal excitation signal with amplitude of 10 mV was applied over a frequency range of 100 mHz-100 kHz. The 0.1M phosphate buffer solution (PBS) with a pH 4 was used as electrolyte.

RESULTS AND DISCUSSION

Synthesis and characterization of the β-CD derivative: The hydrophobic β-CD derivative (β-CDMeAl) was obtained via the direct allylation of the hydrophilic methylated cyclodextrin (β-CDMe) (Scheme 1). A conventional procedure for the Williamson reaction was adopted, using NaH/DMF system.



Scheme 1: Allylation reaction of the β-CDMe.

The modified β-CD was found to have good solubility in common volatile organic solvents such as THF and chloroform; its macromolecular structure was confirmed by FT-IR and NMR spectroscopies. The FT-IR spectrum of β-CDMeAl (Figure 2) proves the totally disappearance of the OH groups characteristic bands (stretchings at 3400 cm^{-1} and bendings at 1650 cm^{-1}) and reveals two bands at 1730 cm^{-1} and 3080 cm^{-1} corresponding to the vinylic C=C and C-H stretching vibrations of the allyl groups. The ^{1}H NMR spectrum shows the characteristic peaks of the allylic protons as illustrated in Figure 3. By comparing the integration of these signals with those corresponding to CD and methoxy protons, the average methylation and allyation degrees were estimated to 12 and 9, respectively. This result was in agreement with the MALDI-TOF MS analysis (Figure 4), which indicates a number-average molecular weight of 1672 g.mol^{-1}. The spectrum shows a narrow mass distribution (monodisperse Ip ~1) and reveals the presence of six macromolecular species containing from 7 to 12 allyl groups per cyclodextrin.

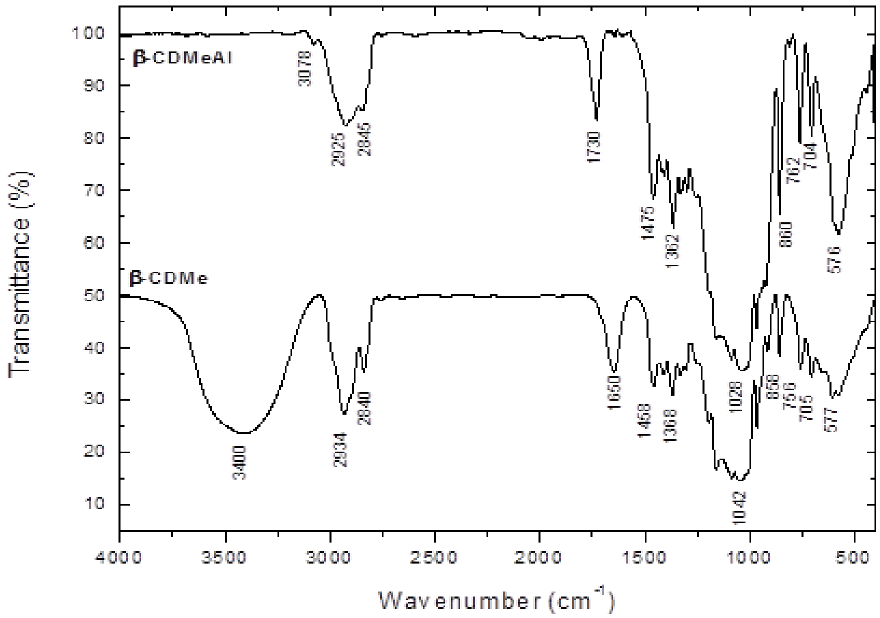


Figure 2: The FT-IR spectrum of β-CDMeAl, in comparison with β-CDMe FT-IR spectrum.

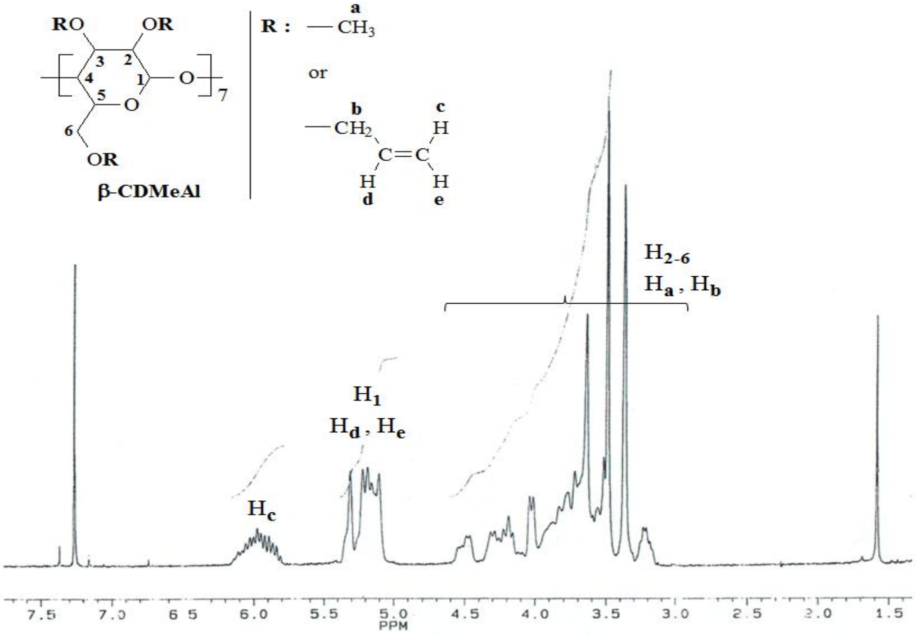


Figure 3: ^{1}H NMR spectrum of β-CDMeAl ($CDCl_3$, 200 MHz).

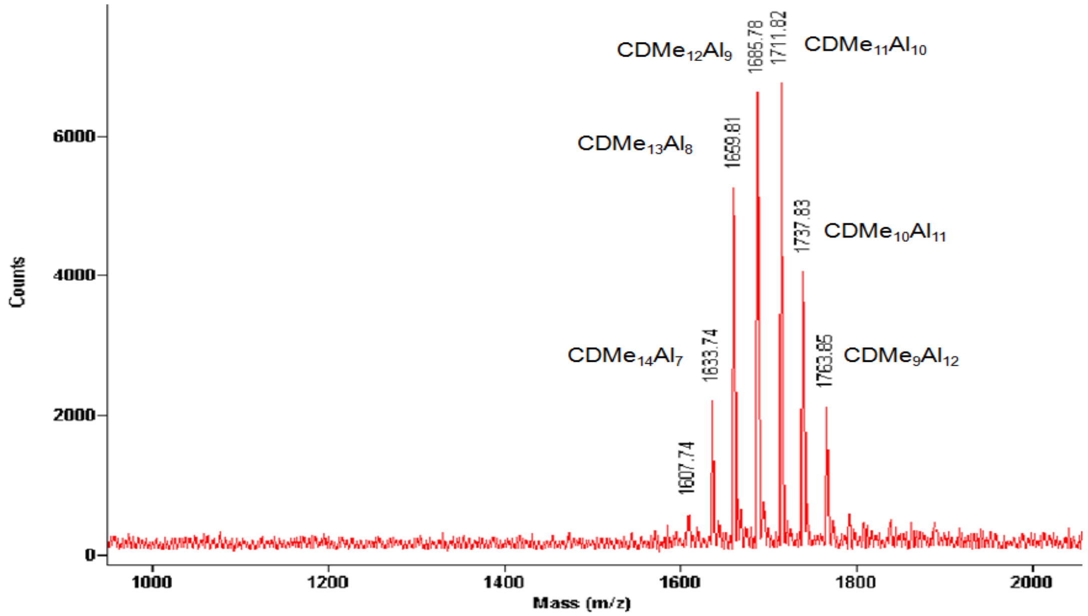


Figure 4: MALDI-TOF mass spectrum of β-CDMeAl.

Wetting properties: The wettability of the β-CDMeAl deposited on gold electrode was evaluated using contact angle measurements. The obtained data for the bare electrode and the β-CDMeAl membrane are summarized in Table I. The gold surface shows a contact angle of 69°, which is similar to the previously reported value [30]. The contact angle corresponding to the β-CDMeAl surface is higher, confirming the increase of the hydrophobicity due to the presence of the allyl and methyl grafted groups. Surface energies and wetting envelopes were determined by the van Oss model using three test liquids (distilled water, diiodomethane and formamide); [31] the obtained values were summarized in table I. We notice that the polar energy component decreases while the apolar energy component increases after modification of the gold surface by the cyclodrextrin derivative. As consequence, a slightly higher surface energy was estimated for this membrane, in comparison with clean bare gold electrode.

Table 1. Contact angle measurements

	θ_{water}(°)	γ^+(mJ.m^{-2})	γ^-(mJ.m^{-2})	γ^{AB}(mJ.m^{-2})	γ^{LW}(mJ.m^{-2})	γ^s(mJ.m^{-2})
Gold surface	69	3.8	3.4	7.2	42.3	49.5
Gold/β-CDMeAl	74	0.3	10.8	3.6	48.3	51.9

γ^+: acid energy component; γ^-: basic energy component ; $\gamma^{AB} = 2(\gamma^+\gamma^-)^{1/2}$:polar energy ; γ^{LW}: apolar energy ; $\gamma^S = \gamma^{AB} + \gamma^{LW}$: surface energy.

Equivalent circuit modeling: The gold/β-CDMeAl/electrolyte interfaces were studied by the electrochemical impedance spectroscopy. The obtained Nyquist plot shows an overlap of two semi circles which appear as a single one with a large diameter (Figure 5).

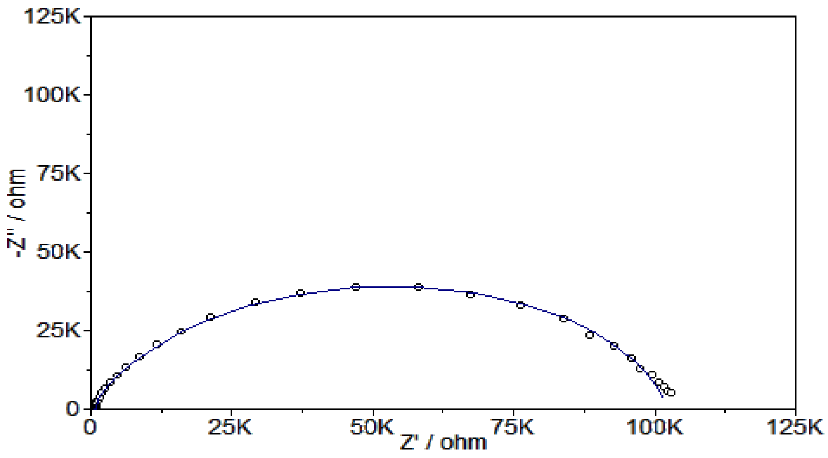


Figure 5: Nyquist diagram (o) and fit (—) of the gold/CDMeAl membrane in 0.1M PBS (recorded at -0.5 V versus SCE; frequency range: 100 kHz-100 mHz ; amplitude: 10 mV).

The impedance diagram was modeled by an equivalent electrical circuit to investigate the diverse processes taking place at the different interfaces. The equivalent circuit was determined by fitting the experimental impedance data using the FRA2 software (Figure 6); it consists of three components: (i) The first component corresponds to low frequency range and relates the gold electrode/membrane interface; it is composed by a charge transfer resistance (R_{ct}) and a constant phase element (CPE_1). The corresponding impedance can be expressed by the following relation:[32] $Z(CPE) = 1/Q(j\omega)^n$, where Q is a constant, j is the imaginary number, ω is the angular frequency and n is a correction factor $(0 < n \leq 1)$. The CPE is a non-ideal capacitance that takes into account the interfacial irregularities (porosity, roughness and geometry); [33,34] particularly, it becomes more capacitive when the n value tends to 1. (ii) The second component, which is in series with the first one, represents the membrane /electrolyte interface at high frequency range. This component is composed by a dipole based on parallel R_m and CPE_m, where R_m is the resistance of the membrane and CPE_m is its constant phase element. The CPE_m can be associated to the exchange of ions between the electrolyte and β-CDMeAl layer [31]. Indeed, due to the porosity of the membrane, the electrolyte molecules can penetrate into the pores and reach the electrode surface; so, this parameter depends essentially on the membrane morphology. (iii) The solution resistance (R_s), which relates to the electrolyte resistivity out-side the pores, was added in series.

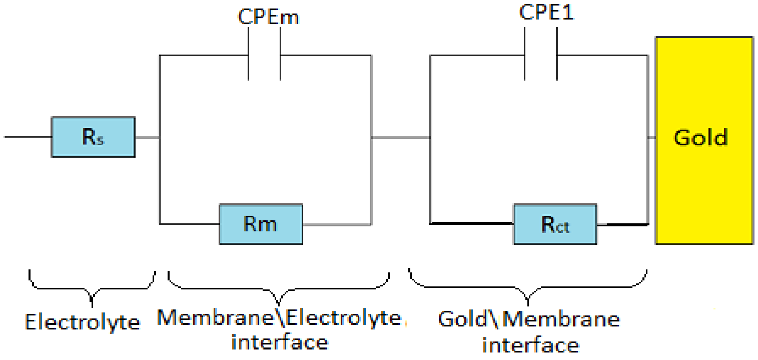


Figure 6: Equivalent circuit of the gold/β-CDMeAl /electrolyte interfaces
(R_s : electrolyte solution resistance; R_{ct} : charge transfer resistance; CPE_1 : constant phase element; CPE_m : constant phase element of the membrane; R_m : membrane resistance).

Sensitivity of β-CDMeAl-modified gold electrode towards hydroquinone: The sensing properties of the β-CDMeAl membrane deposited on gold electrode towards hydroquinone (HQ) have been investigated by electrochemical impedance technique. The figure 7 shows the responses of this membrane after addition of different amounts of HQ; the diameter of Nyquist plot decreases with increasing the HQ concentration. The fits of the experimental Nyquist plots for different concentrations were estimated and the values of electrical parameters were summarized in table 2.

Table 2. Fitting electrical data of gold/β-CDMeAl membrane, for different concentrations of HQ.

p[HQ]	4.9	4.6	4.4	4.2	4.1	3.9	3.6	3.3	3.0
R_m(kΩ)	90.1	82.7	75.7	70.3	65.0	61.5	50.9	37.9	25.7
CPE_1(μF)	0.550	0.560	0.580	0.596	0.597	0.679	0.965	1.635	0.501
n	0.860	0.860	0.858	0.856	0.858	0.848	0.836	0.818	0.702
R_{ct} (kΩ)	5.25	5.43	5.59	5.81	5.76	7.79	14.4	21.05	36.5
CPE_m(μF)	0.720	0.707	0.665	0.640	0.630	0.585	0.510	0.432	0.417
n	1	1	1	1	1	0.980	0.944	0.922	0.871
R_s(Ω)	799	798	794	793	791	788	786	785	781
$\chi(10^{-3})$	8.68	8.83	9.88	13.10	12.60	19.70	27.60	32.90	40.80

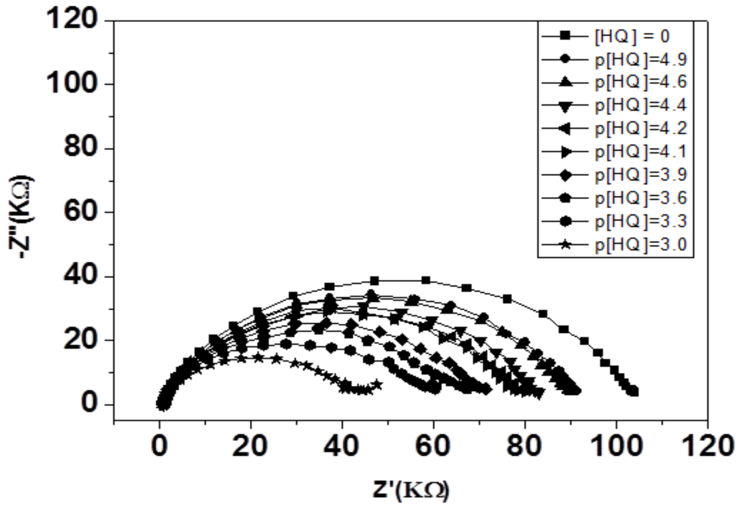


Figure 7: Nyquist diagrams of the gold electrode based on β-CDMeAl thin membrane, for different HQ concentrations.

The Figure 8-a shows the variation of the membrane resistance (R_m) as a function of the HQ concentration cologarithm. We observe that the R_m value decreases with increasing the HQ concentration, indicating an enhancement of the membrane conductivity [35]. This behavior can be attributed to the complexation of HQ by β-CDMeAl. Indeed, due to its hydrophobic apolar cavity, the β-CD derivative can form inclusion complex with hydrophobic HQ molecules. In aqueous solution, the cavity is occupied by water molecules;

the latter, being in a situation energetically disadvantaged (polar-apolar interaction), can be easily replaced by the less polar molecules of HQ [36]. The constant phase element (CPE_m) decreases by adding hydroquinone in the aqueous solution, as shown in Figure 8-b. This behavior can be attributed to the incorporation of the HQ molecules through the membrane, which leads to increase the thickness and then to decrease the CPE_m value. At low concentrations of HQ, we notice the minor variation of the R_{ct} and CPE_1 (Figures 8-c and 8-d); the value of the *n* tends to1 indicating that the CPE_1 becomes more capacitive. From a HQ concentration of 8.10^{-4} M, an increase of these parameters was observed, which suggests that the electron transfer to the electrode was slowed down due to the spatial hindrance of the HQ molecules [37].

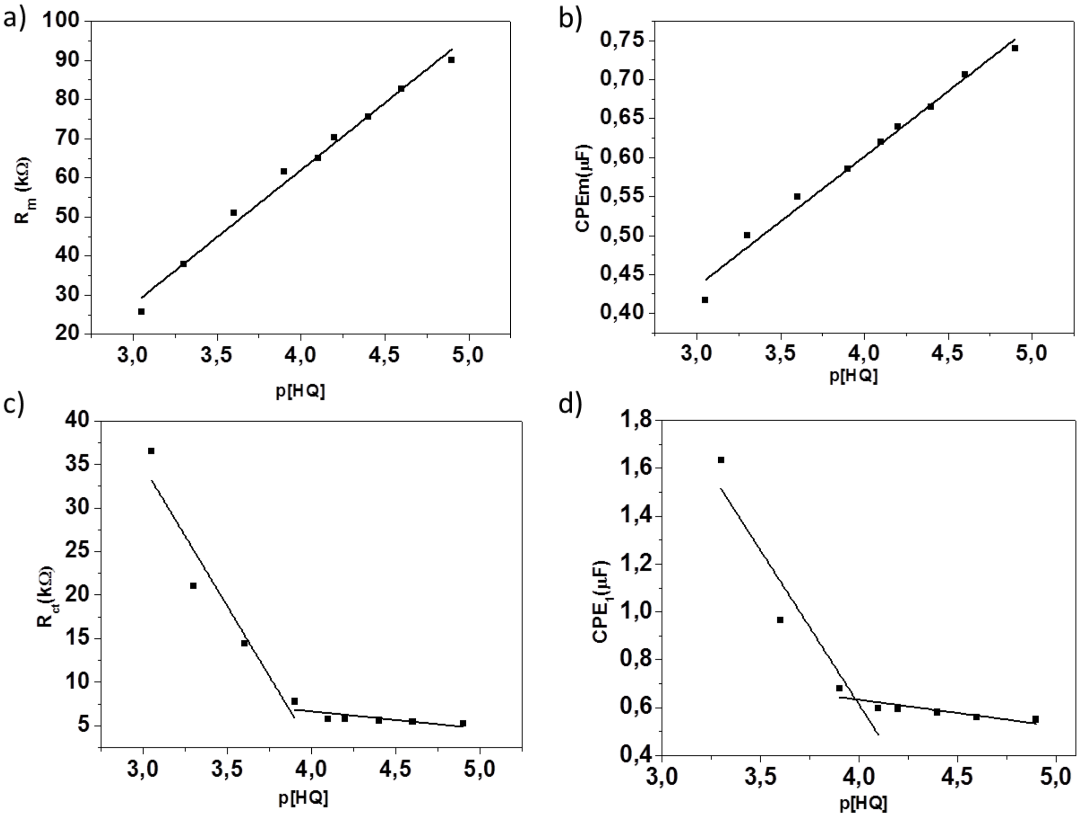


Figure 8: Variation of the R_m (**a**), variation of the CPE_m (**b**), variation of the R_{ct}, (**c**) and variation of the CPE_m (**d**) *vs* p[HQ] of the gold/β-CDMeAl membrane.

APPLICATIONS

The bio-based sensitive membrane studied in this work can be used in the development of impedimetric sensors for the hydroquinone in sea, river, well or industrial waste waters.

CONCLUSIONS

A new hydrophobic derivative of the β-CD (β-CDMeAl) was synthetized and characterized. The β-CDMeAl membrane spin-coated on gold electrode shows a good stability in water and its surface properties were examined by contact angle measurements. The gold/β-CDMeAl/solution interfaces were investigated by electrochemical impedance spectroscopy and the obtained data were fitted using an equivalent electrical circuit. The response of the gold/β-CDMeAl membrane towards hydroquinone was studied and the results show a good sensitivity to this molecule.

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