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Electrochemical capacitive K^+ EMIS chemical sensor based on the dibromoaza[7]helicene as an ionophore for potassium ions detection

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Abstract

A K^+ -sensitive capacitive electrolyte-membrane-insulator-semiconductor (EMIS) based on a novel dibromoaza[7]helicene ionophore has been developed. An ion-sensitive membrane based on polyvinylchloride (PVC) doped with the ionophore was deposited on the $Si_3N_4/SiO_2/Si-p/Cu-Al$ transducer. The properties of the K^+ -EMIS chemical sensor were investigated by electrochemical impedance spectroscopy (EIS). All the developed devices upon being tested have shown good sensitivity and linearity responses within the range 10^{-6} M to 10^{-1} M of potassium activity, with good selectivity over a wide variety of other cations (Na^+ , Li^+ , Cu^{2+} , Ca^{2+} , and Mg^{2+}). To our knowledge, this is the first time that a capacitive field-effect sensor has been fabricated using helicene as a carrier for a K^+ -detection, combined with the structure $Si_3N_4/SiO_2/Si-p/Cu-Al$ as a transducer.

Keywords: Capacitive field-effect chemical sensor; dibromoaza[7]helicene; potassium sensitivity; electrochemical impedance spectroscopy; silicon nitride.

1. Introduction

Potassium ions (K^+) exist in plants, tissue of animals, extracellular spaces and biological fluids [1-2]. They play key roles in nature and biological system by maintenance of muscular strength, enzyme activation, regulation of blood pressure and pH in living cells [3-6]. This is why elevation or depletion of the potassium amount can cause many problems and, in extreme cases, even death [7]. Therefore, maintaining consistent levels of potassium in the blood and cells is vital to any bodily function. The concentration of K^+ ions in blood is between 3.8 and 5.4 mmol L⁻¹ [8,9]. For this reason, potassium monitoring is very important in biological systems and in the medical field [10-11]. Therefore, it is essential to monitor and detect this ion at trace level with high sensitivity.

In literature, there are many examples of potassium sensors that have been developed, which are based on different technologies, including flame atomic absorption spectrometry [12], ion chromatography [13], surface Plasmon resonance [14], and electrochemical methods [15-17]. These latter play an important role in the development of biosensors due to their fast response, high sensitivity, simple instrumentation, low production cost, and portability. A number of chemical sensors based on the field-effect in semiconductor structures such as ion-sensitive field-effect transistors (ISFETs) or electrolyte-membrane-insulator-semiconductor (EMIS) have been extensively studied in the last two decades for detection of potassium ion. However, most of them are based on polymeric membrane doped with ligands like valinomycin [18-19] or based on 1,3-(di-4-oxabutanol)-calix[4]arene-crown-5 [22], or at times the sensing layers are fabricated by implanting K^+ and Al^+ ions into SiO_2 [23]. Up until the present day there have been numerous studies on the development of novel ionophores for the molecular recognition of this biologically important ionic guest.

In the last few years, several theoretical studies have been carried out using density functional theory (DFT) computational methods to study the interaction between helicenes and atoms/ions [24-25]. The binding energies in these cation- π complexes comprise mainly electrostatic, polarization and charge transfer contributions. All the obtained results have shown that the complexes of helicene with lithium ions (Li^+), sodium ions (Na^+), and potassium ions (K^+) express large interaction energies that increase with the size of helicenes. These are intriguing polycyclic aromatic compounds that combine a helical structure with a conjugated system [26], containing more than six benzene rings (carbohelicenes) or seven heteroaromatic rings (heterohelicenes). They possess a rigid helical framework [27-28] and are very stable towards acids, bases, and relatively high temperatures [29].

We have recently published an article on the use of helicene for ion chemical sensors, based on cation- π interaction [15]. Based on the same principle, we report in the present study a new K^+ -electrolyte-membrane-insulator-semiconductor (K^+ -EMIS) capacitive electrochemical sensor based on simple dibromoaza[7]helicene ionophore molecules within the plasticized polyvinylchloride (PVC) membranes. Here we report about the fabrication processes and the impedimetric characterization of dibromoaza[7]helicene based chemical sensors. The sensitivity and selectivity of the electrochemical sensor toward K^+ ions was also studied and compared with different types of cations. [30-32].

2. Experimental

2.1. Reagents

All reagents used were of analytical grade. Dioctyl sebacate (DOS), potassium tetrakis(4-chlorophenyl)borate (KTPClPB), polyvinylchloride (PVC), and tetrahydrofuran (THF) were obtained from *Fluka Analytical*, France. The chloride salts of all analyzed cations were of the highest purity available and they were used without further purification (all from *Fluka Analytical*, France). The ligand: dibromoaza[7]helicene was used as the neutral carrier in the ISE- K^+ selective devices and it was prepared at the Asymmetric Organic Synthesis and Homogeneous Catalysis Laboratory, Monastir, Tunisia. The analytic metal ions that were studied consisted of: Na^+ , K^+ , Li^+ , H^+ , Ca^{2+} , and Mg^{2+} . All solutions were prepared with deionized water that was purified by a Milli-Q Element System (resistance: 18.2 M Ω .cm).

2.2. Synthesis of the Ionophore

The synthesized macrocyclic ionophore dibromoaza[7]helicene cited in the text as compound **4** (Fig. 1) was prepared as previously reported in our recent publication [15]. This compound can be used for applications in organic optoelectronic materials and also for sensing applications which act as an ionophore for metal ions [15, 24-25].

Fig. 1: Chemical structure of the dibromoaza[7]helicene. This molecule contains 49 atoms, 17 hydrogen atoms, 29 carbon atoms, two bromine atoms and one atom of nitrogen. The potassium cation is retained by cation- π interaction between the two last benzene rings.

The synthesis was carried out by conducting palladium-catalyzed vinylation using appropriate aryl/vinyl halides, commonly known as Mizoroki-Heck reaction which is followed by oxidative photocyclization (Scheme 1). Starting from the commercially available tricyclic ring system, named N-methylcarbazole **1**, bromine was introduced in positions 3 and 6 by treatment with two equivalents of N-bromosuccinimide (NBS) in dichloromethane (DCM). The quantitative yield (99%) of the resulting dibrominated derivative **2** was obtained after purification by flash chromatography. The latter was then linked to 4-bromostyrene (2.8 equiv.) through a double-Heck coupling reaction using 2% of Hermann's catalyst, sodium acetate as the base, and N,N-dimethylacetamide (DMA) as the solvent. The desired coupled product **3** was obtained at a 66% yield by heating for two days at 140°C. It was assumed to have (E,E)-stereochemistry at the double bond, based on a ^1H NMR study. The (Z,Z)- and/or (Z,E)-isomers were neither isolated nor identified unambiguously as minor products in the reaction mixture (Scheme 1).

Scheme 1: Schematic illustration of the synthesis of the helically chiral heptacyclic system **4**.

In order to obtain the helically chiral helicene **4**, bis-styrylcarbazole **3** was subjected to a double photocyclization using a 500 W high-pressure mercury immersion lamp. We optimized the reaction conditions for the double cyclization to find that the highest yield of the racemic dibromoaza[7]helicene **4** was obtained on a 150 mg scale per run for about one night in the presence of a stoichiometric amount of iodine as the oxidizing agent, that was in a mixture of toluene and tetrahydrofurane (95:05) at room temperature. The resulting target: aza[7]helicene **4** produced a significantly pure yellow solid giving a 71% yield, after purification by column chromatography (Scheme 1).

2.3. Capacitive Field-Effect chemical sensor preparation

The planar sensor was fabricated from a p-type silicon substrate, with <100> orientation and 4-40 Ω cm resistivity, covered with 78 nm of thermally grown silicon dioxide layer (SiO_2) and 100 nm of silicon nitride (Si_3N_4) prepared by Low Pressure Chemical Vapor Deposition (LPCVD). The electrical contact on the silicon backside was obtained by over doping it with boron ions and deposition of 1 μm of Al/(1%Cu) alloy. Finally, the wafers consisting of Al-Cu/Si-p/ SiO_2 / Si_3N_4 were diced into single chips of 1 cm^2 .

The ionophore (1 wt.%), PVC (33 wt.%), plasticizer (65.5 wt.%), and KTpCIPB (0.5 wt.%) were mixed and dissolved in a solution of THF (7mL) for the preparation of the polymeric membrane. After complete dissolution of the membrane material, 10 μL of the resulting solution was drop casted on the top of the Si_3N_4 surface for three times with an interval of 5 min between each drop cast. Finally the chemical sensor was left overnight at room temperature in order to totally evaporate the solvent from the membrane. After complete evaporation of the solvent, a transparent layer of the sensing membrane was formed with high adhesion onto the modified capacitive field-effect surface. The resulting K^+ sensitive capacitive electrolyte membrane insulator semiconductor (K^+ -EMIS) sensors were preconditioned by incubation in 1 mM KCl solution for at least 30 min before potassium detection.

2.4. Contact Angle Measurements

Contact angle measurement is a quantitative analysis by measuring the angles formed by a liquid droplet and the substrate, at the three-phase boundary where a liquid, gas, and solid intersect [33,39]. The measurements were performed using the “Digidrop” instrument

from the GBX society (France). Contact angle measurements for three different liquids (distilled water, diiodomethane, and formamide) were carried out at room temperature. The contact angles were determined from the droplet image using the tangent method. The liquid was deposited on solid surfaces with a micrometric syringe and controlled by means of a camera. Contact angle measurements were repeated 5 times for each solvent and the average value was taken for each surface. Van Oss acid–base theory was used, to determine the surface energy components: total energy (γ^S), dispersive energy (γ^{LW}), acid-base energy (γ^{AB}), acid energy (γ^+), and base energy (γ^-). Here, the wettability of the PVC-Helicene membrane deposited on the capacitive field-effect surface was evaluated using contact angle measurements (CAM). Before and after membrane deposition, CAMs were analyzed with water as the liquid probe.

2.5. Electrochemical Impedance Spectroscopy (EIS)

The EIS measurements were performed using an EC-LAB version 10.31 VMP3 multi-channel system, with up to 16 channels, from Bio-Logic that included a potentiostat, galvanostat, and an integrated impedance spectroscopy system. EIS measurements were carried out using an electrochemical cell with a volume of 25 mL and consisting of three electrodes: (1) the working device Al-Cu/Si-p/SiO₂/Si₃N₄/Membrane, (2) a platinum (Pt) auxiliary electrode, and (3) a saturated calomel electrode (SCE) as a reference that were placed inside a Faraday cage. The EIS measurements were carried out at the frequency range from 100 mHz to 200 kHz using a modulation voltage of 10mV. The measurements were performed in a Tris-HCl buffer solution at pH 7.0. Data acquisition and analysis were accomplished using the EC-Lab software (Bio-Logic SAS).

2.6. FT-IR study

K⁺-EMIS Membranes were characterized using the chemical technique, Fourier transform infra-red (FTIR) to study the influences of detection process on membrane composition, and lifetime of the proposed sensors. This FT-IR method allows us to get the characteristic peaks for the K⁺-PVC membrane before K⁺ detection and after 21 days of potassium detection. All the membranes were characterized by FTIR analysis using a Perkin–Elmer Spectrum One FT-IR spectrometer (Thermo Scientific Nicolet IS50ATR) according to the Attenuated Total Reflectance (ATR) technique.

3. Results and discussion

3.1. Characterization of the Dibromoaza[7]helicene

The obtained dibromoaza[7]helicene was found to have good solubility in common organic solvents including dichloromethane, chloroform, toluene, ethyl acetate, and tetrahydrofuran. The results showed a violet fluorescence when dissolved. Aza[7]helicene has a rigid helical framework and is stable in solid state towards oxidation under air atmosphere for months.

The thermal behavior of sample 4 was studied by differential scanning calorimeter (DSC) with a heating rate of 10°C/min from 25 to 300°C, under a nitrogen atmosphere. DSC indicated that compound 4 has a clear and high melting point of 255°C (Fig. S1 supplementary material). In addition, helicene 4 also has a high glass transition temperature (T_g) of 189°C. These results show the good thermal stability of helicene.

3.2. Contact angle measurement

Table 1 (Supplementary material) shows the evolution of the surface energy components as a function of the treatments performed on the Si₃N₄ substrate. In all the measurements deionized water which has a surface tension of 71.970 10⁻³ Nm⁻¹ at a room temperature (25 °C) was used. In the first step, the Si₃N₄ surface was cleaned with acetone and the contact angle was measured at 51.5°. In the second step, the surface was activated with piranha solution (H₂SO₄:H₂O₂, 3:1 v/v) for 20 min and the Si₃N₄ was placed top side down at the liquid/air interface to prevent the Al contact from etching. Here, the contact angle value was decreased to 32.8° and the surface became more hydrophilic. In the final step, the contact angle after the deposition of the membrane was measured and an increase in the contact angle value was observed from 32.8° to 89.3° (Fig. 2). This result proves that the surface becomes more hydrophobic by deposition of the helicene/PVC-membrane onto the Si₃N₄ surface. This is in agreement with the other studies of the wettability of the silicon nitride surface throughout the cleaning step [15, 39].

Fig. 2: Contact angle measurements for: (a) bare Si₃N₄ electrode, (b) activated electrode, and (c) PVC-membrane modified electrode

The values of the surface tension components and parameters were determined by measuring the contact angles of liquids of known properties in contact with the solid in question. Two polar liquids must be used to determine the acid energy γ^+ and base energy γ^- . These two parameters are used to determine the polar component: $\gamma^{AB} = 2(\gamma^+ \gamma^-)^{1/2}$. The surface energy is the sum of polar and apolar energy: $\gamma^s = \gamma^{AB} + \gamma^{LW}$. The results showed a decrease in the surface energy from 56.5 mJm⁻² for bare electrode to 52.4 mJm⁻² for the modified device by addition of the K⁺-PVC membrane. However, surface energy depends on the hydrophobic and hydrophilic feature. It can be described by the entire polar part of the surface tension of the material such as the γ^{AB} (acid-base) component [39].

3.3. Effect of pH

The influence of pH on the impedimetric response of EMIS based on dibromoaza[7]helicene with (DOS) as plasticizer was examined using a 10⁻¹ M Tris-HCl solution over a pH range from 2 to 10.3. The variation of the pH solution was obtained by addition of HCl (0.1 M). The Al-Cu/Si-p/SiO₂/Si₃N₄/Membrane showed no significant pH influence between pH 2 and 10.3. Therefore, for the rest of experimental procedures, the pH of the electrolyte solution was kept constant at pH 7.

3.4. Impedance analysis of the K⁺-EMIS chemical sensor

3.4.1. Polarization potential optimization

The polarization of the membrane was used at -2500 mV/SCE within the frequency range 100 mHz to 200 kHz. The amplitude of 10 mV was chosen for all experiments in order to work within the linearity range of impedance response (Fig. S2 supplementary material). The potential polarization used for these measurements has been previously optimized as described in our recent work [15].

3.4.2. Potassium detection

The properties and the sensitivity of the membrane have also been evaluated by EIS measurements in Tris-HCl buffer solutions (0.1 M). This was used as the supporting electrolytes in all experiments. The K⁺-EMIS membrane was tested for different potassium (K⁺) concentrations ranging from 10⁻⁶ to 10⁻¹ M at a potential of -2.5V with amplitude of 10 mV.

Fig. 3: Nyquist impedance spectra of PVC-membrane/ $Si_3N_4/SiO_2/Si-p$ structure for different K^+ concentrations : (★) 0M, (◀) $10^{-6}M$, (◊) $10^{-5}M$, (▼) $10^{-4}M$, (▲) $10^{-3}M$, (●) $10^{-2}M$ and (■) $10^{-1}M$, vs saturated calomel reference electrode (SCE) (frequency range: 200 kHz–100 mHz, amplitude of 10 mV sinusoidal modulation, and polarization potential of -2500 mV in 0.1 M TRIS-HCl (pH 7) solution). Inset: the equivalent circuit used for fitting of the impedance data.

Fig. 3 shows a significant variation of Nyquist plot semi-circles by increasing K^+ concentrations. Here it is observed that the most significant variation of the Nyquist semi-circles occurs at low frequencies. This variation was due to the interaction of the helicene molecule with potassium ions.

Fig. 4: Nyquist diagram (★) and fit (—) of PVC-membrane/ $Si_3N_4/SiO_2/Si-p$ structure vs saturated calomel reference electrode (SCE) (frequency range: 200 kHz–100 mHz, amplitude of 10 mV sinusoidal modulation, and polarization potential of -2500 mV in 0.1 M TRIS-HCl (pH 7) solution). Nyquist plot semi-circle was formed from a combination of three interfaces (3 semi-circles)

Fig. 4 shows an individual Nyquist plot semi-circle in order to highlight the behavior of the membrane towards potassium as a function impedance analysis. Here the Nyquist plot semi-circle was formed from a combination of three interfaces (3 semi-circles). These interfaces correspond to the membrane/electrolyte, membrane/electrode and the capacitance layers of the electrode on itself. This justifies the choice of three component equivalent circuit (Fig. 3 inset). The experimental data was fitted using this electrical circuit and the model has provided the best fit to the experimental data. The quality of the fitting to the equivalent circuit was accurately evaluated by measuring the χ^2 which was found to be in the order of 10^{-2} . The resistance of the electrolyte is described by R_s in the equivalent circuit, which characterize the behavior of the electrolyte solution. The electrical characteristics of the silicon nitride working electrode at the interface (Si/SiO₂/Si₃N₄)/(PVC)-membrane, were simulated by a capacitance (constant phase element) CPE₁, parallel to the resistance R_1 and in series with capacitance CPE₂, parallel to the resistance R_2 in the equivalent circuit. Finally, the interface of the PVC-membrane and the electrolyte solution corresponds in the electrical equivalent circuit to R_3 which is related to the polarization resistance, in parallel with the corresponding CPE₃. The values of interfacial capacitance CPE₃ and polarization resistance R_3 are referred to as the geometric area of the working electrode. This was considered as an electric capacitor consisting of the electrode and the electrolyte, with the helicene/PVC-membrane as the dielectric. The double-layer can be assumed to act as a parallel-plate capacitor; where its capacitance is given by [37-38]:

$$C = \varepsilon \varepsilon_0 \frac{rA}{d}$$

Where ε is dielectric constant of the medium and ε_0 the dielectric permittivity of vacuum, d is the distance between the charged layers, and r is the ratio of effective surface area A_{eff} to geometric area A . The interfacial capacitance and polarization resistance are directly related to the effective surface area.

The constant phase element CPE₃ was used instead of a capacitance to account for the non-ideal capacitive response. The CPE impedance is represented by [30-36]:

$$Z_{CPE} = 1/Q(j\omega)^n$$

Where: Q is a constant, j is an imaginary number, ω is the angular frequency, and $0 < n < 1$. CPE becomes more capacitive, when the value n tends to be 1.

The variation of resistance polarization standardization $\Delta R_3 = (R_3^i - R_3^0)$, was plotted as a function of potassium concentration (Fig.5), where: R_3^0 is the polarization resistance value without potassium cations in the solution while R_3^i corresponds to the polarization resistance

for different potassium concentrations. The variation of ΔR_3 , was due to the fact that the helicene- K^+ binding caused a change of the geometrical factor of the interface producing an increase in the polarization resistance caused by a change in the dielectric and the conductive properties of the EMIS surface [34].

The normalized data curve (Fig. 5II) can be characterized using a linear relation; $\Delta R_3 = 47,213 - 7,845 \log[K^+]$. It reveals the linear range of the 10^{-6} M to 10^{-1} M with correlation coefficient of $R^2=0.959$ and the detection limit of less than 10^{-6} M. At this concentration, the ΔR_3 was at least three times higher than ΔR_3 of all other interferences present in the same medium. The K^+ -EMIS was highly sensitive and selective towards the corresponding K^+ when compared to the other ion interferences (Fig. 5II). All detection measurements were repeated at least three times to examine the reproducibility of the sensor. The K^+ -EMIS sensor showed good reproducibility of measurements and the value exhibits a relative standard deviation less than 3%.

3.4.3 Sensitivity and selectivity of membrane

The properties and the sensitivity of the PVC-membrane without helicene have been evaluated by using EIS measurements in Tris-HCl buffer solutions (0.1 M). The EMIS fabricated without aza[7]helicene was tested for different potassium (K^+) concentrations ranging from 10^{-6} to 10^{-1} M. Fig. 6 provides Nyquist plots of the (Si/SiO₂/Si₃N₄)/(PVC)-membrane without addition of the ionophore. The first Nyquist plot semi-circle corresponds to the PVC membrane (0 M of K^+). By increasing the potassium concentrations from 10^{-6} to 10^{-1} M, no significant increase between Nyquist plot semi-circles has been observed. The normalized data of this Nyquist plot semi-circles has been compared with the previous detection of K^+ using membrane with ionophore curve (Fig. 5I). This clearly shows that the response of the chemical sensor was due in particular to the ionophore Aza[7]helicene. Without the latter, the analyte would be incapable to divide up into the organic membrane. Aza[7]helicene is a chelating agents, who complexes selectively the potassium cations. The important characteristic of this molecule is its cavity which presents dimensions approximately similar to potassium cations.

Selectivity is one of the most important characteristics of a sensor. The K^+ -EMIS chemical sensor exhibited a higher preference for K^+ when compared to a weak linear tend that has been obtained for the other examined metal ions (Mg^{2+} , Ca^{2+} , Na^+ and Li^+) (Fig. 5II). Therefore, as the potassium cation comes close to the helicene molecule, the two terminal

overlapping rings are in the form of a tweezers' jaw. This jaw opens up to receive the incoming K^+ and then closes down on it [20].

Fig. 5: Calibration curves describing the relative variation of $\Delta R_3 = (R_3^1 - R_3^0)$, as a function of potassium concentrations using PVC membrane with ionophore compared to: (I) K^+ detection using PVC membrane without ionophore, (II) detection of other interferences.

Indeed, the dibromoaza[7]helicene can function as a chiral “molecular tweezers” for a potassium cation. The Na^+ cation, with its greatest positive charge density, polarizes the π cloud of the helicene more than potassium cation. While for the dibromoaza[7]helicene- K^+ complex, the electrostatic contribution to binding is much higher than polarization contribution due to a much lower positive charge density on the cation. Hence, for the helicene- K^+ complex, electrostatic interactions contribute more to binding than polarization. The cation- π interaction arises from the electrostatic interaction of a cation with the face the π -system in the last two benzene rings [24]. The modified electrode has a low response

towards other tested ions in comparison to the response obtained for the K^+ ion. Here, all the other ions: Mg^{2+} , Ca^{2+} , Cu^{2+} , Na^+ and Li^+ were not retained in the jaws of helicene molecule and this did not produce any interference to the K^+ -EMIS. The high selectivity of the sensing method is due to the fact that the Aza[7]helicene shows high affinity for K^+ against many other metal ions.

Fig. 6: Nyquist impedance spectra of PVC-membrane/ $Si_3N_4/SiO_2/Si-p$ without ionophore for different K^+ concentrations : ($\blacktriangleright$) 0M, ($\blacktriangleleft$) $10^{-6}M$, ($\blacklozenge$) $10^{-5}M$, ($\blacktriangledown$) $10^{-4}M$, ($\blacktriangle$) $10^{-3}M$, ($\bullet$) $10^{-2}M$ and ($\blacksquare$) $10^{-1}M$, vs saturated calomel reference electrode (SCE) (frequency range: 200 kHz–100 mHz, amplitude of 10 mV sinusoidal modulation, and polarization potential of -2500 mV in 0.1 M TRIS-HCl (pH 7) solution).

3.5 Chemical characteristics of EMIS-membranes.

In order to investigate the good adhesion of the constituents of the membranes containing PVC + DOS + Helicene, FTIR was investigated to characterize the EMIS-membranes before K^+ detection and after 21 days of potassium detection. (Fig.7).

Fig. 7. FTIR spectrum of K^+ -EMIS composed of a PVC membrane containing [7]helicene as ionophore deposited on a Al-Cu/Si-p/SiO₂/Si₃N₄ before and after use for potassium detection.

The presence of the bands between 2800 and 3000 cm^{-1} is attributed to the stretching vibration of $-C-H$ and $-CH_2-$ present in all membrane constituents. An absorption band at 1460 cm^{-1} assigned to the CH_2 group and the peak at 1379 cm^{-1} are attributed to CH_3 bend of dioctyl sebacate (DOS). The absorption at 1248 cm^{-1} is assigned to the $H-C-Cl$ bend of PVC. The absorption at 692 and 632 cm^{-1} are assigned to the $C-Cl$ stretching vibration of PVC. The presence of DOS as plasticizer in the PVC-membrane compositions based on helicene ionophore was confirmed also by the strong absorption bands related to $C-O$ stretching appearing at 1100-1300 cm^{-1} region and $C=O$ stretching appearing at 1730 cm^{-1} . The chemical structure of the membrane was similar after 21 days of incubation in water which confirms the good adhesion of the membrane onto Si₃N₄ substrate. The bands between 3697 and 3065 cm^{-1} and the band at 1646 cm^{-1} are attributed to the stretching vibration of $O-H$ and indicate the presence of water in the membrane pores.

4. Conclusions

In this study, we have fabricated and characterized an impedimetric chemical sensor for potassium detection based on Si-p/SiO₂/Si₃N₄ structures. This new K^+ -EMIS biosensor is composed of a PVC membrane containing aza[7]helicene as ionophore deposited on a working electrode based on Al-Cu/Si-p/SiO₂/Si₃N₄. The importance of this new ionophore is its ability to form complexes with potassium cation. The developed biosensor exhibits a

higher preference for K^+ when compared with other examined metal ions. A linear range was observed between 10^{-6} to 10^{-1} M and a detection limit of 10^{-6} M. In addition, it has shown good selectivity over a wide variety of other cations (Na^+ , Li^+ , Cu^{2+} , Ca^{2+} , and Mg^{2+}). As this method is fully compatible with the standard complementary metal–oxide–semiconductor (CMOS) process, these results are very promising for the production of Ion Selective Field Effect Transistors (ISFET) devices sensitive to potassium using the helicene-like ionophores membrane.

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