Journal Academica Vol. 1(1), pp. 18-31, May 6 2011 - Environmental Science - ISSN 2161-3338 (post assignment) - online edition www.journalacademica.org © 2011 Journal Academica

Full Length Research Paper

IMMOBILISATION OF CALIX[4]ARENE ONTO MODIFIED SELF AUTOASSEMBLED MONOLAYER GOLD SURFACE FOR ALKALI IONS DETECTION IN WATER

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Accepted May 4 2011

Calixarenes are currently the subjects of study as chemical sensors, biosensors and selective receptors due to their important functionalization and complexations possibilities. A chemical sensor for the detection of alkali ions based on surface-plasmon resonance (SPR) phenomenon was elaborated by using a gold thin film, of which surface was modified with a Calix[4]arene-self-assembled monolayer (SAM). The immobisation of calixarene onto modified SAM gold surface was confirmed by impedance spectroscopy. The SPR sensor signal based on resonance angle shift is dependent on the concentration of ion in the range from 0 to 1 µM. Three alkalin ions were used K+, Na+ and Ca+2 and the influence of pH on ions detection was studied and optimized for each ion. The sensor shows a high sensitivity and a low limit of detection for different alkali ions. The sensitivities obtained are 0.992, 0.742 and 0,122 µM-1 for Na+, K+ and Ca+2, respectively. Regeneration of the sensor chip surface was achieved by a pulse injection of 10 mM EDTA.

Key words: *calixarene*, SAM, SPR, alkali ions, sensor, gold surface

1. INTRODUCTION

The determination of alkalin ions is important for routine quality control of beverage products and in medicine and environment fields (Wicker et al., 2002; Wicker et al., 2003; Malon and Maj-Zurawska, 2005; Ammann, 1986; Qin et al., 2000). A macrocyclic complexes of alkali metal cations have been extensively investigated in aqueous solutions and in a wide variety of neat non-aqueous solvents (Popov and Lehn, 1985; Izatt et al., 1991; Mosier-Boss and Popov,1985). The complexation reactions of these complexes in mixed solvent systems have been investigated only to a very limited extent (Izan et al., 1985;

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David, 1989; Antesberger et al., 2005). Calixarenes are currently the subjects of study as chemical sensors and selective receptors due to their important functionalization and complexations possibilities. Among this sensors, different calixarene derivative may be found in ions selective electrodes and in chromogenic sensors (McMahon et al., 2003; Nachtigall et al., 2002; Atwood et al., 2002; Thallapally et al., 2005; Purse et al., 2005; Kumar et al., 2006; Jain et al., 2005; Lu et al., 2004). Many work was carried out based on calixarene molecule using polymer support and different measurement techniques to detect traces of ions were reported (Duncan and Cockayne, 2001; Pérez-Jiménez et al., 1998; Chen et al., 2000; Bouazizi et al., 1999; Lu et al., 2002; H. Barhoumi et al., 2005; N. Levit et al., 2002; Love, et al., 2005). The use of polymer as support for calixarene decrease the sensitivity of the sensor (T. Baumgart et al., 2003; Park et al., 1999). It is shown that surface adsorption and bulk adsorption of polymers affect the sensitivity and the response time of sensor and exhibiting low vapor permeability.

A self-assembled monolayer (SAM) is a flexible and simple system that permits the interfacial properties of a metal substrate to be tailored for a well-designed functional surface (Ulman, 1991; Gao and Siow, 1996; Sato and al, 1996). The advantages of SAMs include simplicity of preparation, versatility, stability, reproducibility and the possibility of introducing different chemical functionalities with high level of order on a molecular dimension (Freire and Kubota, 2004; Steinberg and Rubinstein, 1992; Mandler and Turyan, 1996; Flink et al., 1998). One of the most widely used systems in the molecular self-assembled method is the chemisorption of sulfur derivatives (i.e. thiols, disul- fides) on gold surfaces (Boussaad et al., 2000; Zacher and Wischerhoff, 2002; Georgiadis et al., 2000).

A large number of physico-chemical techniques such as NMR spectrometry, calorimetry, polarography, spectrophotometry, conductometry and potentiometry have been used to study complexation of alkali metal cations in solutions (Haymore et al., 1982; Sinta et al., 1983; Ungaro et al., 1976; Takeda et al., 1985; Fenton et al., 1981; Lim and Jeong, 2006; Kruppa et al., 2006; Kudo et al., 2006; Bendikov and Harmon, 2006; Katsuta et al., 2005). Surface plasmon resonance (SPR) spectroscopy is a powerful tool for the in situ real-time characterization of a solid/liquid interface and to study interactions between larger molecules (Chah et al., 2004; Boussaad et al., 2000; Zacher and Wischerhoff, 2002; Georgiadis et al., 2000; Sarkar and Somasundaran, 2003; Chah et al., 2002; Chah et al., 2002)..

In this work, an SPR sensor based on gold surfaces modified by self-assembled monolayer of cysteamine was developed and the response of the SPR sensor to alkali ions was investigated. To functionalize SPR sensor, pyridine was made to protect oxygen provider group and catalyze the reaction between the SAM and the alcohol group calixarene.

2. EXPERIMENTAL

2.1. SPR material and Principle:

Surface Plasmon Resonance Spectrometer BIO-SUPLAR 2 (Analytical μ-Systems, Germany) produced by Biacore campany was used. It is based on the Kretschmann type prism and GaAs solid-state laser (λ= 670 nm).

The principle of detection is that SPR is detected by measurement of the intensity of the reflected light. At the SPR angle a sharp decrease or 'dip' of intensity is measured. The position of the SPR angle depends on the refractive index in the substance with a low-refractive index close to the sensing surface. The refractive index near the sensor surface changes because of binding of ions to the surface. As a result, the SPR angle will change according to the amount of bound ions.

During a binding analysis SPR changes occur as a solution is passed over the surface of a sensor chip. To perform an analysis, one interactant is captured on a sensor surface. The sensor surface forms one wall of a flow cell. Sample containing the other interactant(s) is injected over this surface in a precisely controlled flow. Fixed wavelength light, in a fan-shaped form, is directed at the sensor surface and molecular binding events are detected as changes in the particular angle where SPR creates extinction of light. This change is measured continuously to form a sensorgram (Figure 1), which provides a complete record of the progress of association or dissociation of the interactants.

2.2. Synthesis of the chromogenic amide derivative Calix[4]arene:

The synthesis of tetra-O-substituted Calix[4]arene derivative was performed by the reaction sequence depicted in Figure. The treatment of p-tetrakis(phenylazo)Calix[4]arene with tertiary acetamide (α-chloro-N,N-diethylacetamide) in the presence of CaH2 as base gave p-tetrakisphenylazoCalix[4]arene tetra-amide derivative in cone conformation figure 2 (Sarkar and Somasundaran, 2003).

2.3. Reagents and solvents

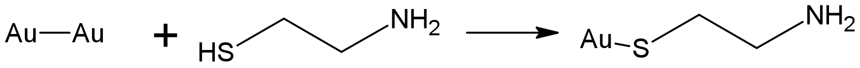
Several samples necessary to elaborate sensor were prepared. First, 10-2 M of cysteamine solution was prepared in which sensor was immersed. Calix[4]arene solution was prepared by dissolved 5 mg of Calix[4]arene powder in 2 ml of chloroform. Calix[4]arene was deposited on the sensor by dip-coating technique. This technique makes it possible to have homogeneous layers. PCC or pyridinium chlorochromate, known as Corey's reagent (Chah et al., 2002), was prepared. To 22 ml of 6 M HCl was added 12 g of CrO3. After ultrasonic mixing during 10 min, 9,5 g of pyridine was added to the homogeneous solution. Ultrasonic mixing over 5 minutes and cooling to 0o. A dilute sulfochromic oxidant solution and aqueous solutions containing 0 µM to 1 µM of the ions K+, Na+ and Ca+2 were prepared. Phosphate buffer solution PBS was prepared at pH equal 8.

2.4. Immobisation of calixarene onto modified SAM gold surface

To functionalize Calix[4]arene-SAM onto gold surface in order to make an SPR sensor for ions detection, four stages are necessary:

1. In SPR chip the adhesion between gold layer and glass is only physical. Pirhana was not made to clean gold surface. So, acetone and ethanol were used,
2. Grafting of SAM on the gold surface: the sensor is immersed in 15 mM of cysteamine during two hours,

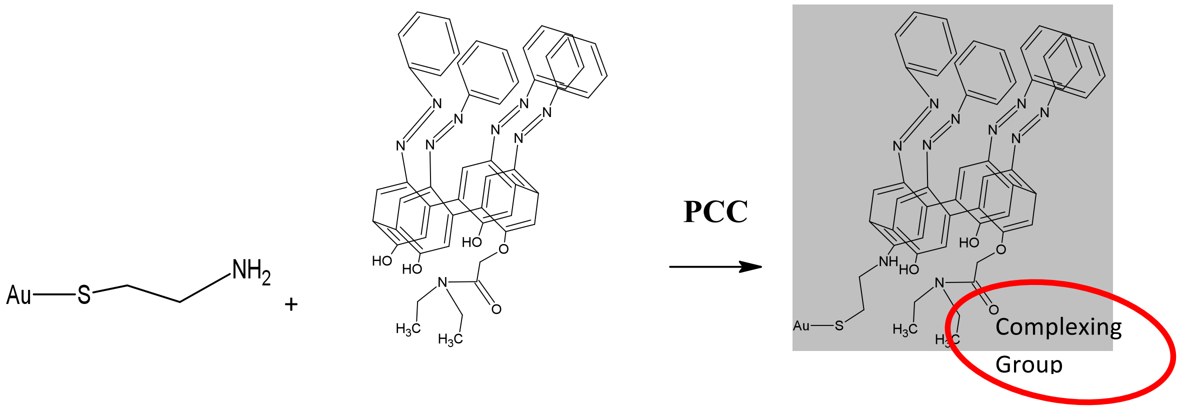
Diagram 1 Grafting of SAM on the gold surface



3. Cleaning of SAM by ethanol for few minutes and drying by nitrogen gas,

4. Deposition of Calix[4]arene onto SAM of cysteamine in presence of PCC solution. The PCC was made to protect oxgen provider group and catalyse the reaction between the SAM and alcohol group of calixarene (Halouani et al., 2002; Corey and Suggs, 1975; Shervedani and Mozaffari, 2005). Deposition solution was prepared by mixing 1 ml of calixarene solution with 0.5 ml of PCC for six hours at room temperature (cf. figure 3). After, 30 µl of mixture solution was deposited onto modified sensor by thin film method.

Diagram 2 Deposition of Calix[4]arene onto SAM of cysteamine in presence of PCC solution



3. RESULT AND DISCUSSION

All tests were made using SPR method. The influence of pH on ions detection was studied and optimized for each ion. The regeneration of the sensor was made by injection of 10 mM EDTA.

3.1. Characterization of modified sensor by electrochemical impedance spectroscopy (EIS)

The EIS is a powerful technique for characterization and studying electrical and electrochemical properties of a large variety of systems.

All electrochemical measurements were carried out using VOLTALAB 40 analyzer (PGZ301 & VoltaMaster 4). A three-electrode electrochemical cell was used, with the chemically gold electrode as the working electrode; A calomel electrode was used as the reference electrode and a platinum was used as the auxiliary electrode. Measurements were used in buffer solution at adjusted pH for about 7.3.

Concerning the use of EIS to characterize thin films in contact with electrolyte solutions, three different contributions, bulk, interfacial and electrolytes may be determined (Sun et al., 1998; Xiao et al., 1999; Delvaux and Demoustier-Champagne, 2003). From an electrochemical point of view, when a metal is placed in contact with an electrolyte, a potential is generated due to the unequal distribution of charge across the interface, in addition, hydrated ions will not be able to approach indefinitely close to the interface.

In order to confirm immobisation of calixarene onto modified SAM gold surface faradaic impedance spectra were presented as Nyquist plots (Zim vs. Zre) for gold, SAM of cysteamine and SAM-Calixarene (cf. Figure 4).

We show that the covalent attachment of each layer increases the charge transfer resistance. The bare Au electrode exhibits an almost straight line (curve a) that is characteristic of a mass diffusional limiting electron-transfer process. Assembly of the cysteamine monolayer on the electrode surface (curve b) generates a layer on the electrode that introduces a barrier to the interfacial electron-transfer. The deposition of Calix[4]arene onto SAM cysteamine layer results in an increase of the electron-transfer resistance (curve c).

3.2. pH optimization

SPR method was used for pH optimization and tests sensors. pH detection of the sensor was optimized for each ion at 1µM concentration. The pH of buffer solution was adjusted by using 0.1 M of HCl or NaOH solution. Figure 5 shows that ions detection will be made in basic solution at about 8. This is in agreement with proton/ion exchange (Hudlicky, 2005; Hunsen, 2005). At low pH, quinone protonated and ion complexation does not take place. At pH>7, oxygen was deprotenated making the sensor surface become negatively charged. Thus, the incorporation of ion by the Calix[4]arene-SAM also can be favored by electrostatic interactions (Sato et al., 1996). Such coupling of favorable characteristics is probably the key to achieving the remarkable sensitivity to ions of the proposed sensor.

3.3. Sensor detection

For all ions, we observed that output refractive index increases with increasing ions concentration. As shown in (Hunsen, 2005) ions are coordinated with the oxygen atoms of the amide group and its complexatation takes place.

As shown in figure 8, detection limit reached are lower than 10-5µM for the most ions used. Detection limits reached are 9 10- 5, 10-4 and 5 10-3 µM for Na+, K+ and Ca+2 ions, respectively (cf. figure 6).

Three zones of detection were observed between 0 and 1 µM.: high concentration zone from 0.1 to 1µM (figure 7 a)), second zone between 10-3 and 10-2µM (figure 7 b)) and third zone between 10-4 and 10-5 µM (figure 7 c)). In order to determine the sensitivity of sensor, linear smooting curves were plotted for each zone detection. In figures 7 a), b) and c), a linear variation of signal was showed for each ions in all detection zones. The slopes of stringhts represent the sensitivities of sensor in µM-1. A recapitulative table which gives sensitivity of sensor for each zone was drawn (table 1). The results obtained in table 1 show different sensitivities of sensor for alkali ions. In the zone of high concentration, low sensitivities were observed 10-2,1.4 10-3 and 2.4 10-3 µM-1 for Na+, K+ and Ca+2, respectively. In the second zone, the sensitivities increase and the values obtained are 0.122, 0.034 and 0.0039 µM-1 for Na+, K+ and Ca+2, respectively. In the range between 10-4 and 10-5µM, high sensitivity values were observed for alkali ions in which the border of detection limits were reached. As shown in table 1, the sensitivities obtained are 0.992 and 0.742 µM-1 for Na+ and K+.

Comparative results show that signal is proportional to the capacity of adsorbed ions on the surface of sensor which is in agreement with literature (Muzart, 1992; Macdonald, 1987).

Different limits detection observed for various ions can be explained by several parameters: adsorption potential and formation of various metal hydroxides which not the same for different heavy metals ion, oxygen deprotenation making the sensor surface become negatively charged (Hsu et al., 2001; Ding et al., 2005; Norlin et al., 2002; Profumo et al., 2006; Parsons et al., 1995). So, the incorporation of ion by the Calix[4]arene-SAM can be favored by electrostatic interactions which influences directly the stability of complex formed and its association binding (Sato et al., 1996; Karlsson and Falt, 1997). Although the ionic force in aqueous medium and interactions between host and guest such as π-stacking, dipolar-dipolar interactions have a strong influence on the stability of the complexes (Paarmann et al., 2002; Ma et al., 2001; Muñoz and Palmero, 2004; Farghaly, 2003; Tsukube, 1997).

4. Conclusion

In conclusion, this work demonstrates that alkali ions can be detected using an SPR sensor elaborted by immobilization of Calix[4]arene onto modified SAM gold surface and open the way to biosensor for ions detection and to the use of Calix[4]arene in biochemistry field. SPR sensor developed shows a high sensitivity and a low limit of detection for different alkali ions. Since the magnitude of the SPR response is proportional to the molecular masses of the interacting species, the system is ideally suited to study complexation of small molecules.

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FIGURE CAPTIONS

Figure 1:	SPR sensing principle
Figure 2:	Reaction sequence for the synthesis of p-tetrakisphenylazocalix[4]arene tetra-amide derivative
Figure 3:	SAM-Calix[4]arene scheme for ions detection
Figure 4:	EIS measurement of sensor in buffer solution: a) Gold b) SAM c) Calixa[4]rene-SAM
Figure 5:	pH optimization for each ion
Figure 6:	Calibration Curve of SPR Calix[4]arene SAM sensor for alkali ions detection
Figure 7:	Behavior of alkali ions adsorption on calixarene-SAM in different zones of detection: a) zone 1 b) zone 3 c) zone 3
Table 1:	Sensitivities of SPR sensor for different detection zones

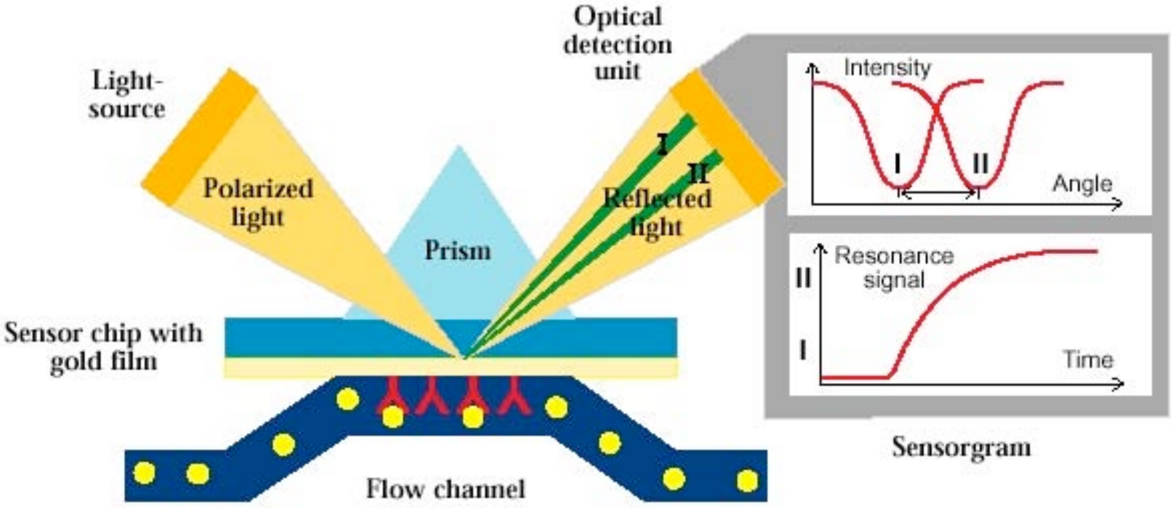


Figure 1. SPR sensing principle

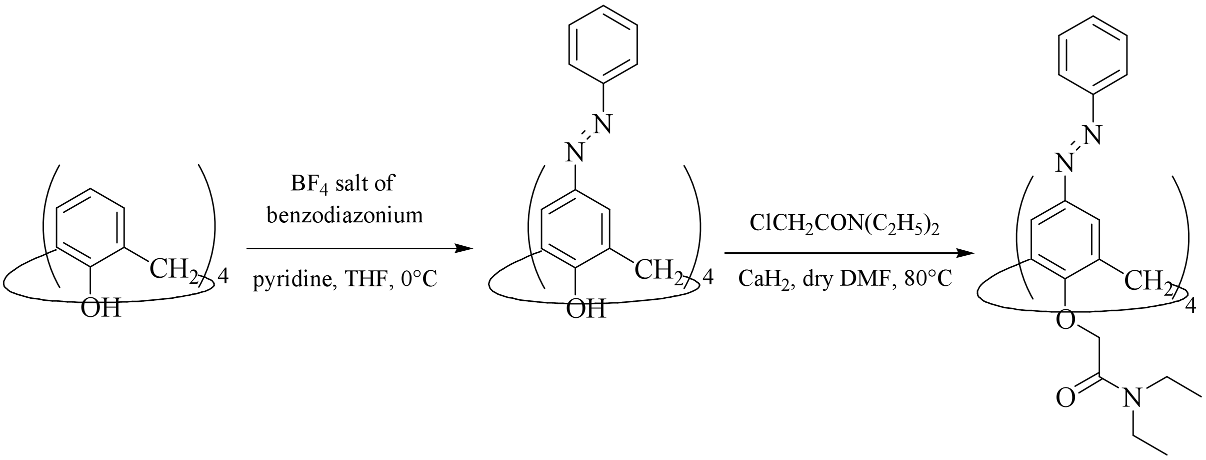


Figure 2. Reaction sequence for the synthesis of p-tetrakisphenylazocalix[4]arene tetra-amide derivative

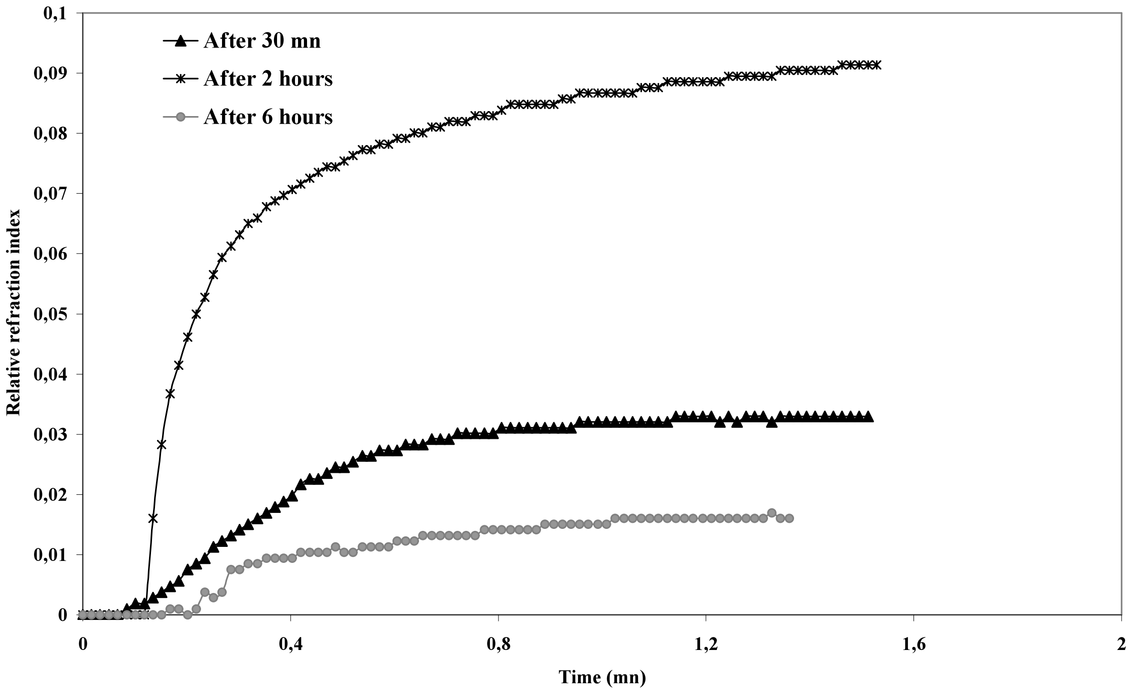


Figure 3. Optimization of time

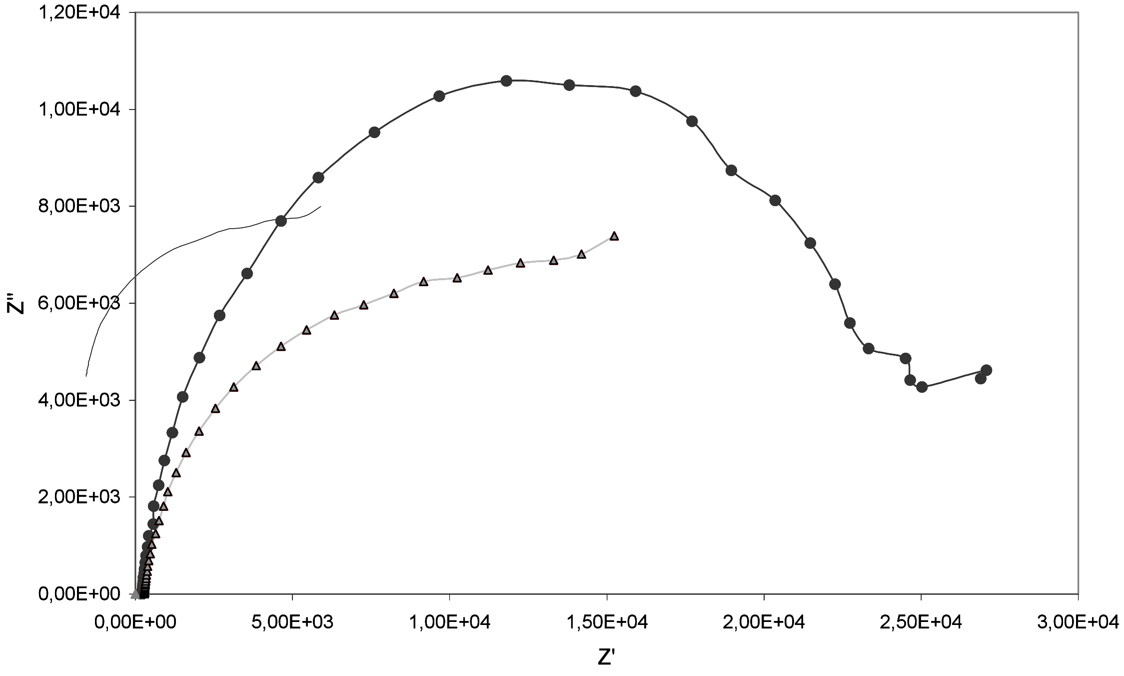


Figure 4. EIS measurement of sensor in buffer solution:
a) —— Gold b) —△— SAM c) —●— Calixa[4]rene-SAM

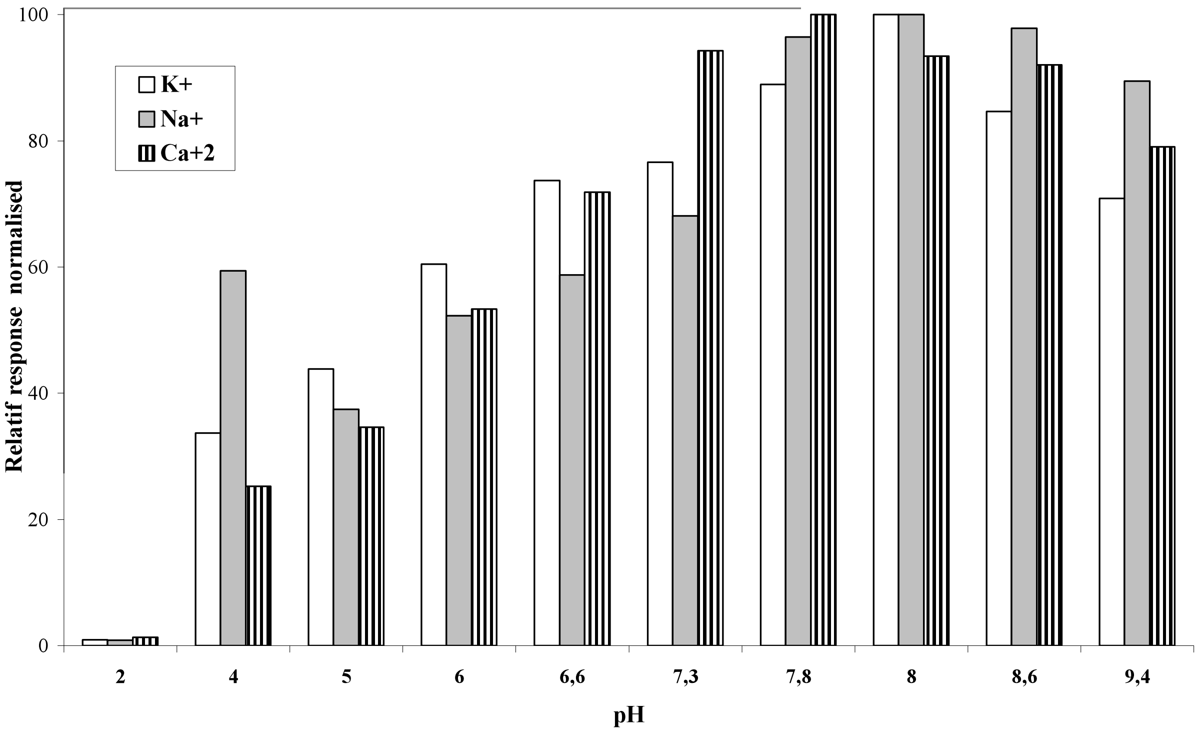


Figure 5. pH optimization for each ion

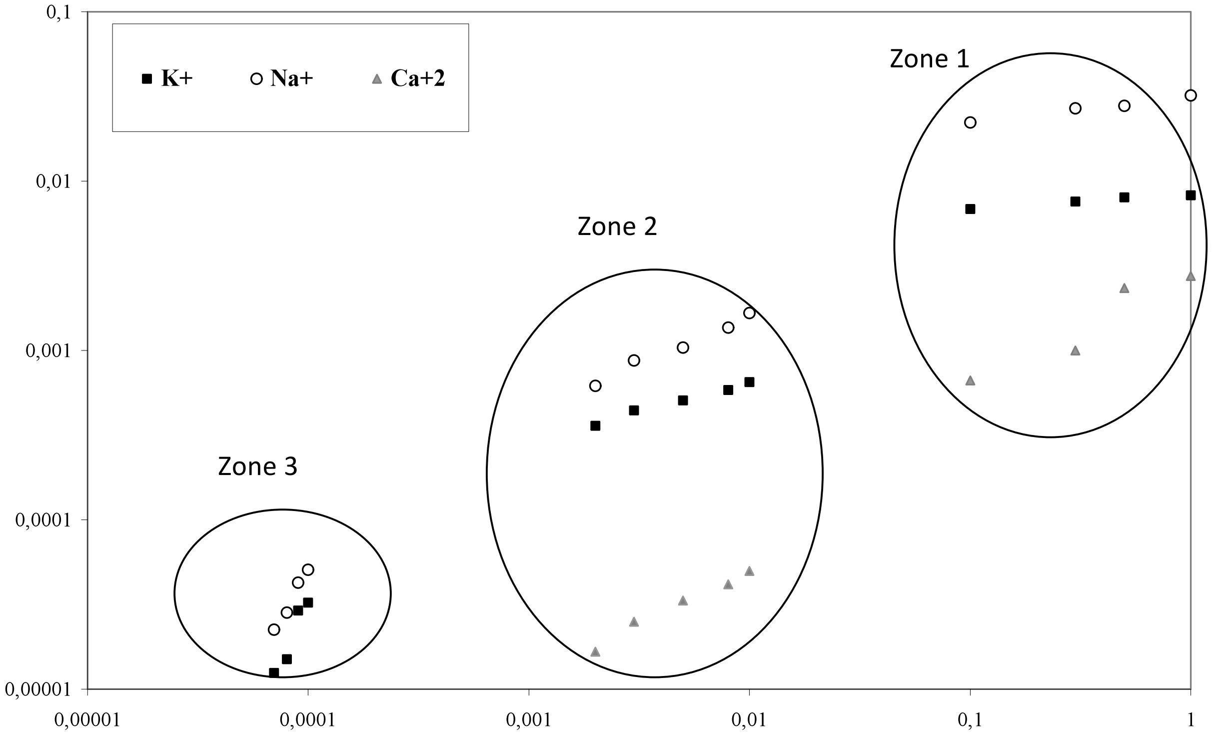
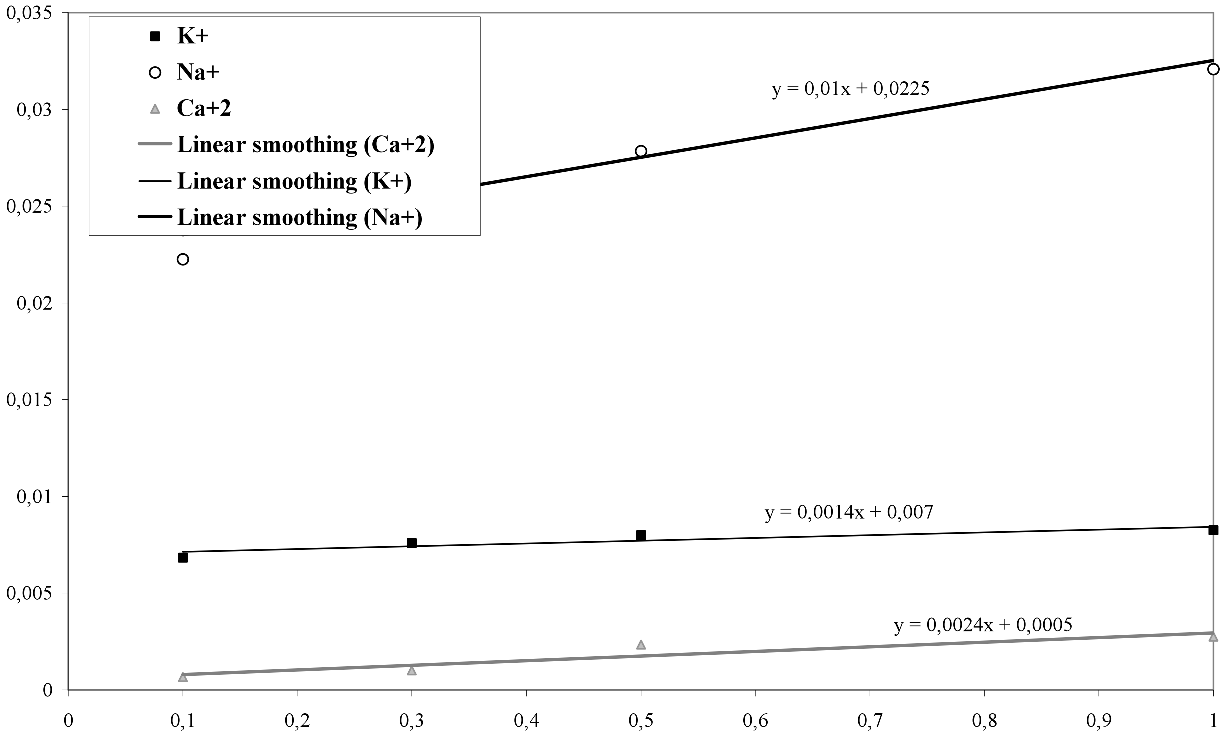
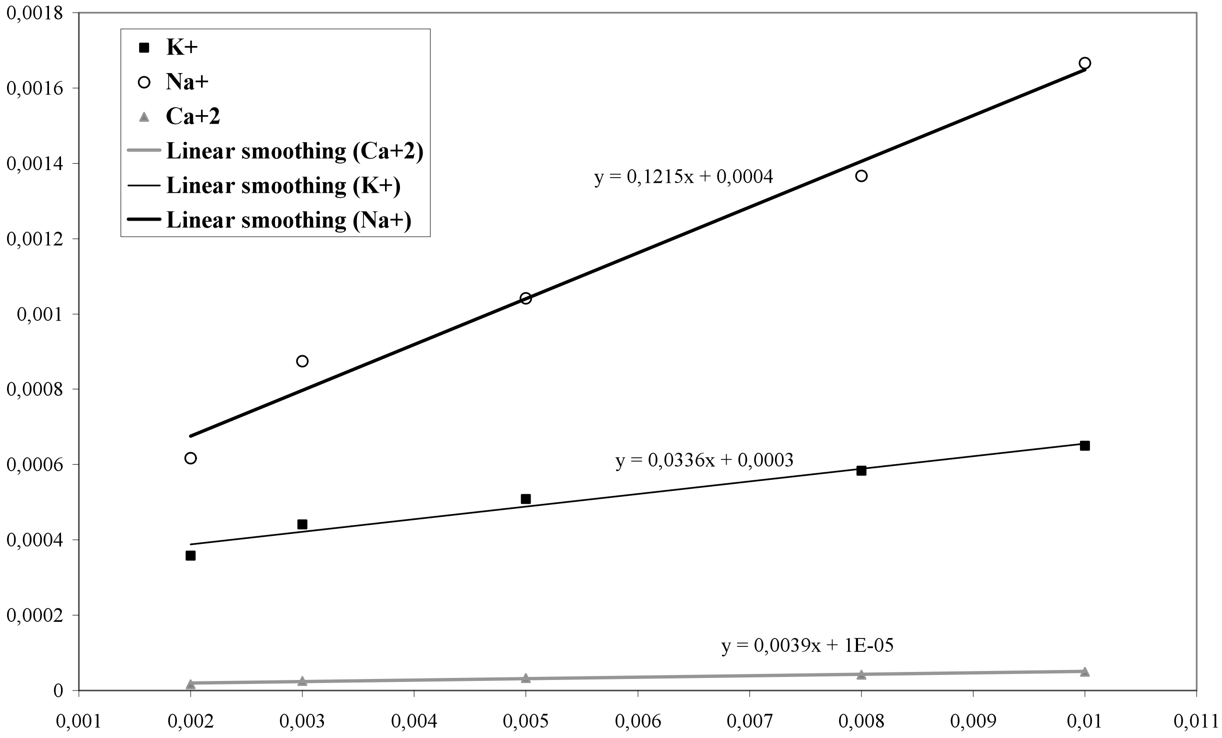


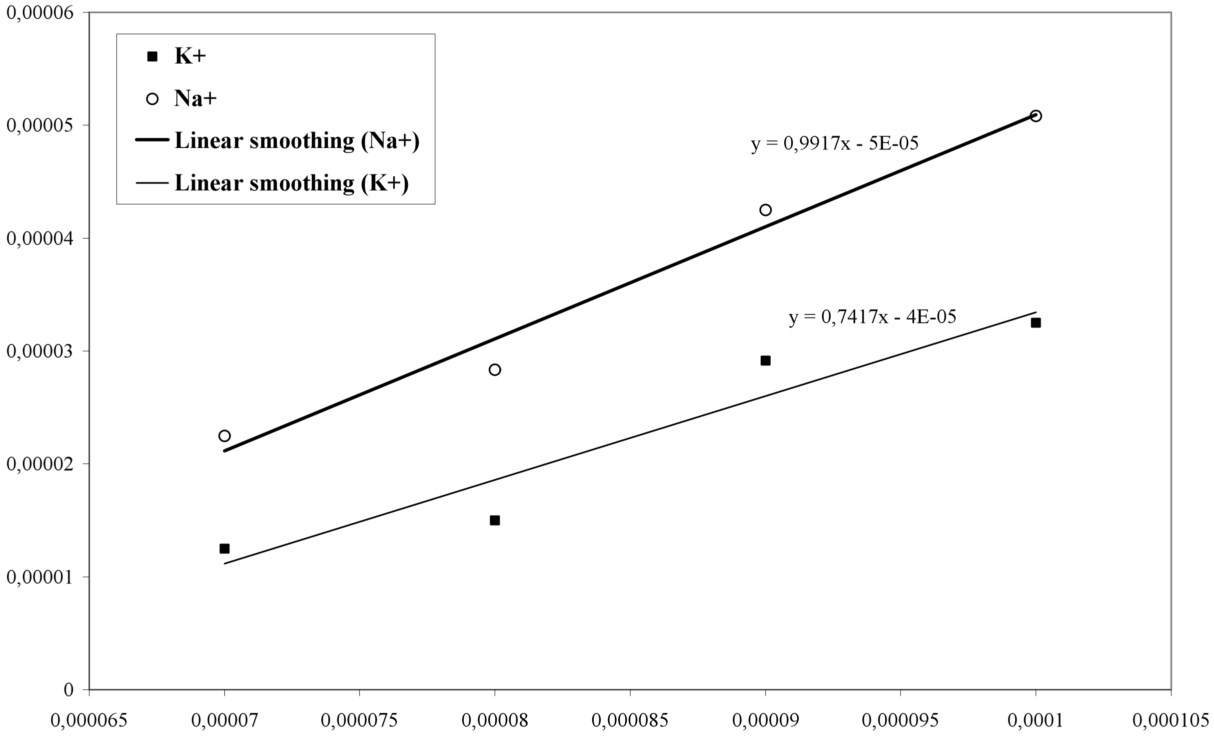
Figure 6. Calibration Curve of SPR calix[4]arene SAM sensor for alkali ions detection



a) Zone 1



b) Zone 2



c) Zone 3

Figure 7. Behavior of alkali ions adsorption on calixarene-SAM in different zones of detection: a) zone 1 b) zone 2 c) zone 3

	Sensitivity μM^{-1}		
	Zone 1	**Zone 2**	**Zone 3**
Na^+	0.01	0.1215	0.992
K^+	0.0014	0.0336	0.742
Ca^{+2}	0.0024	0.0039	-

Table 1. Sensitivities of SPR sensor for different detection zones