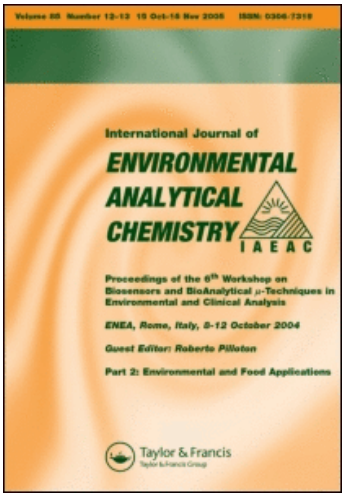

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Development of an electrochemical chemosensor for the rapid detection of zinc based on air stable lipid films with incorporated calix4arene phosphoryl receptor

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Development of an electrochemical chemosensor for the rapid detection of zinc based on air stable lipid films with incorporated calix[4]arene phosphoryl receptor

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This work describes the preparation of a selective receptor for the rapid, selective, and sensitive electrochemical flow injection analysis of zinc using air stable lipid films supported on a methacrylate polymer on a glass fibre filter with incorporated artificial receptor. The selective receptor was synthesised by transformation of the –OH groups of resorcin[4]arene receptor into phosphoryl groups. These lipid films were supported on a methylacrylate polymer (i.e. methacrylic acid was the functional monomer for the polymerisation, ethylene glycol dimethacrylate was used as the crosslinker and 2,2′-azobis-2-methylpropionitrile as an initiator). A minisensor device was constructed for the electrochemical flow injection analysis of zinc based on air stabilised lipid films supported on a polymer. The device can sense the analyte in a drop (75 μL) of sample. Zinc was injected into flowing streams of a carrier electrolyte solution. A complex formation between the calix[4]arene phosphoryl receptor and zinc takes place. This enhances the pre-concentration of zinc at the lipid membrane surface which in turn causes dynamic alterations of the electrostatic fields and phase structure of membranes; as a result ion current transients were obtained and the magnitude of these signals was correlated to the substrate concentration. The response times were ca 5 s and zinc was determined at concentration levels of nanomolar. The analytical curve was linear in the concentration range $1.00 \times 10^{-7} - 1.20 \times 10^{-6}$ M with detection limit of 5.00×10^{-8} M and a relative standard deviation lower than 4%. The effect of potent interferences included a wide range of other metals. As an analytical demonstration, trace concentrations of Zn(II) were successfully detected in real samples of waters without any laborious and time-consuming treatment.

Keywords: electrochemical chemosensor; lipid films; artificial receptor; calix[4]arene phosphoryl receptor; zinc

1. Introduction

Toxic and persistent substances in the environment continuously increase owing to anthropic activities. In particular, the rapid diffusion of heavy metals as environmental contaminants has called for attention to their determination at trace and ultratrace levels [1].

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Zinc is the second most abundant heavy metal ion in the human body, and its concentration may be as high as 10 μM in serum [2]. It is also an essential element of many enzymes, and plays critical roles in many biological activities [3–6]. In addition, the quantification of Zn^{2+} in environment samples is also very important [7].

The speciation of zinc in natural water is a critical factor to consider when assessing the environmental impact of zinc. In uncontaminated waters zinc concentration is usually very low and can span a wide range from 10^{-10} to 10^{-6} M [8]. Concentrations of zinc greater than 5.0 mg L^{-1} affect the potable water nature in alkaline waters.

Because of the importance of zinc, simple and sensitive analytical methods for the determination of trace levels of zinc are required. The commonly used analytical methods for the quantitative determination of zinc are graphite furnace atomic absorption spectrometry (GF-AAS) [9], flame-AAS (FAAS) [10], inductively coupled plasma mass spectrometry (ICP-MS) [11,12], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [13,14], microprobe X-ray [6], spectrophotometry [15–17], and electroanalytical techniques [18]. Although, these methods exhibit low detection limits, however, they are time consuming, expensive, and could suffer from serious matrix interference. A number of fluorescent chemosensors for the determination of zinc have recently been developed [19–21]; these sensors have attractive advantages such as high sensitivity (i.e. nanomolar detection limits) and selectivity, however, they have the disadvantage that they are not portable for the determination of zinc in fields.

In the past decades, calixarenes as third generation supramolecules have drawn considerable attention among synthetic chemists due to their various binding properties. A review article has demonstrated the sensor applications of these intriguing molecules [22]. Calixcrowns, combining the unique properties of the two supramolecular systems in one molecule, are especially attractive ionophores for chemical sensors. In recent years, the use of resorcinarenes for the synthesis of artificial receptors for the construction of chemosensors has increased greatly [23,24]. Recently, the advantage of the incorporation of a novel resorcinarene (actually pyrogallarene) in planar freely-suspended bilayer lipid membranes (BLMs), composed of phosphatidylcholine (PC) and dipalmitoyl phosphatidic acid, for the rapid selective detection of dopamine has been reported [25]. Recent work has investigated the selectivity of these resorcinarene receptors towards catecholamines [25–28].

The present article describes the use of a phosphoryl derivative of a resorcin[4]arene receptor for the development of a chemosensor for the rapid, selective, and sensitive electrochemical flow injection analysis (FIA) of zinc in natural tap, synthesised and mineral water, without any laborious and time-consuming treatment; the sensor is based on stabilised after storage in air lipid membranes in which the receptor was incorporated. The device can sense an analyte in a drop (50–100 μL) of sample. Injections of zinc were made into flowing streams of a carrier electrolyte solution. A complex formation between the calix[4]arene receptor and zinc takes place that enhances the pre-concentration of zinc at the lipid membrane surface which in turn causes dynamic alterations of the electrostatic fields and phase structure of membranes; as a result ion current transients were obtained and the magnitude of these signals was correlated to zinc concentration, which could be determined at the nanomolar level. The response times were ca 5 s. The investigation of the effect of potent interferences included other metals and compounds usually found in real samples of waters.

2. Experimental

2.1 *Materials and apparatus*

Dipalmitoyl phosphatidylcholine (C16 : 0) (DPPC) was supplied by Sigma, St. Louis, MO, USA and was used as lipid for the formation of the films supported on a polymer. The functional monomer, methacrylic acid, and the crosslinker, ethylene glycol dimethacrylate, were both supplied by Aldrich (Aldrich-Chemie, Steinheim, Germany). The initiator, 2,2′-azobis-(2-methylpropionitrile) (AIBN), was supplied by Merck KgaA (Darmstadt, Germany). Water was purified by passage through a Milli-Q cartridge filtering system (Milli-Q, Millipore, El Paso, TX, USA) and had a minimum resistivity of 18 MΩ cm. All other chemicals were of analytical-reagent grade. The filters and (nominal) pore sizes that were used in the present experiments were glass microfiber (0.7 and 1.0 μm, Whatmam Scientific Ltd., Kent, UK).

The elemental analysis was performed on a Perkin–Elmer 2400 C,H,N elemental analyser. The IR spectra were measured on a Perkin–Elmer, FT-IR Spectrometer, System 2000. The ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were measured on a Varian 300 UnityPlus.

A Perkin–Elmer differential scanning calorimeter (Model DSC-4) was used for the DSC experiments; the thermograms were processed by means of the Thermal Analysis Data Station (TADS) of the DSC-7.

2.2 *Procedures*

2.2.1 *Preparation of the receptor*

The preparation of the receptor molecule having the chemical structure of the 2,8,14,20-tetraundecylpirogallol[4]arene receptor was previously reported [25,27].

The phosphoryl derivative of the receptor was synthesised as follows: 50 mL of aqueous NaOH (50%) were added dropwise under vigorous stirring into a mixture containing 700 mg of the 2,8,14,20-tetraundecylpirogallol[4]arene receptor, 10 mL of diethylchlorophoshate, and 200 mg of tetra-*n*-butulammonium bromide in 100 mL of dichloromethane. After this addition, the reaction mixture was refluxed for 6 h and cooled. The organic layer was then collected and washed with an aqueous solution of NaCl and then with water. This layer was dried over anhydrous Na_2SO_4, and finally concentrated *in vacuum* to provide the phosphoryl derivative. The yield was 34%.

2.2.2 *Procedures*

Stabilised lipid films were prepared by polymerisation that was previously described in the literature [27–30]. The polymerisation took place by using UV irradiation instead of the thermal polymerisation; 5 mg of DPPC were mixed with 0.070 mL of methacrylic acid, 0.8 mL of ethylene glycol dimethacrylate, 8 mg of 2,2′-azobis-(2-methylpropionitrile), 1.0 mL of acetonitrile, and 0.29 mg of the phosphoryl receptor. The mixture was sparged with nitrogen for about 1 min and sonicated for 30 min. This mixture could be stored in the refrigerator. For the preparation of the stabilised lipid films, 0.15 mL of this mixture was spread on the microfilter. The filter with the mixture was then irradiated using the UV deuterium lamp. Raman Spectrometry was used to monitor the kinetics of the process of polymerisation [30]. The polymerisation was completed

within 4 h. These membranes were stable in storage in air, for repetitive uses, for periods of more than 2 months.

The apparatus for the present electrochemical experiments consisted of two Plexiglas chambers. One of the Plexiglas chambers (upper) was machined to contain a circular hole with a diameter of 0.4 cm and depth 0.5 cm. The thickness of the Plexiglas chamber was 0.5 cm. It was found that a thinner Plexiglas chamber could not be used because it could allow leakage of electrolyte solution. The other Plexiglas chamber (lower) with a thickness of 1 cm was machined to contain a circular electrochemical cell (diameter 1.5 cm and depth 0.5 cm) connected with a plastic tubing for the flow of the carrier electrolyte solution.

Those two Plexiglas cell chambers were separated by a Saran Wrap^{TM} (PVC, PVDC) partition of a thickness of ca 10 μm. This plastic sheet should extend beyond the limits of the edges of the chambers so that no ion current leakage could occur around the barrier. For the same reason the chambers should be clamped tightly, but should not pinch or stretch the plastic sheet at points where the corners of the chambers meet. This partition was cut to more than twice the size of the contact area of the faces of the chambers with a paper cutter and folded in half; an orifice of 0.32 mm diameter was made through the double layer of the plastic film by punching with a perforation tool.

The microporous filter disk (diameter of about 20 mm) with the stabilised lipid film on a polymer and incorporated receptor was placed between the two plastic partition layers, with the filter centred on a 0.32 mm orifice. The plastic partition with the filter in place was then clamped between the two Plexiglas chambers. We have found that by using four screws at each corner of the device, did not allow any electrolyte leakage. The holes of the upper cell chamber were used as microwell to deposit ca 50 μL of electrolyte solution to act as one cell chamber; whereas the circular cells with the flowing electrolyte solution acted as the opposing cell.

The stock solution of zinc was 0.00100 M. The dilute aqueous solutions of zinc were prepared daily just before use. The BLMs were supported in a 0.1 M KCl electrolyte solution.

Two Ag/AgCl reference electrodes were used for the present experiments. One of these reference electrodes was immersed in the waste of the carrier electrolyte solution; whereas an Ag/AgCl reference electrode was placed into the round cell of the upper Plexiglas chamber and an external 25 mV d.c. voltage was applied across the lipid membrane between the two reference electrodes. A digital electrometer (Model 614, Keithley Instruments, Cleveland, OH) was used as a current-to-voltage converter. A peristaltic pump (Masterflex with SRC Model 7020 speed controller and 7014 pump head) was used to carry the electrolyte solution from the reservoir. Repetitive injections of analyte sample (75 μL) can be made in close proximity to the detector system with a Hamilton repeating dispenser with a disposable tip (Hamilton Co., Nevada). A modified version of this experimental setup containing an upper Plexiglas (dimensions: $6.7 \times 4.3 \times 0.5\,cm^3$) with 12 holes and one lower Plexiglas chamber (dimensions: $6.7 \times 4.3 \times 1\,cm^3$) with 3 circular holes as previously described can be used to simultaneously monitor three different analytes. The electrochemical cell and electronic equipment were isolated in grounded copper screen Faraday cage. Figure 1 shows the upper and lower Plexiglass chamber cells used for the measurements. A simplified schematic diagram of the measuring apparatus has been recently given in a large number of our recent publications [31–33]. All experiments were made at $25 \pm 1^{\circ}C$.

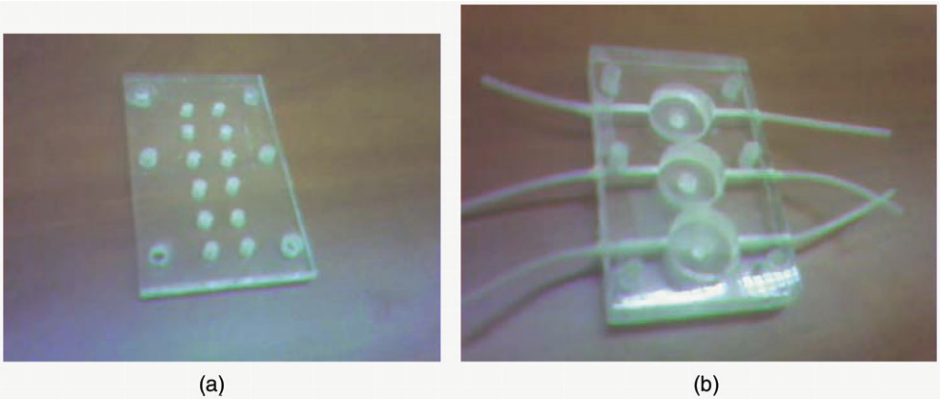

Figure 1. Upper (a) and lower (b) plexiglass chamber cells used for the measurements.

2.3 *Application to real samples*

Recovery experiments were also conducted by spiking the samples with appropriate amounts of zinc in order to simulate real-life conditions.

3. Results and discussion

3.1 *Identification of the receptor*

Analytical calculations for the phosphoryl receptor structure ($C_{120}H_{220}O_{48}P_{12}$) provided the values: C 51.42%, H 7.86%, P 13.29%, whereas the values found using element analysis was: C 51.35%, H 7.90%, P 13.23%. Analysis for the phosphoryl receptor has given the following results ^{1}H NMR ($CDCl_3$) (ppm relative to TMS): δ0.90 (36H, CH_3CH_2O), 1.24 (72H, CH_2), 4.20 (4H, Ar–C*H*–Ar), 4.25 (24H, CH_3CH_2O), 7.15 (s, 4H, Ar*H*), 7.24 (4H, O*H*). ^{13}C-NMR ($CDCl_3$): δ16.07, 16.16 (bridged CH_3H_2OP) and the ^{31}P-NMR ($CDCl_3$) (ppm relative to H_3PO_4): $\delta -12.22, -6.12, -5.66, -5.35, -5.20, -4.89$. The latter signals were attributed to the pendant diethyl phosphate groups, and the former to the bridging phosphoester [34]. The IR spectrum of the calixarene receptor and the analysis of the peaks have been previously presented [27]. Most importantly, the phenolic ν_s(OH) gives the 3468 cm^{-1} peak and 3369 cm^{-1} shoulder. This band and shoulder completely disappear in the IR spectrum of the phosphoryl derivative of the receptor, and new bands 1265, 1180, 1030, 964 cm^{-1} showing that all the hydroxy groups are fully transformed into phosphoryl groups during the organic synthesis.

3.2 *Use of the receptor for the development of an electrochemical chemosensor for the rapid detection of zinc*

Figure 2 shows recordings of the signals obtained with injections of zinc in continuous flowing streams of carrier electrolyte solution of pH 6.0 (0.1 M KCl). Experiments were done using a continuous flow of the carrier electrolyte solution and flow rates of 1.0 mL min^{-1}. It can be seen in this figure that a transient current signal as a single event is obtained by the interactions of zinc with the stabilised filter-supported BLMs. A constant time delay for the appearance of the transient currents of (5.0 ± 0.3) s is observed in Figure 2.

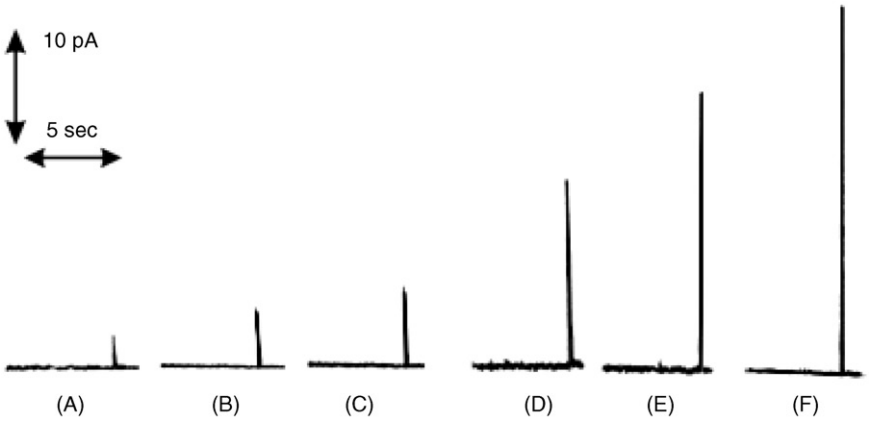

Figure 2. Typical recordings of the stabilised lipid film chemosensor responses to zinc concentration changes in electrolyte solution. The lipid films were composed of DPPC. These films were stabilised with polymerisation and were supported in glass microfiber filters. Zinc concentrations of the solutions injected (75 μL) in the carrier electrolyte solution (μM): (a) 0.10; (b) 0.15; (c) 0.25; (d) 0.50; (e) 0.75 and (f) 1.00. The electrolyte solution was 0.1 M KCl. The injection of each sample was made at the beginning of each recording. The recordings shown were chosen randomly from a number of injections made. Experiments were done at $25 \pm 1^{\circ}$C.

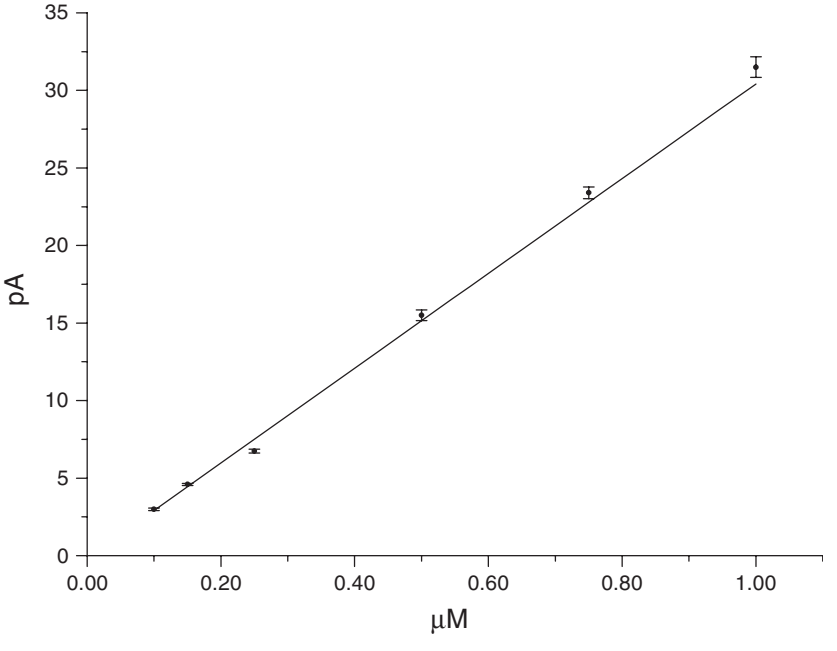

Figure 3. Calibration of analytical signal for zinc determination.

The magnitude of these transient responses is in direct proportion to zinc concentration between 0.1 and 1.2 μM in the carrier electrolyte solution [I(pA) = 31.9C (μM) − 0.49, $r^2 = 0.9990$]. Figure 3 is calibration graph for zinc determination and shows the reproducibility of each measurement ($N = 5$). The maximum RSD was ±4%.

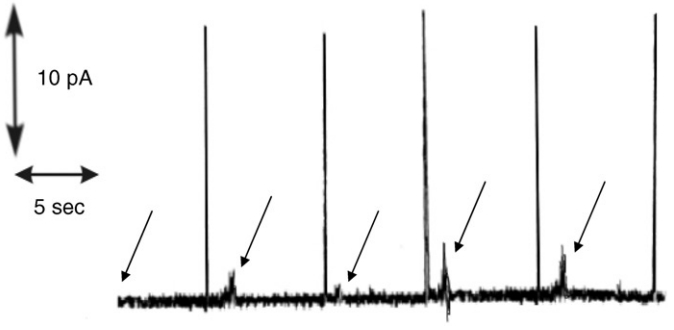

Figure 4. Continuous recordings of the stabilised lipid film chemosensor responses to zinc concentration changes in electrolyte solution. Conditions were described in Figure 1, but the zinc concentration of the solutions injected was 0.5 μM. The arrow shows where the injection of each sample was made.

The detection limit (based on the lowest concentration that could be measured) was ca 0.05 μM ($s/N = 3$). Repetitive cycles of injection of zinc have shown no signal degradation during each cycle (30 sequential injections). Figure 4 shows a batch of signals as recorded continuously during repetitive cycles of injection and exhibits the reproducibility of the method.

The pH (between 5.0 and 8.0) and the ionic strength effect were investigated and were found not to have any effect on the phenomenon as experimentally was observed. This provides an advantage to the sensor because the samples can directly be used without any addition of any pH and ionic strength adjusters.

3.3 *Investigations of signal generation*

When the phosphoryl receptor molecules are incorporated in the structure of polymerised lipid films, the polymer with the lipid film becomes more flexible due to the incorporation of the receptor in the structure of the polymer [35,36]. The formation of a complex between zinc and the phosphoryl group of the receptor enhances the preconcentration of zinc at the lipid membrane surface which in turn results in a phase alteration of the lipid film. The lipid film becomes more flexible with the introduction of the receptor in the lipid membrane. The preconcentration of zinc into the lipid film surface and the formation of the complex make the lipid film more fluid.

In order to investigate the mechanism of signal generation, differential scanning calorimetric (DSC) experiments were presently made. The phase transition temperature (T_m) of the DPPC was found to be 62 ± 1.0°C. Note that the T_m of DPPC liposomes is 42°C. However, presently DPPC in lipid films is polymerised and therefore exists in the solid state. Therefore, a small piece of microporous filter glass fibre disk was cut with the polymerised stabilised lipid film in a size to fit inside the cell of the DSC. To test whether the phase transition of the lipid films were modulated by the glass substrate, a polymerisation step has taken place on a glass substrate and a small amount of pulverised polymerised lipid film was placed inside the DSC cell. The results obtained were similar to that of the solid DPPC (i.e. T_m ca 62). When the receptor was

incorporated within the lipid film, the phase transition temperature was decreased to $55 \pm 1.0^{\circ}C$. These results show that the fluidity of the lipid film is increased. The presence of zinc results again in a further decrease of the phase transition of the lipid film to $54 \pm 1^{\circ}C$ (in the presence of 1×10^{-5} M of zinc), to $52 \pm 1^{\circ}C$ (in the presence of 1×10^{-4} M of zinc), and $49 \pm 1^{\circ}C$ (in the presence of 1×10^{-3} M of zinc), which shows that the lipid film becomes more fluid; therefore, these experiments clearly show that the analyte binding makes the membrane more fluid and the phenomenon is an effect of the phase stage. These results show that the receptor decreases the transition temperature of lipid vesicles and is therefore incorporated in the lipid membrane through its hydrophobic tails leaving its hydrophilic groups towards the electrolyte solution. The results show that the incorporation of the receptor in the lipid membrane destabilises the gel phase of the lipid film. In the presence of zinc, the gel phase of the lipid membranes is destabilised which is reflected by the decrease of the T_m value of the liposomes [35,36]. The fluidity of these vesicles in the presence of this substance is increased which is in agreement with the electrochemical signals. Presently our electrochemical experiments are performed in $25^{\circ}C$. However, it is well known even at this temperature, there is a coexistence of solid (gel) and fluid (liquid-crystalline) phases and phase separation of the lipid molecules [35–37]. It is well known and provided in the literature [37] that other cations, i.e. calcium ions may affect the rigidity of a lipid membrane, in the presence only of dipalmitoyl phosphatidic acid. In the absence of this acidic lipid, the ionic conductivity of unmodified membranes is practically not affected [37]. Similar results were presently obtained and zinc did not practically affect the transition temperature of unmodified membranes in the absence of the receptor. These results are in agreement with the mechanism that was currently described and is based on both electrochemical double layer and cation concentration changes at the lipid/water interface [29]. Presently the current is not of capacitive nature and the mechanism of the signal generation in the case that when an organic molecule interacts with these stabilised lipid films with incorporated receptor was previously explained [25,27].

We recently have synthesised a variety of artificial receptors [25,27,38]. The structure of the chemoreceptor before and after phosphorylation is presented in a simplified form in Figure 5.

Presently, zinc interacts with the phosphate groups of the receptor and forms a complex. The results of Figure 2 and DSC experiments show that there is a coexistence of solid (gel) and fluid (liquid–crystalline) phases. Such a lateral phase separation results in defects that are located at the dilatation regions at the boundaries between the phases [31,38,39]. The number density of defects will vary dynamically in the presence of zinc. If a structural defect appears at the same time (when zinc forms a complex with the phosphoryl groups of the receptor), then the ions diffuse through the defect sites which are increased. The fraction of ions that permeate through the lipid film depends on the speed of channel opening and the diffusion of ions from the surface to the bulk solution. A slow channel formation implies that the majority of ions will be dissipated into the bulk solution [31,39] which would result in a capacitive current. If the channel formation is fast, which is the present case, then an appreciable portion of the ions will pass through the membrane (i.e. ionic current changes, see [31]). The latter phenomena are presently observed in our flow experiments; due to the nature of our flow experiments, the baseline returns back to its initial value due to the flow of the electrolyte solution.

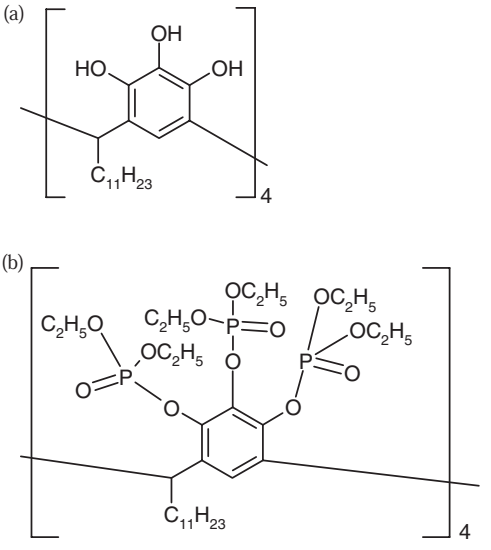

Figure 5. Simplified form of the structure of the chemoreceptor (a) before and (b) after phosphorylation.

Table 1. Interference effect of various metals.

Interferent	I (pA)
None	15.5
K^+	15.1
Na^+	15.2
NH_4^+	15.4
Ca^{2+}	15.8
Mg^{2+}	14.9
Al^{3+}	16.4
Fe^{3+}	16.5

Note: The concentration of zinc was 5.00×10^{-7} M and the concentration of interferent was 0.01 M except Fe^{3+} and Al^{3+} which was 1.00×10^{-4} M.

3.4 *Interferences*

Interfering studies were conducted to determine whether other trace elements or anions interfere with the determination of zinc during the proposed chemosensor. Various amounts of the potential interferants were added to a concentration level of 0.01 M. in the presence of 5.00×10^{-7} M of zinc and the signals were compared to that of a solution containing only Zn(II). The metals examined were selected with respect to their toxicity and presence in real samples and the results of these studies are collected in Table 1. As can be seen, the tested cations, at concentration levels higher than those usually present in real samples, were not found to impair the effectiveness of the proposed method. Our present results show that, for example, calcium ions do not interfere with our zinc determination as

Table 2. Determination of Zn^{2+} in water samples.

Sample	Zn^{2+} spiked level (μM)	Zn^{2+} found (μM)	Recovery (%)	RSD (%)
Tap water	0.00	n.d.	–	–
	0.25	0.24	96	3.7
	0.50	0.52	104	2.7
	0.75	0.73	97	1.9
Synthesised water	0.00	0.46	102	1.8
	0.30	0.73	97	3.1
Mineral water	0.00	n.d.	–	–
	0.30	0.29	97	1.6
	0.60	0.62	103	2.2

Note: Synthesised water was prepared by tap water by adding 0.45 μM Zn^{2+}, 30 μM $N\alpha^{+}$, K^{+}, Mg^{2+} and Ca^{2+}.

was previously described. Also the present results show that monovalent cations, i.e. sodium, potassium, ammonium etc. do not also interfere as is experimentally expected [40]. The selectivity factor as defined by Wang *et al.* [41,42] can be calculated from Table 1 and has a value of ca 1.

Various anions were also tested for their effect on the determination of zinc. Phosphates, organic matter in the form of humic acids, citrates, tartarates, oxalates, fluoride, and nitrates (20 mg L^{-1}) were not found to impair the effectiveness of the proposed method.

3.5 *Analysis of real samples*

Tap water (containing no Zn^{2+}), synthesised water (by adding Zn^{2+} and other metal ions to tap water), and commercial bottled water (mineral water) were analysed by the proposed method under optimised condition (Table 2). All the results were satisfactory, and it could be found that alkali and alkali earth metal ions in high concentration did not interfere with the quantification of Zn^{2+}.

4. Conclusions

The present article describes the preparation of a novel phosphoryl calixarene receptor and sensor based on a lipid film supported on a polymer with the incorporated receptor that can be used for the rapid electrochemical screening of zinc and potentially could be commercialised. Many papers have been published on the detection of zinc during the last 30 years but the originality of this paper is based on the mode of detection, i.e. construction of a selective receptor for the direct detection of zinc. The technique has several advantages, i.e. it is direct and rapid and the detection time is in the order of about a few seconds and not several minutes as other techniques. The overall procedure is simple and does not require any tedious and time-consuming steps for sample pre-treatment. As an analytical demonstration, trace concentrations of zinc were successfully determined in various real samples. The results have shown that these lipid films can be reused after storage in air even after a period of more than 1 month and can be reproducibly fabricated with simplicity and low cost.

Acknowledgements

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