A novel self-assembled monolayer (SAM) coated microcantilever for low level caesium detection

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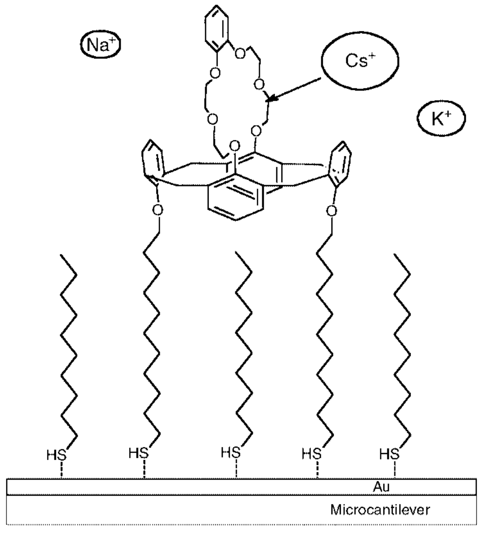
We report a new sensor concept based on an ion-selective SAM modified microcantilever which can detect caesium ion concentrations *in situ* in the range 10^{-11}–10^{-7} M and shows potential for use in developing a new family of real time *in situ* metal ion sensors with high sensitivity/selectivity and low cost, for chemical and biological applications.

Research in the area of sensor development for metal ion detection in chemical and biological applications has received considerable attention in recent years.[1–3] In particular, the application of host–guest chemistry to sensor development has proved to be a very useful detection method.[4] Many different receptors (hosts) including crown ethers, cryptands and calixarenes have been synthesized as molecular recognition agents for the binding of various metal ions (guests).[5–7] Recent results from our laboratory on microcantilever based sensors have revealed that adsorption-induced stress on microcantilevers can be used to detect low concentrations (ppb) of chemical vapors.[8] This adsorption-induced stress can be detected by the change in bending[9] or resonance frequency[10] caused by changes in the cantilever surface. We have shown that microcantilevers can operate in both the gas and liquid phase for chemical sensing applications.[8,9] In liquid environments, the preferable mode of detection appears to be adsorbate induced cantilever bending. Chemical selectivity for inorganic ions can be obtained by coating an ion-selective polymer film or modified SAM containing ion selective binding sites.

Here we report the first example of a selective caesium ion sensor based on an ion-selective SAM coated microcantilever capable of detecting caesium ions in the presence of high concentrations of potassium of sodium ions. Our data shows that the sensitivity of this cantilever based sensor for *in situ* measurements is several orders of magnitude better than the currently available ion selective electrodes (ISE).

The caesium recognition agent used in this work was 1,3-alternate 25,27-bis(11-mercapto-1-undecanoxy)-26,28-calix[4]benzocrown-6 **1**, bound to a gold coated microcantilever. The crown cavity of the 1,3-alternate conformation of calix[4]benzocrown-6 has been shown to be very suitable for accommodating caesium ions with Cs/Na and Cs/K selectivity ratios in excess of 10^4 and 10^2, respectively, by a solvent extraction technique.[11] Binding constant values of 10, 2×10^4 and 2.5×10^6 have also been determined by a fluorescence technique for Na^+, K^+ and Cs^+ in $MeOH–CH_2Cl_2$ (1 : 1) solution.[12] Based on the high selectivity exhibited by these compounds, receptor molecule **1** was designed and anchored onto the gold surface of the microcantilever by standard techniques.[13] Decane-1-thiol was co-absorbed onto the gold surface in a 2 : 1 ratio to fill the gaps present between the two alkyl thiol arms of **1** and the adjacent molecules (Scheme 1) and to enhance the aqueous stability of the SAM.

The experiments were performed in a flow-through glass cell where the SAM coated V-shaped microcantilever was immersed in distilled water at a flow rate of 10 mL min^{-1}. Electrolyte solutions (Cs, K or Na nitrate) were introduced using a syringe pump by switching the syringe delivering pure water to the syringe containing the desired electrolyte solution. The volume of the glass cell was selected to be small enough (4 mL) to insure fast replacement of the liquid in contact with cantilever. The bending of the cantilever was measured by monitoring the position of a laser beam reflected off the top of the microcantilever onto a four-quadrant photodiode. The microcantilever was initially immersed into the cell exposed to a constant flow of distilled water and its deflection (bending) was measured as the background and set to 0 nm. Approximately 30 s later, the flow of distilled water was replaced with caesium ion solution. As the Cs^+ ions diffuse to the SAM coated microcantilever, the bending response of the cantilever changes reaching an equilibrium within 70–80 s (Fig. 1). Based on the large complexation constant calculated (*vida infra*) for caesium and 1,3-alternate calix[4]benzocrown-6, it is reasonable to assume that the initial rapid increase in bending response depends on the concentration of caesium in solution. Fig. 2 shows the observed change in bending response of the microcantilever as the concentration of caesium ions is varied. It is clear from the plot in Fig. 2 that the most dramatic response is exhibited when the concentration of caesium is in the range 10^{-7}–10^{-11} M. In contrast, the cantilever response to potassium ions (the most prevalent interfering ion) in the same concentration range is very small (*e.g.* 20 nm deflection for 1×10^{-8} M solution of K^+ compared to 330 nm deflection for caesium at the same concentration, Fig. 2). For Cs^+ ion concentrations $> 10^{-6}$ M, the bending response at equilibrium reaches its maximum value at *ca.* 330 nm (Fig. 2). A blank test performed on a gold coated silicon nitride cantilever without the SAM revealed that



Scheme 1 Schematic representation of the molecular structure of receptor molecule 1,3-alternate 25,27-bis(11-mercapto-1-undecanoxy)-26,28-calix[4]benzocrown-6 (**1**) co-absorbed with decane-1-thiol on the gold surface of microcantilever by the SAM technique. The synthetic procedure for preparation of the thiol derivative of 1,3-alternate calix[4]arene **1** used in this work will be published elsewhere. The microcantilever is commercially available and has the following dimensions: 200 μm long, 40 μm base and 0.7 μm thick (Park Scientific Instruments, CA). The maximum number of molecules of **1** that can adsorb on the surface of cantilever is $\leqslant 2 \times 10^{10}$. The sensitivity of detection is 10.58 mV nm^{-1}

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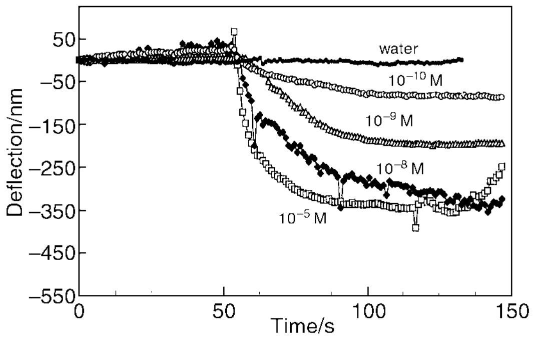

Fig. 1 Bending deflection response of the SAM coated microcantilever as a function of time, *t*, before and after exposure to different concentrations of Cs^+ ions in solution at room temperature. For the *y*-axis, the voltage has been converted to nm using the conversion factor 10.58 mV nm^{-1}.

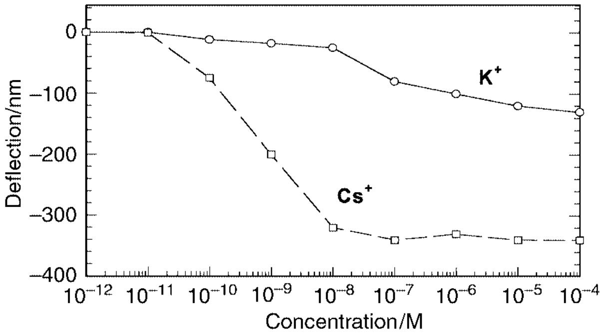

Fig. 2 Bending deflection response of the SAM coated microcantilever as a function of the change in concentration of Cs^+ and K^+ ions. For the *y*-axis, the voltage has been converted to nm using the conversion factor 10.58 mV nm^{-1}.

even at high Cs^+ ion concentration (*e.g.* 10^{-3} M) the bending response was unaffected (same as pure water). Such a finding clearly rules out any contribution to the cantilever bending response by the caesium ions in the absence of receptor molecule, and substantiates the role of molecular recognition agent (receptor) in inducing the observed change in bending response.

The relationship between the cantilever displacement, *z*, and the differential surface stress can be expressed by eqn. (1).

$$z = \left(\frac{3(1-v)L^2}{t^2E}\right)\delta s \qquad (1)$$

where *L* is the length of the cantilever, *v* is Poisson's ratio, *E* is Young's modulus for the substrate, *t* is the thickness of the cantilever, and δ*s* is the adsorption-induced differential surface stress. Since δ*s* is directly proportional to ion absorption by the microcantilever, eqn. (1) can be re-arranged to eqn. (2) where *b* is a constant, *K* is the complexation constant between the ion receptor and the ions present in solution (1 : 1 stoichiometry), [M] is the concentration of ions in solution, and R_0 is the no of mol of ion receptor present on cantilever before complexation.

$$z = b\left(\frac{3(1-v)L^2}{t^2E}\right)\left(\frac{K[\mathrm{M}]R_0}{1+K[\mathrm{M}]}\right) \qquad (2)$$

Since the change in concentration of ions present in solution after absorption by the receptor is essentially unchanged in a continuous flow system, the value of [M] will be the same as the initial concentration of ions. The complexation constants determined from the plot of 1/*z* *vs.* 1/[M] for caesium (K_{Cs}) and potassium (K_K) using eqn. (2) are 2×10^9 M^{-1} and 1.6×10^7 M^{-1}, respectively. These values are much higher (three orders of magnitude) than the corresponding values observed for the derivatives of similar compounds in MeOH–CH_2Cl_2 (1 : 1) solution[12] but the ratio of K_{Cs}/K_K is essentially the same. Similar enhancements in the association constant values for other SAM systems (relative to the free molecule) have also been reported.[14,15] The large value of association constant observed for Cs^+ ions indicates that binding is essentially irreversible. This notion is further supported by our experimental results that showed cycling pure water through the system (to rinse the SAM coated microcantilever containing Cs^+ ions) for several hours failed to regenerate the initial reading (water curve in Fig. 1).

The bending response of the SAM coated microcantilever upon Cs^+, K^+ and Na^+ complexation was also compared for the same concentration of each ion (10^{-5} M). The results indicated that SAM coated microcantilever was much more selective towards Cs^+ ions compared to K^+ and Na^+ ions (not shown). In fact, Na^+ ions have a minimal effect (if any) on the bending response while K^+ ions exhibit enough sensitivity to interfere (as a perturbing ion when present) in the detection of caesium ions.

In summary, our study has shown that the concept of ion-selective-SAM coated cantilever can be applied successfully to detect trace amounts (ppb) of caesium ions (*in situ*) in the presence of high concentrations of interfering potassium ions with remarkable sensitivity. This methodology can be applied to the detection of a wide variety of metal ions of chemical and biological importance. For example, we envision construction of a compact device capable of measuring low levels of metal ions in the blood stream *in situ* using this technique. This concept can be further expanded by constructing a multi-panel array device based on an SAM coated microcantilever for *in situ* detection of different metal ions present in solution or biological fluids. Along these lines, we are currently synthesizing molecular recognition agents containing different size cavities capable of complexing different metal ions.

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