BINDING OF METAL IONS TO SELF-ASSEMBLED MONOLAYERS OF CROWN ETHERS

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0. Abstract

The reversible binding of cations to self-assembled monolayers of (6-mercaptohexyloxy)methyl-12-crown-4 (**1**) and (6-mercaptohexyloxy)methyl-15-crown-5 (**2**) in aqueous solutions is reported. Binding of the electrochemically inactive cations can be monitored by cyclic voltammetry and impedance spectroscopy using $Ru(NH_3)_6^{2+/3+}$ as "reporter ions". As a result of the high surface density of crown ether ligands sandwich complexes are probably formed, which accounts for the observed selectivities of the monolayer.

1. Introduction

Self-assembled monolayers (SAMs) of sulfur-containing molecules, like thiols, disulfides, and sulfides are the subject of numerous investigations.[1] The ease of their preparation, their stability, and the possibility to introduce different functional groups makes them a facile way to create surfaces with tailor-made properties.[2,3] Self-assembly of receptor molecules onto gold enables their use in sensing devices. We have previously shown that self-assembled monolayers of resorcin[4]arene tetrasulfides can be used for the detection of organic compounds from the gas phase.[4] Only a few receptor adsorbates have been used to investigate the binding of guests in solution.[5] Rubinstein *et al.*[6] and Mandler *et al.*[7] have shown that the *voltammetric* detection of electroactive metal ions using self-assembled monolayers is a very sensitive and selective method. Recently, also impedance spectroscopy was used to detect the binding of guests to monolayers. Rubinstein *et al.*[8] reported changes of the monolayer capacitance due to the binding of Fe^{3+} by trishydroxamate SAMs. Henke *et al.*[9] used a cyclodextrin monolayer to bind an organic sulfonic acid which changed the charge transfer resistance of the SAM.

In this poster we describe the reversible and selective complexation of metal ions from aqueous solutions to self-assembled monolayers of 12-crown-4 and 15-crown-5 adsorbates, monitored by cyclic voltammetry and impedance spectroscopy.

2. Experimental

(6-mercaptohexyloxy)methyl-12-crown-4 (**1**) was synthesized by alkylation of 2-(hydroxymethyl)-12-crown-4 with 5 mol equivalents of 1,6-dibromohexane and NaH in DMF. This intermediate product was subsequently converted into the desired product **1** by treatment with thiourea in boiling ethanol, followed by hydrolysis with KOH in boiling water. The 15-crown-5 derivative **2** and the triethyleneglycol derivative **3** were synthesized accordingly from 2-(hydroxymethyl)-15-crown-5 and

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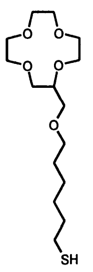
triethylene glycol monomethyl ether, respectively. The structure and purity of the products was verified by TLC, ^1H NMR, ^{13}C NMR, and EI-MS.

The monolayer preparation and the used substrates were applied as discribed before in ref 3c. Experimental details regarding the IR characterization were described in ref 3c. Advancing and receding contact angles were determined automatically on a Krüss G10 Contact Angle Measuring Instrument, equipped with CCD camera, during growth and shrinkage of the droplet by the drop shape analysis routine. Cyclic voltammetry and impedance spectroscopic measurements were performed with an Autolab PGSTAT10 in a three-electrode cell containing a gold working electrode (clamped to the bottom of the cell exposing a geometric area of 0.44 cm^2 to the electrolyte), a platinum counter electrode, and a mercurous sulfate reference electrode. All measurements were conducted in electrolyte containing 1 mM $Ru(NH_3)_6Cl_3$ as a redox couple and a total concentration of the background electrolyte of 100mM. Impedance spectroscopic experiments were conducted at the formal redox potential of $Ru(NH_3)_6^{3+/2+}$, in a frequency range of 10 kHz to 0.1 Hz, with an ac-amplitude of 5 mV. Analysis of the spectra was performed using the software package "Equivalent Circuit" see ref 14.



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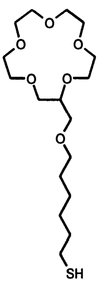

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3. Results and discussion

The monolayers of both crown ether adsorbates showed methylene C-H stretching vibrations at 2930, 2904, and 2859 cm^{-1}, which corresponds with the bulk spectra. The absorption at 1140 cm^{-1} was assigned to the C-O stretching mode of the ether groups.[10] The monolayer of the triethylene glycol adsorbate **3** showed a broad absorption centered around 2870 cm^{-1}, which was assigned to the various C-H stretching modes of the methyl and methylene groups. In addition a peak of the C-O streching vibration was present at 1115 cm^{-1}. Wettability studies of the three SAMs with water showed contact angles that are characteristic for a surface of low hydrophobicity. The self-assembled monolayers of 12-crown-4 **1**, 15-crown-5 **2**, and the triethylene glycol adsorbate **3** had advancing contact angles of 59, 55, and 58 ± 1°, respectively. In the case of both crown ether monolayers **1** and **2**, the hysteresis between the advancing and receding contact angle was 20°. SAMs of **3** showed a slightly smaller hysteresis of 15°, which indicates a more ordered layer.

Characterization of the crown ether monolayers by cyclic voltammetry in the presence of $Ru(NH_3)_6Cl_3$ showed that the heterogeneous electron transfer from the gold electrode to the redox couple in aqueous solution was hardly influenced by the presence of the SAM. The large current density of the redox waves around -0.56 V_{MSE} indicates that the redox couple can easily access the electrode surface.

Addition of NaCl to the electrolyte leads to a *drastic decrease* of the faradaic current for the 12-crown-4 **1** modified electrode as shown in Figure 1. The 15-crown-5 **2** modified gold electrode showed a large attenuation of the redox current when KCl was added to the electrolyte (data not shown).

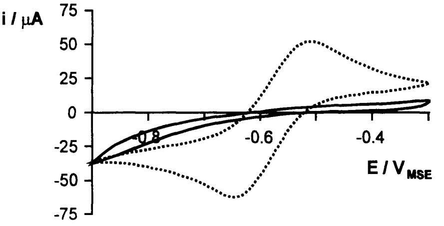

Figure 1. Cyclic voltammograms of a 12-crown-4 1 modified gold electrode in aqueous solutions. The dotted CV is recorded in 100 mM Et_4NCl + 1 mM $Ru(NH_3)_6Cl_3$; the solid CV is recorded in 14 mM NaCl + 86 mM Et_4NCl + 1 mM $Ru(NH_3)_6Cl_3$.

Similar effects have previously been observed by cyclic voltammetry of monolayers with amine or carboxylic acid headgroups which can be charged by protonation and deprotonation, respectively.[11] The influence of a charged monolayer on the electron transfer to a charged redox couple was attributed to the electrostatic forces acting between both, and the shift of the potential drop across the diffuse layer. Hence, complexation of metal cations by the SAM generates a repulsion towards the positively charged redox couple which attenuates its redox current.[11b]

This means that cyclic voltammetry allows the detection of metal cation complexation by the monolayer. However, the application of large potential sweeps (in the range of several hundred mV) might disturb the structure of the monolayer.[12] Impedance spectroscopy is a less interfering technique which enables the simultaneous determination of the electrochemical properties of the monolayer by using a wide frequency range.[13] The impedance spectra of the crown ether SAMs **1** and **2** were best described by the Randles equivalent circuit (Figure 2).[14,15]

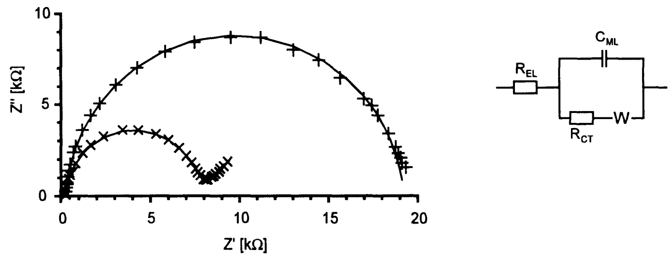

Figure 2. Impedance spectra of 12-crown-4 1 modified gold electrode in solutions containing 1 mM NaCl (x) and 2.5 mM NaCl (+). Fits to the spectra are indicated by the solid line. The Randles equivalent circuit, used to fit the spectra, consists of the electrolyte resistance (R_{EL}), the monolayer capacitance (C_{ML}), the charge transfer resistance (R_{CT}), and a diffusion element (W).

The dependence of R_{CT} on the concentration of sodium demonstrates that binding of metal ions to the monolayer of 12-crown-4 increases its resistance from 250 Ω to a limiting value of 145 kΩ at concentrations above 23 mM (see Figure 3). The initially linear increase of R_{CT} at low concentrations of sodium levels off at concentrations above 10 mM, and finally reaches a plateau value. These observations indicate that the binding sites become saturated at high guest concentrations.

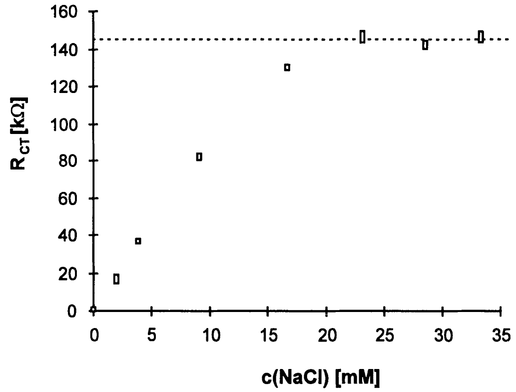

Figure 3. Charge transfer resistance (R_{CT}) of 12-crown-4 monolayer 1 as a function of the sodium concentration. For each concentration at least two impedance spectra were recorded within 30 minutes to establish the stability of the response.

Replacement of the solution by a sodium free electrolyte of 0.1 M Et_4NCl + 1 mM $Ru(NH_3)_6Cl_3$ reduced the charge transfer resistance to the initial value of 250 Ω and the addition of sodium resulted in the same changes of R_{CT} as before. This demonstrates that the binding of sodium to the monolayer is a ***reversible*** process. The monolayer capacitance (C_{ML}), determined simultaneously from the impedance spectra, shows a very weak response to the binding of sodium (6.4 $\mu F/cm^2$ at $[Na^+] = 0$ mM and 6.8 $\mu F/cm^2$ at $[Na^+] > 15$ mM). The slight increase of C_{ML} is probably caused by a change of the relative permittivity ε_r of the monolayer upon binding of cations.[8] The response of the monolayer (ΔR_{CT} vs. salt concentration) was also determined for several other alkaline and alkaline earth salts. Figure 4a shows the change of the resistance of the 12-crown-4 SAM at two guest concentrations (3.8 and 9.1 mM). It is clear that sodium gives the largest response. Also potassium does affect ΔR_{CT}, but the increase of the resistance is roughly a hundred times less than for the same concentrations of sodium. Other ions had even smaller effects on ΔR_{CT}. The selectivity of sodium over potassium makes it possible to *detect sodium concentrations down to 0.1 mM in the presence of 10 mM of potassium.*

A self-assembled monolayer of 15-crown-5 showed a completely different response pattern towards alkaline and alkaline earth cations (Figure 4b). This larger crown ether shows the highest response for potassium. Besides potassium also cesium shows a significant increase of the charge transfer resistance. It is remarkable that sodium gives rise to a signal which is less than one percent of that observed for the same concentration of potassium.

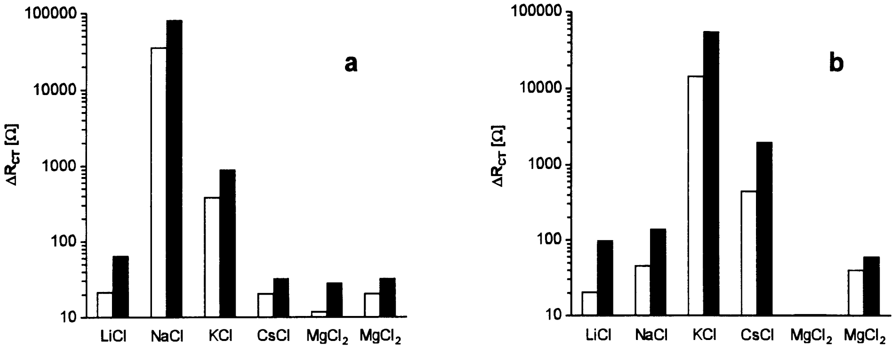

Figure 4. (a) ΔR_{CT} of 12-crown-4 monolayer in the presence of different salts (the white and the black column represent concentrations of 3.8 and 9.1 mM, respectively). (b) ΔR_{CT} of 15-crown-5 monolayer in the presence of different salts (the white and the black column represent concentrations of 2.0 and 9.1 mM, respectively).

Monolayers of the triethylene glycol adsorbate **3** showed no detectable change in both parameters (R_{CT} and C_{ML}) upon addition of alkaline metals. Hence, the binding of metal ions to the crown ether SAMs is a result of the macrocyclic structure of the receptor adsorbates. On the basis of the association constants determined for the 1:1 complexes of 12-crown-4 and 15-crown-5 with metal ions in aqueous solutions preferential binding of sodium and potassium to monolayers of 12-crown-4 and 15-crown-5 would not be expected.[16] The fact that the metal ions are bound to a monolayer with its high surface concentration of crown ethers makes the formation of sandwich complexes, in which one metal ion is complexed by two crown ethers, very likely. The influence of sandwich complexation on the selectivity has been studied using ion-selective electrodes.[17] Bis(12-crown-4) exhibits a much larger Na^+/K^+ selectivity than monomeric 12-crown-4. Similarly, bis(15-crown-5) has a higher K^+/Na^+ selectivity than 15-crown-5. The high resemblance of the selectivity reported for these ion-selective electrodes with the responses of the crown ether SAMs **1** and **2** strongly suggests that sandwich complexation in the monolayer occurs.

4. Conclusions

Modification of a gold electrode with self-assembled monolayers bearing crown ether groups enables the reversible binding of metal ions from water. The use of a positively charged redox couple in the electrolyte transduces the binding event into an electrochemically detectable signal. Moreover, the remarkable selectivity of the crown ether SAMs indicates the cooperative binding of one metal ion by two crown ether ligands.

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