Recognition of Cations by Self-Assembled Monolayers of Crown Ethers

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Self-assembled monolayers (SAMs) of crown ether adsorbates on gold reversibly bind metal ions from aqueous solutions. The resulting changes of the electrochemical properties of the monolayers were monitored by impedance spectroscopy. The increased dielectric constant of the layer due to the complexation of ions results in an increase of the monolayer capacitance (C_{ML}). Analysis of the response curves with a Langmuir isotherm enables the determination of association constants of the SAMs with various metal ions. The cation binding also influences the charge-transfer resistance (R_{CT}) of a redox couple Ru(NH₃)₆^{2+/3+} in the electrolyte. Comparison of both responses allows an accurate interpretation of the origin of the resistive response. Furthermore, the association constants enable the quantitative determination of interactions between SAMs and metal ions, using either capacitive or resistive responses.

Introduction

The modification of gold surfaces with self-assembled monolayers has attracted much interest since the first publication by Nuzzo and Allara.¹ It is a simple and versatile method of attaching molecules to a substrate in a densely packed arrangement and thereby influencing the physical properties (e.g., surface free energy) of the exposed surface.^{2,3} Alternatively, the introduction of functional groups in the adsorbates allows the development of rapidly responding chemical sensors. Monolayer-based systems that are suitable for sensing devices should combine at least two properties. First, the existence of a specific and reversible interaction between guest and SAM which enables the selective recognition. Second, the binding of a guest to the monolayer has to be transduced into a detectable signal. IR spectroscopy,⁴ mass sensitive devices,⁵ SPR,⁶ fluorescence spectroscopy,⁷ and electrochemical measurements⁸ have successfully been applied in the detection of host-guest interactions at SAMs.

Electrochemical impedance spectroscopy (EIS) is a valuable technique for the characterization of self-assembled monolayers and the study of recognition processes. It has been used by Rubinstein et al.⁹ and Vogel et al.¹⁰ to detect capacitance changes upon the binding of metal ions to SAMs of ionophores. Recently, we have demonstrated that EIS can also be used to detect changes of the charge-transfer resistance, caused by the binding of metal ions.¹¹ It was shown that SAMs of 12-crown-4 and 15-crown-5 adsorbates form sandwich complexes, which results in sodium selectivity for the 12-crown-4 SAMs and potassium selectivity for the 15-crown-5 SAMs.

In this paper, we present a detailed study of the binding of alkali metal ions to self-assembled monolayers of several crown ether adsorbates. SAMs of two different 18-crown-6 adsorbates were used to study the capacitive detection of metal ions from aqueous solutions. We have developed a model that quantitatively relates the magnitude of the capacitive response with the structure of the adsorbates. Comparing the capacitive response and the simultaneously determined change of the charge-transfer resistance reveals the mechanism of the latter response. This allowed the interpretation of the titrations in terms of adsorption isotherms and gives the values for the association constants of various metal ions with SAMs of 12-crown-4, 15-crown-5, and 18-crown-6 adsorbates (Chart 1).

Experimental Section

Chemicals. All chemicals for synthesis were obtained from Aldrich and used as received. The syntheses of 2-(6-mercaptohexyloxy)methyl-15-crown-5 (**3**) and 2-(6-mercaptohexyloxy)methyl-12-crown-4 (**4**) have been described previously.¹¹ All reactions were conducted under an argon atmosphere. Electrolyte solutions were freshly prepared from nitrogen-purged, high-purity water (Millipore). The salts were obtained from Merck and were of "pro analysis" purity. Ru(NH₃)₆Cl₃ was purchased from Alfa Products.

2-(p-Toluenesulfonyloxy)methyl-18-crown-6 (5). A solution of 2-(hydroxymethyl)-18-crown-6 (1.00 g, 3.40 mmol), ptoluenesulfonyl chloride (1.90 g, 9.97 mmol), and triethylamine (1.00 g, 9.78 mmol) in dichloromethane (100 mL) was stirred at room temperature for 16 h. Then, 1 M HCl (100 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (3 \times 100 mL). The combined organic fractions were dried over MgSO₄ and filtered, and the solvent was evaporated to give the crude product, which was purified by column chromatography (Al₂O₃, eluent gradient CH_2Cl_2 to EtOAc) to yield 5 as a colorless oil (1.44 g, 95%): ¹H NMR (300 MHz, CDCl₃) δ 2.45 (s, 3H), 3.50-3.76 (m, 22H), 3.79-3.88 (m, 1H), 4.04-4.20 (m, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.5 Hz 2H); ¹³C NMR (75 MHz, CDCl₃) δ 21.63, 69.78, 70.04, 70.13, 70.63, 70.69, 70.85, 70.98, 128.00, 129.76, 132.99, 144.68; FAB MS m/z 471.1 ([M + Na]⁺, calcd for C₂₀H₃₂O₉SNa 471.2).

2-(Mercaptomethyl)-18-crown-6 (1). A solution of **5** (1.24 g, 2.76 mmol) and thiourea (0.42 g, 5.53 mmol) in ethanol (50 mL) was heated under reflux for 16 h. The solvent was evaporated under reduced pressure. Potassium hydroxide (0.31 g, 5.53 mmol) and nitrogen-purged water (50 mL) were added to the residue, and the reaction mixture was heated under reflux for 2 h. After the mixture was acidified with 1 M HClO₄ (50

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mL), the aqueous layer was extracted with dichloromethane (3 \times 100 mL). The combined fractions were dried over MgSO₄ and filtered, and the solvent was evaporated to give the crude product, which was purified by column chromatography (Al₂O₃, eluent gradient EtOAc to EtOAc/EtOH 9/1) to yield **1** as a colorless oil (0.25 g, 30%): ¹H NMR (300 MHz, CDCl₃) δ 2.64–2.80 (m, 2H), 3.50–3.57 (m, 1H), 3.58–3.92 (m, 22H); ¹³C NMR (75 MHz, CDCl₃) δ 26.04, 69.81, 70.69, 70.87, 72.10, 80.08; FAB MS *m*/*z* 333.1 ([M + Na]⁺, calcd for C₁₃H₂₆O₆-SNa 333.2).

2-(6-Bromohexyloxy)methyl-18-crown-6 (6). A suspension of 2-(hydroxymethyl)-18-crown-6 (2.11 g, 7.17 mmol) and sodium hydride (55% in mineral oil; 0.5 g, 11.5 mmol) in 100 mL of DMF was stirred at room temperature. After 30 min, 1,6-dibromohexane (8.0 mL, 52.0 mmol) was added and the reaction mixture was stirred overnight. Subsequently, the reaction was quenched with methanol and the solvent was evaporated under reduced pressure. The residue was taken up in CH₂Cl₂ (100 mL) and washed with water (3 \times 100 mL). After drying over MgSO₄, the solvent was evaporated and the residue was purified by column chromatography (Al_2O_3 , eluent gradient hexane to EtOAc) to yield $\mathbf{6}$ as a colorless oil (1.70 g, 52%): ¹H NMR (250 MHz, CDCl₃) δ 1.28–1.50 (m, 4H), 1.50-1.65 (m, 2H), 1.80-1.92 (m, 2H), 3.35-3.50 (m, 6H), 3.55–3.85 (m, 23H); ¹³C NMR (62.5 MHz, CDCl₃) δ 25.31, 27.97, 29.43, 32.73, 33.94, 69.93, 70.62, 70.64, 70.71, 70.74, 70.79, 70.83, 70.86, 70.88, 71.34, 71.77, 78.40; FAB MS m/z 457.2 ($[M + H]^+$, calcd for C₁₉H₃₈O₇Br 457.2), 479.2 ([M + $Na]^+$, calcd 479.2).

2-(6-Mercaptohexyloxy)methyl-18-crown-6 (2). 2-(6-Bromohexyloxy)methyl-18-crown-6 (6) was converted into the thiol **2** as described above for **1**. The crude product was purified by column chromatography (Al₂O₃, eluent gradient hexane to EtOAc) to yield **2** as a colorless oil (1.25 g, 66%): ¹H NMR (250 MHz, CDCl₃) δ 1.25–1.48 (m, 4H), 1.48–1.70 (m, 4H), 2.51 (dt, $J_A = J_B = 7.3$ Hz, 2H), 3.35–3.55 (m, 4H), 3.56–3.85 (m, 23H); ¹³C NMR (62.5 MHz, CDCl₃) δ 24.59, 25.59, 28.17, 29.50, 33.96, 69.95, 70.63, 70.65, 70.72, 70.76, 70.81, 70.83, 70.87, 70.89, 71.43, 71.80, 78.42; FAB MS *m*/*z* 433.2 ([M + Na]⁺, calcd for C₁₉H₃₈O₇SNa 433.2).

Gold Substrates. Gold substrates were prepared by resistive evaporation of gold (200 nm) on glass slides of 25 mm diameter. A layer of 2 nm of chromium was evaporated onto the glass prior to the deposition of the gold layer in order to improve the adhesion of the gold to the substrate.

Monolayer Preparation. All glassware used to prepare monolayers was cleaned in boiling piraña (solution of 1:4 30% H_2O_2 and concentrated H_2SO_4) and rinsed several times with

high purity water. **Caution:** Piraña is a very strong oxidant and reacts violently with many organic materials. The gold substrates were cleaned in an oxygen plasma (5 min) and subsequently immersed in ethanol for 10 min to remove the oxide layer.¹² Formation of the self-assembled monolayer was achieved by immersion of the gold substrate into a 1 mM solution of the adsorbate in ethanol for 18 h. After the substrate was taken from the solution, it was rinsed with ethanol (three times) and water (two times) to remove any physisorbed material.

Instrumentation. ¹H NMR and ¹³C NMR spectra were recorded with a Brucker AC 250 or a Varian Unity Inova 300 spectrometer in CDCl₃ using the traces of nondeuterated solvent as an internal standard. FAB mass spectra were obtained with a Finnigan MAT90 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. Contact angles were measured on a Krüss G10 contact angle measuring instrument, equipped with a CCD camera. Advancing and receding contact angles were determined automatically during growth and shrinkage of the droplet by the drop shape analysis routine.

Electrochemical Measurements. Electrochemical measurements were conducted with an Autolab PGSTAT10 using a three-electrode cell containing a monolayer-covered 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 (0.61 V_{SHE}). After the cell was filled with the electrolyte solution, nitrogen was bubbled through the solution for at least 3 min. During the measurements, a constant flow of nitrogen was maintained over the solution. Electrochemical measurements without redox couple were performed in a background electrolyte of 0.1 M Et₄NCl and titrated with solutions of metal chlorides ([MCl] = 0.1 M). The impedance spectra were collected at a potential of $-0.2 V_{MSE}$ in a frequency range of 10 kHz to 0.1 Hz, with an ac amplitude of 5 mV. Electrochemical measurements in the presence of a redox couple were performed in a background electrolyte of 0.1 M Et₄NCl + 1 mM Ru(NH₃)₆Cl₃ and titrated with solutions of 0.1 M MCl + 1 mM Ru(NH₃)₆Cl₃ to ensure a constant concentration of the background electrolyte and the redox couple. The impedance spectra were recorded at the formal redox potential of $Ru(NH_3)_6^{2+/3+}$ (-0.56 V_{MSE}), in a frequency range of 10 kHz to 0.1 Hz, with an ac amplitude of 5 mV. The spectra were analyzed using the software package "Equivalent Circuit", which uses a nonlinear least-squares fit to determine the parameters of the elements in the equivalent circuit.¹³

Results and Discussion

Monolayer Characterization. Analysis of the monolayers by grazing-incidence infrared spectroscopy is a very useful technique to identify functional groups of the adsorbates. The SAM of the hexyloxy-containing 18-crown-6 adsorbate 2 showed three absorptions due to methylene stretching vibrations. These absorptions, centered at 2859, 2904, and 2930 cm⁻¹, originate from the hexyl chain and the ethylene groups of the crown ether ring.¹¹ Due to the absence of the alkoxy spacer, monolayers of adsorbate 1 lack the absorption at 2930 cm^{-1} , which originates from asymmetric CH2 stretching vibrations of alkyl chains. The remaining peak at 2859 cm⁻¹ and its shoulder around 2905 cm⁻¹ originate from the symmetric and asymmetric CH₂ stretching vibrations of the crown ether ring, respectively. Besides this, both monolayers show an intense absorption at 1139 cm⁻¹, which is assigned to the C–O stretching mode of the ether groups.¹⁴ The similar height of the C–O absorptions (0.0033 and 0.0038 for SAMs of 1 and 2, respectively) suggests similar densities of adsorbates for both SAMs.



Figure 1. Capacitance plot of 18-crown-6 modified gold electrodes (SAM of 1 (\bullet); SAM of 2 (\odot)) at $-0.2 V_{MSE}$ in 0.1 M Et₄NCl, with $C'' = 1/j\omega Z''$ and $C' = 1/j\omega Z'$. Fits to the spectra are indicated by the solid lines. The inset shows the equivalent circuit used to fit the spectra. It contains an electrolyte resistance (R_{EL}), a monolayer capacitance (C_{ML}), and a constant-phase element (Q).

Wettability studies of monolayers of 18-crown-6 adsorbates 1 and 2 demonstrated that both surfaces have almost identical hydrophobicities. SAMs of the longer adsorbate 2 have advancing and receding contact angles of 60° and 23° , respectively. The short adsorbate 1 produces SAMs with the same advancing contact angle, but the receding contact angle of 17° is slightly smaller. This indicates that in both adsorbates the crown ether is exposed to the outer interface, which will enable them to interact with ions from solution.

Cation Binding to SAMs. The electrochemical impedance spectra of self-assembled monolayers of crown ethers, performed in a background electrolyte of 0.1 M Et₄NCl, are presented in Figure 1 as the complex capacitance plot.^{8b} In this representation, the real component of $1/j\omega Z$ is plotted versus its imaginary component. The advantage of the capacitance plot over the more commonly used Nyquist plot is the simple analysis of the impedance spectra. The impedance spectra of gold electrodes covered with a SAM of 1 and 2, respectively, are shown in Figure 1. Analysis of the spectra showed that the system is best described by an equivalent circuit consisting of the electrolyte resistance $R_{\rm EL}$ in series with the monolayer capacitance $C_{\rm ML}$ and a constant-phase element Q in parallel (see inset Figure 1). The constant-phase element, which has values for n between 0.4 and 0.6, is a diffusion-like element that we attribute to the diffusion of ions in and out of the monolayer under the influence of the applied ac potential. Deviation from the ideal Warburg, for which n = 0.5, is attributed to the roughness of the electrode surface.15

From the impedance spectra, we determined that monolayers of the long 18-crown-6 adsorbate **2** have a capacitance of 4.2 \pm 0.1 μ F cm⁻², whereas SAMs of the short 18-crown-6 adsorbate **1** have a capacitance of 6.8 \pm 0.1 μ F cm⁻². The capacitance of a monolayer-covered electrode is inversely proportional to the layer thickness as given in eq 1 (where ϵ_0 is the permittivity of vacuum, ϵ_r is the relative permittivity of the monolayer, and *d* is the average layer thickness). This means that SAMs of **2** have a larger average thickness than SAMs of **1**, in agreement with their molecular structure.

$$C_{\rm ML} = \frac{\epsilon_0 \epsilon_{\rm r}}{d} \tag{1}$$



Figure 2. Influence of potassium chloride in the electrolyte on the monolayer capacitance for SAMs of adsorbates $1 (\Box)$ and $2 (\diamondsuit)$.



Figure 3. Electrochemical model of modified gold electrodes with monolayers of 18-crown-6 adsorbates 1 and 2.

The addition of aliquots of a 0.1 M KCl solution to the background electrolyte of 0.1 M Et₄NCl gives rise to an increased $C_{\rm ML}$ in both cases (see Figure 2). We attribute this effect to the binding of potassium ions to the monolayer. The binding of ions to the initially neutral monolayer increases the relative permittivity of the layer and results in the observed response. Similar findings have previously been reported for other monolayers that bind metal ions or protons.^{9,16}

To account for the different response amplitudes of both crown ether SAMs, we assume that the total capacitance of a gold electrode covered with a monolayer of 2 can be divided into C_{crown} and C_{chain}, as illustrated in Figure 3. C_{crown} represents the part of the monolayer capacitance that changes due to the binding of metal ions and the corresponding change of the relative permittivity. C_{chain} is the part of the monolayer capacitance that is not influenced by the binding of metal ions. Consequently, the total monolayer capacitance $C_{\rm ML}$ of 2 can be described by C_{crown} and C_{chain} which are in series; thus, $1/C_{\text{ML}}$ = $1/C_{\text{crown}} + 1/C_{\text{chain}}$. Binding of metal ions to the crown ether monolayer, and the subsequent change of C_{crown} , results in a change of $C_{\rm ML}$ that is attenuated by the presence of the invariable C_{chain} . The absence of the alkyl chain in the short crown ether adsorbate 1 results in a monolayer capacitance of $C_{\rm ML} = C_{\rm crown}$. For this SAM, the change of C_{crown} due to the binding of cations is equal to the detected change of $C_{\rm ML}$ and consequently larger than that for the monolayer of the longer crown ether adsorbate 2.

A more detailed examination of the data in Figure 2 reveals that the capacitance of SAM 2 increases from $4.2 \pm 0.1 \ \mu\text{F}$



Figure 4. Adsorption isotherm of potassium cations on crown ether SAM **1**. The surface coverage (Θ) of potassium complexes was calculated from capacitance changes using eq 2 with $C_{\text{complex}} = 8.6 \,\mu\text{F}$ cm⁻² and $C_{\text{ligand}} = 6.8 \,\mu\text{F}$ cm⁻². The solid line is the fitted Langmuir isotherm with $K = 10400 \,\text{M}^{-1}$.

cm⁻² to a maximum value of $4.7 \pm 0.1 \,\mu\text{F cm}^{-2}$. The monolayer capacitance of the short adsorbate **1** increases from $6.8 \pm 0.1 \,\mu\text{F cm}^{-2}$ to $8.6 \pm 0.1 \,\mu\text{F cm}^{-2}$. From these data, the resulting value for the invariable capacitance was calculated as $C_{\text{chain}} = 10.8 \pm 0.2 \,\mu\text{F cm}^{-2}$. The fact that this value is somewhat larger than the reported value of $8.3 \,\mu\text{F cm}^{-2}$ for a heptanethiol SAM in 1 M KCl¹⁷ is not very surprising, since the large size of the 18-crown-6 headgroup does not allow a close packing of the alkyl chains such as in a monolayer of alkane thiol.

Changes in the monolayer capacitance ($C_{\rm ML}$) can be used to characterize the process of ion binding to the SAM. Under the assumption that total monolayer capacitance is determined by the fraction of surface covered by complexes and the rest of the surface that is covered by free ligands, the system can be described by the corresponding two capacitors ($C_{\rm complex}$ and $C_{\rm ligand}$) in parallel. Consequently, $C_{\rm ML}$ changes according to eq 2,

$$C_{\rm ML} = \Theta C_{\rm complex} + (1 - \Theta) C_{\rm ligand}$$
(2)

where Θ is the fraction of occupied binding sites, C_{complex} is the capacitance of the monolayer with metal ions bound to all binding sites, and C_{ligand} is the capacitance of the monolayer in the absence of metal ions. Both C_{ligand} and C_{complex} can be obtained from the titration curves shown in Figure 2. The resulting adsorption isotherm for the binding of potassium ions to the monolayer of 1 is shown in Figure 4. We have focused on the titration curves with SAMs of the short adsorbate 1, since they have the largest capacitance changes and hence the smallest relative error.¹⁸

To characterize the recognition process in the crown ether SAM, the adsorption isotherm was fitted with the Langmuir, Temkin, and Freundlich isotherms.¹⁹ Both Temkin and Freundlich isotherms include terms that account for interactions between bound guests. In contrast, the Langmuir isotherm assumes equal binding energies for all binding sites. We found that our titrations with SAMs of **1** are best described by a Langmuir isotherm, implying that the cation binding sites are well shielded from each other. From the fitted isotherms, the association constants for Na⁺ and K⁺ were determined to be 1080 \pm 90 and 10400 \pm 800 M⁻¹, respectively.²⁰

An alternative method for the detection of metal ion binding to the SAM uses a positively charged redox couple. Electrostatic interactions between the redox couple and the monolayer-bound



Figure 5. Resistive (\diamond) and capacitive (\Box) response of crown ether SAM 1 caused by the addition of aliquots 0.1 M KCl + 1 mM Ru-(NH₃)₆Cl₃ to the background electrolyte of 0.1 M Et₄NCl + 1 mM Ru(NH₃)₆Cl₃ determined simultaneously from impedance measurements at $-0.56 V_{MSE}$. The inset shows the Randles equivalent circuit used to fit the spectra. It contains an electrolyte resistance (R_{EL}), a monolayer capacitance (C_{ML}), a charge-transfer resistance (R_{CT}), and a diffusion element (W).

cations result in an increase of the charge-transfer resistance ($R_{\rm CT}$), which can be measured by impedance spectroscopy.¹¹ Under these conditions, the system is best described by the Randles equivalent circuit (as shown in the inset of Figure 5).²¹ Apart from the charge-transfer resistance, also the monolayer capacitance ($C_{\rm ML}$) is a part of the equivalent circuit used. Therefore, these two electrochemical properties of the monolayer ($R_{\rm CT}$ and $C_{\rm ML}$) can be monitored simultaneously during the titration experiments.

The electrochemical properties of crown ether SAM 1 during the titration of the background electrolyte (0.1 M Et₄NCl and 1 mM Ru(NH₃)₆Cl₃) with a solution of 0.1 M KCl and 1 mM Ru(NH₃)₆Cl₃ are shown in Figure 5. Changes of the monolayer capacitance are identical to those determined in the absence of the redox couple. This indicates that the complexation of the metal ions is not influenced by the presence of Ru(NH₃)₆^{2+/3+} or the more cathodic potential under which these measurements are performed (-0.56 V_{MSE} vs -0.2 V_{MSE}). A comparison of the capacitance and the resistance titration curves immediately shows that both properties respond very differently to the binding of cations. $C_{\rm ML}$, which changes linearly with the fraction of occupied binding sites Θ , shows the characteristics of a Langmuir isotherm. In contrast to this, $R_{\rm CT}$ is increasing linearly with the KCl concentration of the electrolyte. The fact that both measurements show different response curves can be qualitatively understood by the fact that the capacitance is changing with the fraction of occupied binding sites (Θ) , whereas the charge-transfer resistance is probed with a redox couple that is only able to penetrate the monolayer at vacant binding sites (1 $- \Theta$). Since changes of $C_{\rm ML}$ and $R_{\rm CT}$ are related to the same event (the binding of metal ions), it is possible to establish the exact relation between Θ and the change of $R_{\rm CT}$. The capacitive response of the monolayer is linearly proportional to the Langmuir isotherm,

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$$C_{\rm ML} \propto \Theta = \frac{Kc}{1+Kc} \tag{3}$$

where K is the association constant and c is the concentration of metal ions in solution. Linearization of the Langmuir isotherm gives

$$\frac{\Theta}{1-\Theta} = Kc \tag{4}$$

Consequently, R_{CT} should be multiplied by $(1 - \Theta)$ in order to obtain the desired relation between the charge-transfer resistance and the fraction of occupied binding sites.

$$R_{\rm CT}(1-\Theta) = R_0 \tag{5}$$

Combination of eqs 4 and 5 gives

$$Kc = \frac{R_{\rm CT}}{R_0} - 1 \tag{6}$$

where R_0 is the charge-transfer resistance of the monolayer in the absence of metal ions. The linear relation between $R_{\rm CT}$ and *c* in eq 6 increases the concentration window in which the metal ion can be detected compared to the capacitive detection. The monolayer capacitance is changing for metal ion concentrations between $1/_{10}K_{\rm ass}$ and $10/K_{\rm ass}$, whereas the charge-transfer resistance is responding at every concentration above $1/_{10}K_{\rm ass}$. However, we have found that at very high guest concentrations, the resistance response is deviating from eq 6, until it eventually reaches a maximum value.¹¹ We attribute this to the fact that $R_{\rm CT}$ cannot increase to infinite values.

The experimentally derived relation between the association constant and the charge-transfer resistance of the monolayer as given in eq 6 was used to calculate the association constants of alkali metal ions with several crown ether monolayers (see Table 1). Since the titration curves deviate from linearity at very high metal concentrations, only the concentration range where eq 6 is valid was used for the determination of the association constants. A striking feature of the determined association constants is that they are higher than those reported for the complexes in aqueous solutions.²² A much better resemblance is found to the corresponding association constants of the complexes in less polar solvents such as methanol. This indicates that the environment inside the monolayer has a lower polarity than the contacting aqueous solution.²³ In the two cases where the association constants were determined by capacitive and resistive measurements, the obtained values are identical within the experimental error, which confirms the validity of eq 6. Besides this, both 18-crown-6 adsorbates form monolayers that exhibit similar selectivities: $K_{\rm K^+} > K_{\rm Cs^+} > K_{\rm Na^+} > K_{\rm Li^+}$. Also, monolayers of the 15-crown-5 adsorbate have the highest affinity for potassium ions. The other alkali metal ions have association constants that are almost 2 orders of magnitude smaller. Monolayers of adsorbates with the smallest crown ether ring exhibit sodium selectivity. These remarkable selectivities of the 12-crown-4 ($K_{Na^+}/K_{K^+} = 30$) and 15-crown-5 ($K_{K^+}/K_{Na^+} = 450$) SAMs have been attributed to the formation of sandwich complexes.¹¹ The fact that in these cases the metal ions are bound in a sandwich complex does not contradict the requirements of the Langmuir isotherm (i.e., independence of binding sites), since the two crown ethers involved in the complexation can be regarded as being one binding site.

Conclusions

Self-assembled monolayers of crown ether adsorbates are able to bind cations from aqueous solutions. The binding of ions

 TABLE 1: Association Constants of Metal Ions with

 Different Crown Ether SAMs Determined from Changes of

 the Charge-Transfer Resistance^a

	18-crown-6 (1)	18-crown-6 (2)	15-crown-5 (3)	12-crown-4 (4)
$K_{L^{i+}}$	100	50	30	90
$K_{\rm Na^+}$	1000 (1080)	230	60	15800
$K_{\rm K^+}$	11000 (10400)	8500	27100	500
K_{Cs^+}	4600	1500	770	50

^{*a*} Association constants determined from capacitance changes are given in parentheses. The relative error in the association constants is 10%.

influences the dielectric constant of the layer, resulting in an increase of the monolayer capacitance. The magnitude of the capacitive response is related to the chemical structure of the used adsorbates. Longer adsorbates that have an alkyl spacer to attach the ionophore to the gold substrate show a smaller response due to the invariant capacitance of the spacer.

Comparison of capacitive and resistive changes of the crown ether SAM caused by the binding of metal ions unraveled the origin of latter response. Both responses can now be used to determine the association constants of the monolayer with metal ions. However, the magnitude of the resistance change and its linear dependency on the metal concentration in the solution enables its detection over a much wider range compared to the capacitive detection.

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