Redox-Active Self-Assembled Monolayers for Solid-Contact Polymeric Membrane Ion-Selective Electrodes

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With a view to the miniaturization of ion-selective electrodes (ISEs), thin (10−20 μm) polymer membranes are directly contacted to Au covered with a redox-active, lipophilic self-assembled monolayer (SAM). Several homogeneous and mixed monolayers are characterized by reflection−absorption infrared spectroscopy, ellipsometry, scanning tunneling microscopy, cyclic voltammetry, and contact angle measurements. These Au/thiol surfaces are combined with different K^+-selective sensing membranes based on poly(vinyl chloride) (PVC), polyurethane (PUR), or PVC/PUR blends as a matrix and valinomycin as an ionophore. The sensors are investigated with regard to their potential stability in the presence of O_2 and redox-active species. The occurrence of potential drifts upon changing the conditioning KCl solution to a NaCl solution is used as an indicator for the formation of an aqueous film between the membrane and Au/SAM. Stable systems are obtained with mixed monolayers (advancing contact angle $\theta_a \approx 83°$) and PVC membranes with a lower than usual plasticizer content (33 wt %), the ternary systems PVC/PUR/plasticizer (1:1:1), and PUR with 33 wt % plasticizer. On the other hand, a water film is formed between Au/SAM and conventional PVC membranes having 66% plasticizer and with less lipophilic monolayers uniquely based on a redox-active compound ($\theta_a \approx 70°$). The new solid-contact ISEs are promising both for miniaturization and for improving lower detection limits.

Introduction

Polymeric membrane ion-selective electrodes (ISEs) are currently the most widely applied chemical sensors.[1−3] For example, they are used to assess blood or serum ion activities in almost every hospital all over the world.[4] However, they were thought to be inadequate for assessing analytes with submicromolar total concentrations. The situation dramatically changed recently when it was found that both the selectivities[5−8] and the lower detection limits[6−10] of ISEs are better by many orders of magnitudes than hitherto assumed.[1,3] Recent results indicate that many ISEs have a high potential for trace level measurements in the micromolar to picomolar activity range.[6,8] The reason for the insufficient performance of conventional polymer membrane ISEs is a minute ion flux of <1 pmol cm^{-2} s^{-1}, which brings about an analyte concentration of $\approx 10^{-6}$ M in the unstirred Nernstian layer at the membrane surface even if the bulk sample does not contain any analyte.[9,11,12] Consequently, the sensor is insensitive to further dilution of the sample or to the presence of highly discriminated interfering ions. Spectacular improvements of selectivities and lower detection limits of 6 or more orders of magnitude have been achieved by avoiding biases through these ion fluxes.[8]

Conventional ISE membranes are usually contacted on the opposite side of the analyte solution with an aqueous electrolyte, which is in contact with an internal reference element. Analyte ions released from the membrane into the sample originate mainly from the

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inner solution of conventional ISEs[6,13] but also from the membranes themselves, which usually contain ions in concentrations of about 10 mmol kg^{-1}. For typical membranes, this corresponds to 10^{-7} mol, that is, an amount that is present in 100 L of a sample of nanomolar concentration. Therefore, measurements at low concentrations are biased even if only a fraction of these ions is released into the sample. So far, ion release from the membrane has usually been eliminated by carefully adjusting the composition of inner solutions.[6,9,10,14] A more natural way to avoid such biases would be the construction of ISEs that do not contain any inner solution and have miniaturized membranes containing 100−1000 times smaller amounts of ions than the conventional membranes. ISEs without an inner electrolyte, so-called coated wire electrodes, were introduced many years ago.[15] However, they lacked long-term stability[16,17] so that they were only useful for special applications, for example, as chromatographic detectors.[18] Potential instabilities of such systems have been mainly attributed to the lack of a well-defined redox couple at the membrane−metal interface.[16,17] Several authors assumed that an oxygen half-cell is formed at the inner electrode because the membrane is permeable to both O_2 and water.[16,19] To obtain a thermodynamically defined electrochemical interface between membrane and solid contact, it was suggested either to use ISE membranes that contain an appropriate redox-active component, such as a lipophilic silver complex,[20] or to contact the inner electrode via an intermediate polymer layer that is redox-active[17] or has both electronic and ionic conductivity.[21−24] Only recently, it was recognized that the formation of a thin aqueous film between membrane and metal[25] may be another important source of potential instabilities.[26] Such a film is also formed[26] with polymers such as the polyurethane Tecoflex that have better adhesive properties than poly(vinyl chloride) and were, therefore, proposed for solid-contact ISEs.[25] With such a film, there are two phase boundaries on the inner membrane side (membrane/water and water/metal) instead of one (metal/membrane). The phase boundary potential between the aqueous film and the membrane depends on the composition of the film and membrane. Because the latter is permeable to ions and water, it is likely that the composition of this film depends on that of the sample. The slowly changing composition of this layer induces a drift of the inner membrane/water phase boundary potential. With membranes of a thickness on the order of 10 μm and diffusion coefficients of about 10^{-7}−10^{-8} $cm^2\ s^{-1}$,[27−29] the drifts start within a few minutes after a change in the sample composition.

Very recently, lipophilic redox-active self-assembled monolayers (SAMs) have been successfully used for solid-contact ISEs.[30] Their lipophilicity hinders the formation of an aqueous layer between the membrane and the metal, resulting also in stronger adhesion of the ISE membranes to the metal, and the incorporated redox-active groups provide for a coupling of ionic and electronic conductivity.[30] In the study reported here, SAMs were prepared with the previously described redox-active compounds ethyl (8-sulfanyloctyl) 1,2-methano[60]fullerene-61,61-dicarboxylate **1** and 2,3-bis({[5-(1,2-dithiolan-3-yl)pentanoyl]oxy}methyl)-6,7-(ethylenedithio)tetrathiafulvalene **2**.[26,30] Self-assembled thin layers with these compounds as well as mixed monolayers obtained by additional adsorption of *n*-octanethiol were characterized by IR reflection−absorption spectroscopy, ellipsometry, scanning tunneling microscopy (STM), cyclic voltammetry (CV), and contact angle measurements and investigated in solid-contact ISEs. The best behaved system, composed of a mixed monolayer of the tetrathiafulvalene derivative **2** with *n*-octanethiol, was used to further study the influence of the polymer membrane composition on the potential stability of the ISEs.

Experimental Section

Reagents. Valinomycin, potassium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500), bis(2-ethylhexyl) sebacate (DOS), poly(vinyl chloride) (PVC), tetrahydrofuran (THF), dichloromethane, and tetrabutylammonium hexafluorophosphate were from Fluka AG (CH-8071 Buchs, Switzerland). Tecoflex SG 80A (Thermedics Inc., P.O. Box 2999, Woburn, MA 01888-1799) was obtained from Lehmann & Voss Co. (P.O. Box 303424, D-20311 Hamburg, Germany). The synthesis of the redox-active thiol derivatives **1** and **2** was described previously.[30] Aqueous solutions were prepared with deionized water (specific resistance, 18.0 MΩ·cm; NANOpure, Barnstead, CH-4009 Basel, Switzerland). All sodium salts, chloride salts, and iron compounds were p.a. from Fluka or Merck.

Substrate Preparation. Glass microscope slides (7.54 × 2.54 cm) were used as electrode substrates. The slides were chemically cleaned by immersion in 1:4 H_2O_2/ concentrated H_2SO_4 (Piranha solution) at 70 °C for about 20 min, rinsed with H_2O and EtOH, dried under warm air, and kept in bottles under Ar.[31]

Au Evaporation. Metal films were deposited by evaporation at a rate of $\approx$2 nm s^{-1} and with a pressure of 10^{-3} Pa (Kleinbedampfungsanlage MED 010, Balzers AG, Balzers, Liechtenstein). First, a Cr film of 6-nm thickness (99.9%, Balzers AG) was applied as an adhesive layer and a Au film of 200-nm thickness (99.99%, Balzers AG) was deposited on

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it. The thickness of the metal films was measured with an oscillating quartz device (QSG 301, Balzers AG).[32]

Gold Beads Preparation. After a gold wire ($d = 0.5$ mm, 99.995% ChemPur, ChemPur Feinchemikalien und Forschungsbedarf GmbH, D-76206 Karlsruhe, Germany) was cut, Au beads were formed and annealed under an O_2 flame. A glass capillary was inserted from the opposite side of the gold bead and melted onto the wire, insulating the gold electrode.[33]

SAM Preparation. Monolayers of thiol derivatives on gold were prepared by chemisorption, that is, by immersion of freshly prepared Au surfaces in 1 mM solutions of compound **1** or **2** in CH_2Cl_2 for ≈24 h. After removal, the surface was washed with CH_2Cl_2 and dried in a stream of argon. The SAMs were immediately ready to use.[33] Mixed monolayers were prepared by immersion of the SAM of **1** or **2** in a 1 mM solution of *n*-octanethiol in CH_2Cl_2 for 5 h.

Infrared Spectroscopy. IR spectra were recorded at grazing incidence reflection on a Bruker IFS 66 v spectrometer equipped with an Hg−Cd−Te detector. The measurements were performed at an incidence angle of 80° with a fixed-angle inset. To minimize adsorption of contaminants to the samples and interferences by atmospheric bands of water and carbon dioxide, the pressure in the sample chamber was reduced below 1 mbar. Freshly prepared metallic surfaces were used as reference.[32] The spectra of the surfaces were subtracted from the spectra of the polymer-modified substrates. IR spectra of KBr pellets and solutions in $CHCl_3$ were measured with a Perkin-Elmer 1600-FT-IR.

Ellipsometry. Ellipsometric measurements were performed with a Plasmos SD 2300 Ellipsometer, equipped with a He−Ne laser ($\lambda = 632.8$ nm), at an incidence angle of 70°. Prior to measurements, the samples were washed with dichloromethane and blown dry under Ar. The thickness of the layers was measured at 15 positions, on a straight line. Readings were taken for the clean gold, to establish the optical constants of the bare substrate. After monolayer formation, the thickness was calculated with the obtained constants and with an assumed refractive index (n_f) for the monolayer. The obtained thickness strongly depends on the exact value of n_f chosen (see Table 2).[32]

Contact Angle Measurements. The advancing contact angle of water was determined on sessile drops with a Goniometer (Ramé-Hart Model 100-00 Mountain Lakes, NJ 07046) at room temperature under atmospheric conditions. The advancing contact angle, θ_a (H_2O), was obtained by forming a 3-μL drop of water on the surface and by adding an additional 3 μL to the drop. Contact angles were measured very quickly, even if they were stable for many minutes under these conditions. The results are the mean of 36 measurements (6 different positions of 3 samples from both sides of the slides). The experimental error is approximately ±3°.[32]

Cyclic Voltammetric Measurements. Cyclic voltammograms were recorded with 10^{-3} M solutions of compounds **1** or **2** in 10^{-1} M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in CH_2Cl_2, under Ar, using an EG & G Princeton Applied Research Model 263A potentiostat/galvanostat. A gold film, a gold bead, or a glassy carbon minielectrode was used as the working electrode, in combination with a Ag/AgCl electrode (Bioanalytical Systems, West Lafayette, IN) as reference. A Pt wire served as the counter electrode.[33]

The surface coverage was estimated by integrating the area under the curve observed for the first reduction or oxidation peak or for the irreversible reduction of Au−S for *n*-$C_8H_{17}SH$. After removal of the SAM from the Au surface by boiling in a 1:1 HNO_3:H_2O solution for 6 h, the reversible reduction of a 1 mM aqueous solution of $[Ru(NH_3)_6]^{3+/2+}$ in 0.1 M NaCl was investigated. The geometric area of the electrode was obtained from the slope of a linear plot of the cathodic current (i_p in A) vs the square root of the scan rate, γ, using eq 1,

$$i_p = (2.69 \times 10^5) n_e^{3/2} A D_0^{1/2} v^{1/2} c_0^* \quad (1)$$

with A as the electrode surface (cm^2), D_0 the diffusion coefficient (7.5×10^{-6} cm^2 s^{-1}), n_e the number of electrons involved in the process (1), and c_0^* the concentration of the electroactive species (mol cm^{-3}).[34] To study the redox reaction of the dissolved species, 1 mM CH_2Cl_2 solutions of **1** or **2** in 0.1 M Bu_4NPF_6 were used.

Table 1. Composition of the Membranes[a]

membrane type[b]	valinomycin	ETH 500	KTFPB	PVC	PUR	DOS
1:0:2	1.99	2.17	0.83	66.4		142.1
2:0:1	1.98	2.12	0.87	132.1		64.0
1:1:1	2.01	2.38	0.83	64.2	73.9	66.2
0:2:1	10.0	11.5	4.10		661.7	330.2

[a] Amount of components in mg. [b] Mass ratio PVC:PUR:DOS.

STM Measurements. STM measurements were performed in air with a SPM 100 controller from RHK Technology (Troy, MI) and a probe head from Molecular Imaging (Phoenix, AZ) using mechanically cut Pt/Ir tips. Typical bias voltages and currents were 0.8−2.0 V and 0.1−0.5 nA, respectively.

Membranes. The K^+−ISE membranes were based on valinomycin as the ionophore and different amounts of the polymers and additives (see Table 1). They were prepared according to a standard procedure by pouring the solution of membrane components in THF into a glass ring (58 mm i.d.) on a glass plate and letting the THF evaporate slowly at room temperature over 24 h.

Electrodes. Two different geometries for the inner electrode were tested: glass slides covered with gold films and gold beads. On one hand, conventional liquid-contact (LC) ISEs were prepared by punching 4-mm disks from the master membrane and gluing them to plasticized PVC tubing with a THF/PVC slurry. The internal filling solution was 10^{-3} M KCl. On the other hand, ≈150 mg of the master membrane was dissolved in 3 mL of THF, and 50 μL of this cocktail was cast on the gold electrode, resulting in a membrane of 30-μm thickness. Gold beads were repeatedly immersed directly in the same THF solution. Liquid- and solid-contact ISEs were conditioned overnight in 10^{-3} M KCl.

emf Measurements. Measuring solutions were prepared by successive automatic dilution of stock solutions using automated liquid dosing units (Liquino 711 and Dosino 700; Metrohm AG, CH-9010 Herisau, Switzerland) equipped with 50-mL burets. Experiments involving pH-buffered solutions were performed under full computer control in a 100-mL polyethylene beaker or in a special cell with the help of a Liquino 711 and Dosino 700 equipped with 10-mL burets. Potentials were measured with a 16-channel electrode monitor EMF16 (Lawson Labs Inc., Malvern, PA 19355) at room temperature (20−21 °C) in solutions stirred with a rod stirrer, the Ag/AgCl reference electrode (Metrohm, type 6.0729.100) having 1 M LiOAc as a bridge electrolyte. The pH values were determined with a glass electrode (Metrohm). For activity coefficients, the Debye−Hückel approximation was used.[35] All emf values (median of the potentials measured for either 5 or 10 min) were corrected for liquid junction potentials with the Henderson equation. All measurements were performed with three electrodes but only one representative result is shown in the Figures. Potentiometric selectivity coefficients (average obtained with three electrodes) were measured with the separate solution method;[36] the slope of the response function never had a larger deviation from the theoretical value than 2 mV/decade.

Results and Discussion

Homogeneous Monolayers. In this work, redox-active, lipophilic SAMs were investigated with a view

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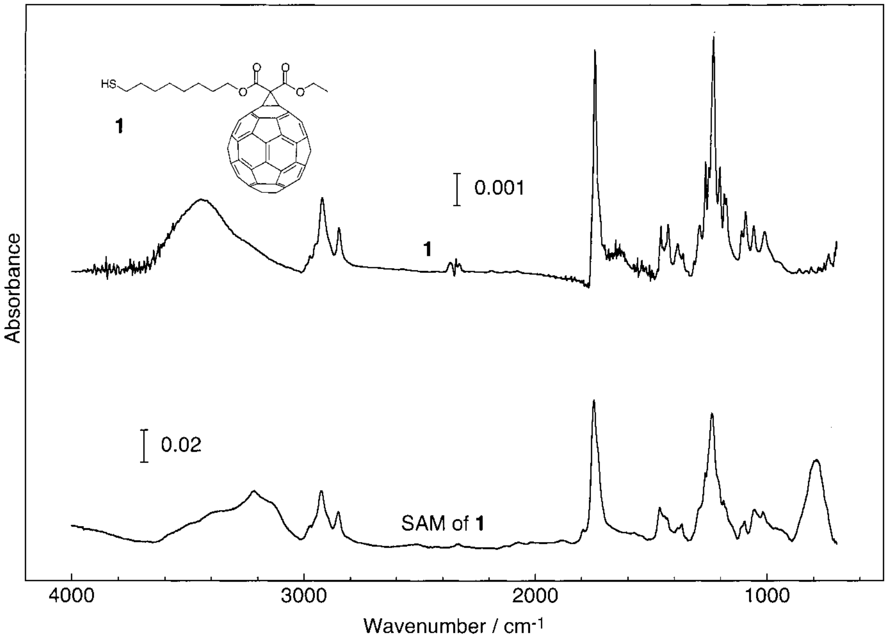

Figure 1. Infrared spectra of **1** in the bulk (KBr pellet, top) and as a SAM on Au film (bottom).

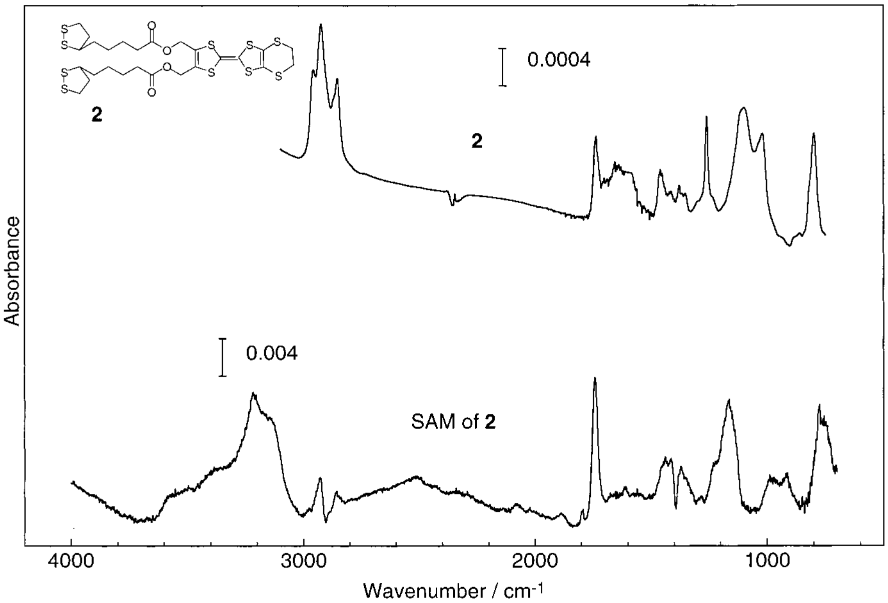

Figure 2. Infrared spectra of **2** in the bulk ($CHCl_3$ solution, top) and as a SAM on Au film (bottom).

to improving potential stabilities of ion-selective membranes directly contacted to a metal electrode. To achieve this goal, a well-defined redox couple must be present[16,17] and the formation of an aqueous film between membrane and metal must be prevented.[20,26] Lipophilic, redox-active derivatives of fullerene **1** (Figure 1) and tetrathiafulvalene **2** (Figure 2) were selected for their ease of reduction and oxidation, respectively. In a first set of experiments, monolayers containing either **1** or **2** were prepared and investigated. In the following, these monolayers will be called "homogeneous", referring to the fact that these layers are formed only by one type of thiol.

The IR spectra of **1** and **2** measured in the bulk (KBr or $CHCl_3$ solution) and on the Au surface are shown in Figures 1 and 2. From the comparison of the spectra it is apparent that SAMs are formed both with **1** and **2**. The symmetric CH_2 stretching vibration frequency of 2924 cm^{-1} is higher in both cases than for highly ordered structures of compounds having long aliphatic chains (2918 cm^{-1}).[37] This behavior is excepted for systems with short chains and rather bulky end groups.[38]

The surface immobilization is further corroborated by cyclic voltammetric measurements in a solution of 0.1 M Bu_4NPF_6 in CH_2Cl_2. As expected for surface-confined electrochemical behavior,[34] the peak current exhibits a linear dependence on the scan rates.[30] At the fairly fast scan rate of 1 V/s, the CVs show only relatively small potential differences between cathodic and anodic peaks of 22 mV for **1** at $E_{1/2} = -680$ mV and 35 mV for **2** at +575 mV (relative to an aqueous Ag/AgCl reference electrode). Considering that the approximate 60-mV

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Table 2. Thickness (in nm) of SAMs with 1 and 2 and Standard Deviation as Calculated with Different Values of the Refractive Index, n_f

n_f	1	2
1.5	11.49 ± 0.3	
1.8	8.45 ± 0.3	3.24 ± 0.3
2.2	6.50 ± 0.3	2.53 ± 0.3

peak separation for these $E_{1/2}$ values in the CVs of the dissolved species (not shown) clearly indicates redox processes involving only one electron per molecule, the peak separations for the immobilizied species confirm the surface-confined nature of the redox reaction. They also show that the electron transfer between the electrode and the surface-confined species is somewhat slow on the time scale given by the 1 V/s scan rate.[34] The SAMs are stable in the potential ranges −400 to −800 mV for **1** and +400 to +1000 mV for **2** and show nearly identical current responses after several sets of 11 scan cycles between 50 and 1000 mV s^{-1}. However, the redox response is eliminated within a few scans if the range is extended to −1200 mV for **1**. This is because at −950 mV **1** undergoes an electrochemically induced *retro*-Bingel reaction that removes the fullerene redox center.[39] The surface coverage of the SAMs was assessed with Au bead electrodes as 3.9 ± 0.1 and $1.9 \pm 0.1 \times 10^{-10}$ mol cm^{-2} for **1** and **2**, respectively (see Experimental Section). These values are almost twice as high for **1** and somewhat lower for **2** than those estimated for the respective monolayers (1.9 and 3.6×10^{-10} mol cm^{-2}, respectively).[33,40,41]

The thickness of the films was estimated from ellipsometric measurements (Table 2). The measurements were evaluated with three different values of the refractive index n_f. The lowest value of 1.5 is what is typically assumed for uncolored compounds. Because both **1** and **2** are colored, a higher value must be assumed. For fullerenes, various values are reported in the range of 1.8−2.2[42] but no reference data are available for tetrathiafulvalenes. Theoretical maximum thicknesses of 1.7 and 2.1 nm are obtained for **1** and **2**, respectively,[43] using MM+ force field calculations with subsequent refining of the generated structures with the semiempirical method AM1.[44] The measured values (Table 2) are thus rather close to the theoretical ones for **2** but larger by a factor of 3−5 for **1**.

To corroborate the high surface coverage of **1** revealed by CV and ellipsometry, the thin layers of **1** were further studied by STM. Initial observations of layers of **1** assembled over 24 h from 1 mM solutions (as described above) showed no regular features at all, but a few locations on the sample had circular structures of ≈1.1 nm width and height, apparently due to the fullerene spheres. Subsequently, the thickness of the layers was observed as a function of time for 0.03, 0.1, 0.3, 1.0, and 3.0 mM solutions of **1**. The results indicated that for all solutions a near-plateau was reached within a day and that a significantly slower adsorption upon further exposure of the samples to solutions of **1** continued to increase the thickness. The STM observation of the samples obtained by 24-h assembly from the 0.03, 0.1, 0.3, 1.0, and 3.0 mM solutions showed that at the lower concentrations submonolayer coverage was possible and resulted in the more frequent observation of fullerene spheres, either completely isolated or in small disordered islands. At higher concentrations, only few fullerene spheres could be observed. An optimum self-assembly concentration that was high enough for full monolayer coverage but small enough to prevent the formation of multilayers was not found. The lower surface coverage determined by CV than the one determined by ellipsometry seems to be due to the slowness of the electron transfer from the electrode to the outer layers of **1**, which makes these outer layers of **1** invisible to CV. It is interesting to note that Shon and co-workers similarly found no evidence of ordering in monolayers of a fullerene derivative with a C_6 linker to the sulfur attaching the buckyball to the gold surface.[45]

Ion-selective membranes based on the K^+-selective ionophore valinomycin[46] and the polyurethane Tecoflex[25] were directly cast onto Au with and without the above-described SAMs as well as with mixed monolayers (see below). For all investigated ISEs, the calibration curves (Figure 3) obtained with the primary ion, K^+, which was also used to condition the membranes, are very similar and show close to Nernstian responses. The most important difference is that the lower detection limit is worse in the absence of SAMs (10^{-5} M as compared to $\approx 10^{-6}$ M with the other systems). The beneficial effect of the redox-active SAMs is also apparent from Figure 4, where the emf of various solid-contact ISEs is recorded in a 10^{-3} M KCl solution under atmospheric conditions and after introducing O_2 or Ar into the solution. Potential drifts on the order of 20 mV are largely eliminated by the SAMs. Because, unlike the redox-active polymer matrixes,[47] the redox-active species are separated from the sample by the membrane, no redox response is observed when varying the ratio Fe(II)/Fe(III) in a 10^{-2} M $FeCl_2/FeCl_3$ solution at constant ionic strength (0.1 M KCl).[30]

Potential drifts upon replacing the primary ions by discriminated interfering ions are indicative of the presence of an aqueous film between the membrane and the solid contact.[26] The phenomenon is well understood in terms of ion transport through the membrane (see also above).[12] Corresponding experiments with and without different SAMs are shown in Figure 5. Upon conditioning the membranes in 0.1 M KCl, at $t = 0$ the sample was changed to 0.1 M NaCl. The virtually instantaneous emf shift of ca. −210 mV reflects the change in the outer phase boundary potential as a consequence of the selectivity behavior of the membrane. Without SAMs (Figure 5, bottom), a positive drift sets in after a short period of time, which can be

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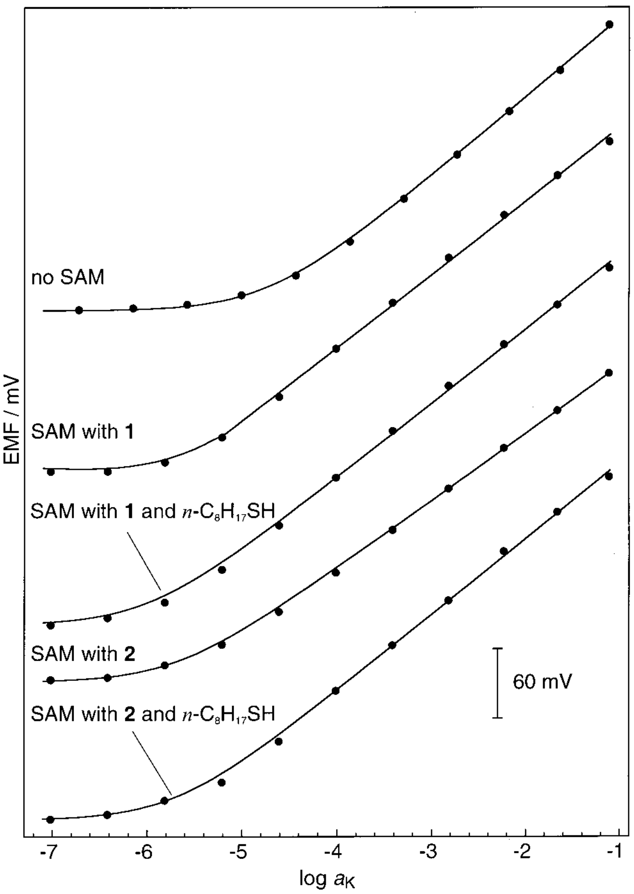

Figure 3. Calibration curves obtained with valinomycin-based Tecoflex SC−ISE membranes cast on a bare Au film and on Au covered with different homogeneous and mixed SAMs.

explained by the decrease of the inner phase boundary potential as a consequence of the exchange of K^+ for Na^+ in the aqueous film formed between the membrane and the metal electrode.[26] Upon changing the sample back to the initial one, an opposite drift sets in after the initial potential step, reflecting the reverse process. As predicted by theory, this reverse step is slower than the initial replacement of the preferred K^+ by the discriminated Na^+.[12,26] The corresponding drifts are strongly reduced but not fully eliminated in the presence of SAMs of **1** (Figure 5, top) and **2** (Figure 5, middle). These results indicate that the SAMs improve the lipophilicity of the metal surface but cannot fully eliminate the formation of an aqueous film.

Mixed Monolayers. To improve the lipophilicity of the metal surface, mixed monolayers were prepared in a two-step process. The initially obtained homogeneous SAMs were further reacted with *n*-octanethiol. The plot of advancing contact angles of water during this process is shown in Figure 6 (right side). The SAM-modified surfaces clearly show higher lipophilicity compared to an unmodified Au electrode (40° ± 7°; obtained with freshly prepared electrodes that were kept under Ar for ca. 30−60 min before measurements) but a lower one than reported for highly hydrophobic densely arranged alkanethiolate SAMs (111°−115°).[45,48,49] This fact apparently reflects the aromatic character of the terminal fullerene and tetrathiafulvalene groups. The measured contact angle of the homogeneous SAM with **1** closely corresponds to those previously reported values for similar systems.[50,51] Upon contact of the initially formed SAMs with *n*-octanethiol, the contact angles increase by about 10° (Figure 6). This indicates that *n*-octanethiol fills the gaps that were formed in the SAMs of **1** and **2**. The strong initial increase of θ_a (Figure 6, left) can be explained by the very fast chemisorption process: If a gold surface is dipped in a solution of **1** and **2**, the respective compound will very quickly assemble onto the clean surface, influencing its advancing contact angle with water. This process is somewhat faster with **1** than with **2**. On the other hand, both SAMs (based on **1** and **2**) behave similarly during the formation of the mixed monolayer: Only after ≈15 min of immersing them in a 1 mM solution of *n*-octanethiol can an increase in θ_a be observed. This behavior can be related to the self-organization (very slow process) of the monolayer. As assesssed from CVs, the surface coverage of the electroactive groups is reduced by the mixed monolayer formation from 3.9 ± 0.1 to 0.8 ± 0.1 and from 1.9 ± 0.1 to $1.1 \pm 0.1 \times 10^{-10}$ mol cm^{-2} for **1** and **2**, respectively. The coverage of *n*-octanethiol is 1.6 ± 0.1 and $3.0 \pm 0.2 \times 10^{-10}$ mol cm^{-2} in the mixed monolayers with **1** and **2**, respectively, as determined from the CVs. These results indicate that *n*-octanethiol not only fills the uncovered hydrophilic Au surface but also replaces in part the electroactive components. This reduction of the concentration has, however, no effect on the emf response of the ISEs (Figure 3). The higher lipophilicity of the mixed monolayer is also indicated by the full elimination of the small dependence of the emf on O_2 as observed with both homogeneous monolayers (Figure 4). An even stronger difference between monolayers with and without *n*-octanethiol is observed when comparing the ISE response to the interfering ion Na^+, which shows a small drift for the homogeneous but no drift for the mixed monolayers (Figure 5).

Oxidized and Reduced Forms. As is apparent from the Nernst equation,[34] a stable redox potential at the membrane−Au interface requires a constant activity ratio of the two redox forms, [ox]/[[red].

$$E = E_0 + \frac{RT}{nF} \ln \frac{[\mathrm{ox}]}{[\mathrm{red}]} \qquad (2)$$

However, a small current of about 100 fA is flowing through the membrane during potentiometric measurements, which slightly alters the concentration of the two forms in the redox-active layer. The electroneutrality condition is fulfilled by the uptake or release of a corresponding amount of analyte ion into or from the membrane. The closer the ratio [ox]/[red] is to 1, the higher the robustness of the electrode that can be expected. The potential stability obtained indicates that a sufficient amount of the reduced form of **1** and oxidized form of **2** is initially present. The emf of the different ISEs prepared with **1** or **2** only varied within ±10 mV,

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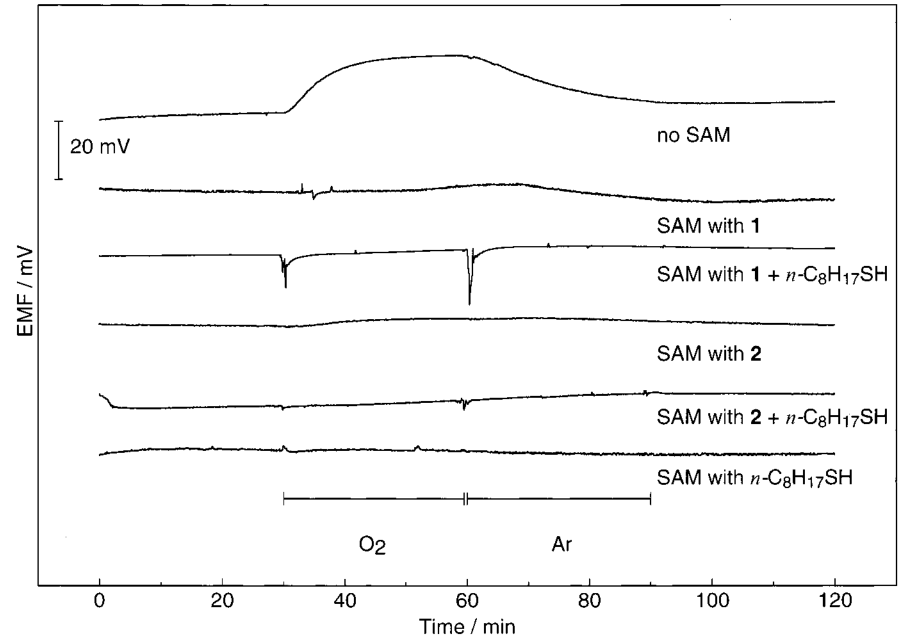

Figure 4. emf response of various SC–ISEs on introducing O_2 or Ar into a 10^{-3} M KCl solution (curves offset for clarity).

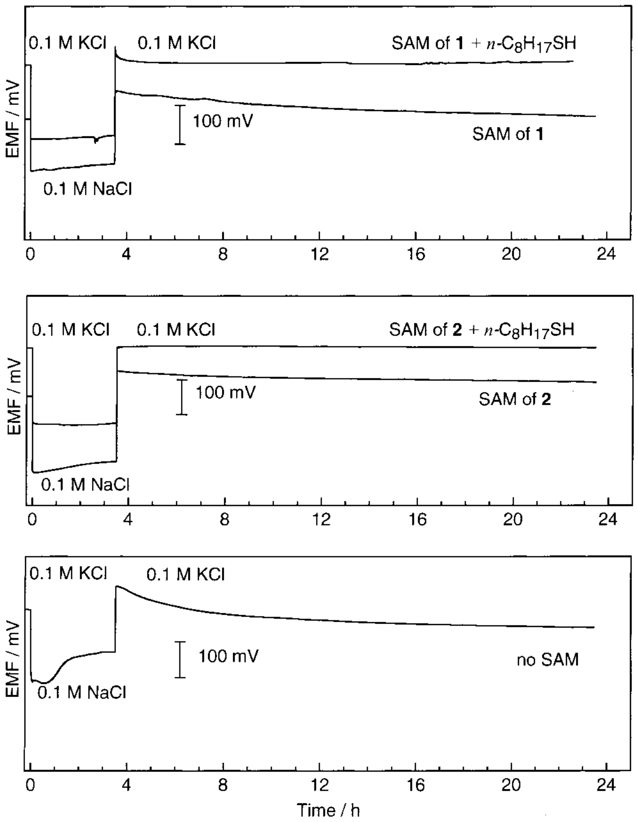

Figure 5. Response of a solid-contact K^+-selective electrode (Tecoflex with 30% DOS) with homogeneous and mixed SAMs of **1** (top), of **2** (middle), and without a SAM (bottom). At $t = 0$, the conditioning solution (10^{-1} M KCl) was exchanged for 10^{-1} M NaCl. At $t = 3.5$ h, the sample was replaced by the conditioning solution.

indicating that the concentration of the reduced **1** and oxidized **2** was rather constant.

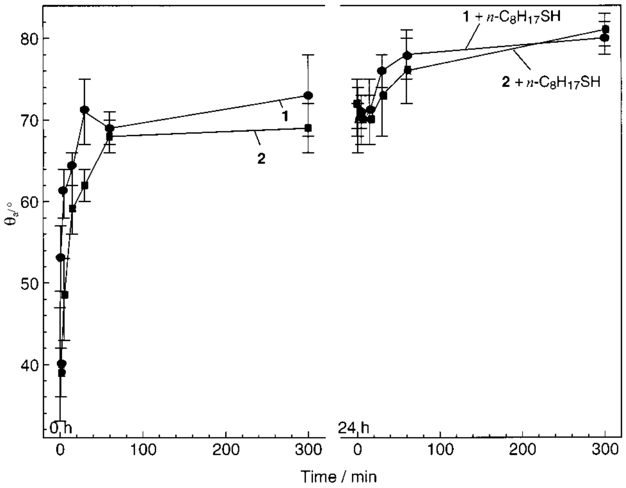

Figure 6. Advancing contact angle (θ_a) of water dependent on the adsorption time. At $t = 24$ h, the sample was changed to a solution of *n*-octanethiol.

To determine the relative concentration of the oxidized form in thin layers obtained directly by self-assembly of **2**, the potential applied to an electrode modified with **2** was raised in a voltammetric experiment from 0 to 500 mV, and the electrode was then disconnected. Subsequent potentiometric measurements with this electrode showed the potential to be stable at 480 mV, which is 95 mV lower than the peak potential. Using the Nernst equation, this allows us to conclude that 2.5% of **2** is oxidized at this potential. The integral from 0 to 480 mV in the cyclic voltammogram indicates that this value is approximately correct, but a quantitative confirmation is not possible because the peak for the first oxidation of **2** partially overlaps with the second peak for the irreversible oxidation of **2** to the dication.

Solid-contact ISEs based on a thin layer with fractions of 2.5% and 97.5% of the oxidized and neutral form of **2**, ($[\mathbf{2}^+]/[\mathbf{2}] = 0.026$), respectively, showed the same characteristics in terms of linear response, insensitivity to O_2, and the variation of the relative concentrations of Fe(II)/Fe(III), but with a shift of 195 mV relative to the response curve for the solid-contacted ISEs based on a self-assembled layer of **2**. From this potential shift, the initial ratio of the oxidized and reduced forms,

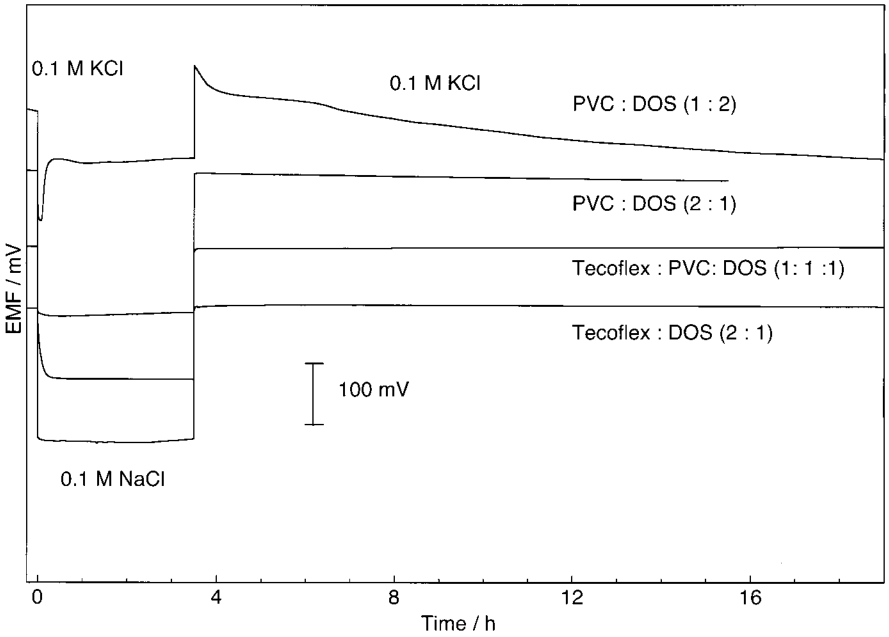

Figure 7. Response of solid-contact K^+-selective electrodes of various membrane compositions with a mixed SAM of **2**. At $t = 0$, the conditioning solution (10^{-1} M KCl) was exchanged for 10^{-1} M NaCl. At $t = 3.5$ h, the sample was replaced by the conditioning solution.

$c_{\mathbf{2}^+(\text{trace})}/c_{\mathbf{2}(\text{initial})}$, can be calculated to be around 1.3×10^{-5} by using eq 3:

$$\Delta E^0_{\mathbf{2}(\text{initial})} - \Delta E^0_{\mathbf{2},10\%\text{ox}} = 195 \text{ mV} = 59.6 \text{ mV} \times \left(\log \frac{c_{\mathbf{2}^+}}{c_{\mathbf{2}}} - \log \frac{c_{\mathbf{2}^+(\text{trace})}}{c_{\mathbf{2}(\text{initial})}}\right) \quad (3)$$

The presence of this small amount of the oxidized form of **2** is apparently sufficient to obtain stable potentials as long as no substantial current is applied. This result is in agreement with the observation of Bobacka et al., who also obtained stable potentials when using the redox polymer poly(*n*-octyl thiophene) in its natural form as the intermediate layer between the metal and the polymeric membrane.[52]

Influence of the Polymer Matrix. For initial experiments, membranes were made with the polyurethane Tecoflex because of its good adhesive properties to silicon nitride[25,53] and polyimide.[54] Such membranes can be applied even without using any plasticizer, but their electrochemical properties[54] and especially their discrimination of H^+ (ref 55) are much better if at least a low amount of plasticizer is added. To investigate the general applicability of the SAM-modified solid-contact ISEs, various polymer compositions were investigated with the mixed monolayer of **2** with *n*-octanethiol, which was found in the above experiments to give the solid-contacted PVC membranes with the most stable emf responses. The corresponding selectivity coefficients indicate that, in the presence of the polyurethane Tecoflex, the H^+ selectivity is worse than that with PVC/DOS membranes (see Table 3). On the other hand, PVC membranes with low plasticizer content have worse Na^+ selectivity. The formation of a water film between the membrane and Au/SAM was investigated as outlined above. With a conventional membrane composition of 33% PVC and 66% DOS, strong drifts are observed after changing the sample from KCl to NaCl and vice versa (Figure 7, top curve). In contrast, stable potentials are obtained with all other investigated membrane compositions. It can be concluded that solid-contact ISEs based on lipophilic redox-active SAMs can be prepared with different polymers.

Table 3. Potentiometric Selectivity Coefficients, log $K^{\text{pot}}_{\text{K,J}}$, of SC-ISEs Based on Various Membranes

J	PUR:DOS (2:1)	PUR:PVC:DOS (1:1:1)	PVC:DOS (2:1)	PVC:DOS (1:2)
H^+	-3.0 ± 0.2	-3.7 ± 0.2	-4.7 ± 0.2	-5.1 ± 0.8
Na^+	-4.1 ± 0.4	-4.1 ± 0.1	-4.8 ± 0.1	-2.8 ± 0.4
NH_4^+	-2.1 ± 0.1	-2.2 ± 0.2	-2.0 ± 0.2	-1.2 ± 0.3
Ca^{2+}	-5.0 ± 0.3	-5.1 ± 0.1	-5.2 ± 0.1	-5.5 ± 0.8

Conclusions

Appropriate solid contacts of polymeric membrane ISEs must provide a reversible redox couple and, at the same time, they must prevent the formation of a liquid layer between the metal electrode and the membrane. In this work, self-assembled layers of the lipophilic, redox-active compounds **1** and **2** have been characterized. The attachment of the fullerene derivative **1** to Au is indicated by STM images, but at higher concentrations/longer reaction times multiple layers are formed and no experimental conditions could be found to generate highly ordered monolayers. However, the presence of both compounds improves the characteristics of the ISEs. Further improvements can be achieved in both cases by forming mixed layers through subsequent modification of the redox-active layers with *n*-octanethiol. Membranes with the K^+-selective iono-

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phore valinomycin and different polymer matrixes were investigated in terms of response characteristics, redox sensitivity to O_2 and Fe(II)/Fe(III) solutions, and the formation of an aqueous layer between the membrane and the metallic electrode contact. Good stabilities were obtained except for conventional membranes with 30% PVC and 70% plasticizer.

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