

EXAMPLE 1

The invention is illustrated with reference to the enclosed figures, in which:

FIG. 1 is a schematic representation of TBEA, TBEA-copper complex and octadecyl mercaptan;

FIG. 2 is a cyclic voltammogram is set out in the Legend to Figures;

FIG. 3 illustrates RA-FTIR spectra of TBEA complexes with a monolayer structure of the invention.

We show here the feasibility of an approach based upon the use of self-assembled mixed monolayers, containing both "active" (monolayer-forming ligand) and "blocking" (surface-sealing long-chain amphiphile) components, so that a specific response for metal ions forming 1:1 complexes with the ligand is achieved. An example relates to the ligand 2,2'-thiobisethyl acetoacetate, $S(CH_2CH_2OCOCH_2COCH_3)_2$ (TBEA, FIG. 1) designed and synthesized as "active" component. The two β -keto ester groups of TBEA form a tetradentate chelating centre, and the sulphur bridge was designed to anchor the ligand to a gold surface. Surface-bound tetradentate TBEA is an excellent candidate for the formation of 1:1 complexes with divalent metal ions, such as Cu^{2+} , but is geometrically unsuited for binding trivalent metal ions, such as Fe^{3+} , that require octahedral coordination. Therefore, in terms of geometric discrimination (and also electrochemical suitability), Cu^{2+} and Fe^{3+} are convenient ionic probes to test the selectivity of the monolayer-coated electrodes.

FIG. 2a shows a cyclic voltammogram of a bare gold electrode in H_2SO_4 solution containing Cu^{2+} and Fe^{3+} . The $Fe^{3+/2+}$ reduction-oxidation peaks are marked with arrows; the small peaks around -0.15 V correspond to underpotential deposition (UPD) of a monolayer of Cu on Au and the peaks at -0.55 V (reduction) and -0.40 V (oxidation) correspond to deposition-dissolution of bulk Cu. Examination of an electrode coated with only TBEA (FIG. 2b) indicates a film structure not sufficiently compact to prevent leakage of Fe^{3+} through uncovered portions of the electrode. TBEA was adsorbed on gold by immersion in a solution containing 3.3×10^{-2} M TBEA in bicyclohexylchloroform, 4:1 v/v, for 3.5 h; the resulting electrodes are denoted Au/TBEA. Evidently the introduction of an appropriate "blocking" element is necessary for the proper functioning of the system. It was expected that addition of a surface-sealing monolayer component to the adsorption solution might result in a continuous mixed monolayer barrier with ion-selective sites embedded within a compact, electrochemically inert matrix. Previous experience pointed to n-octadecyl mercaptan, $CH_3(CH_2)_{17}SH$ (OM, FIG. 1) as a suitable such component. Thus mixed monolayer membranes were prepared on gold substrates by co-adsorption of the two components from a

solution containing 2.0×10^{-2} M TBEA + 2.0×10^{-2} M OM in bicyclohexyl:chloroform, 4:1 v/v, for 3.5 h. These electrodes are denoted Au/(TBEA+OM).

The performance of the mixed (TBEA+OM) monolayer membranes was compared with that of gold electrodes coated with the same ligand, but sealed with a thin electrodeposited polymeric film (~ 10 - 15 Å thick) of 1-naphtol (NP), known to suppress electrochemical reactivity (FIG. 2c). FIG. 2e and f show, respectively, voltammetric curves of an Au/(TBEA + NP) electrode in Cu^{2+} solution and in a mixed solution of Cu^{2+} and Fe^{3+} . Although the electrode is inert to Fe^{3+} , Cu^{2+}

peaks are clearly observed. The voltammogram of the soluble Fe^{3+} -ethylacetoacetate complex in FIG. 2i indicates that the absence of $Fe^{3+/2+}$ peaks in FIG. 2c and f is not due to a possible shift in the redox potentials of complexed Fe^{3+} .

The qualitative behaviour of a typical Au/(TBEA+OM) electrode, shown in FIG. 2d and g for solutions containing Fe^{3+} or both Cu^{2+} and Fe^{3+} ions, respectively, is similar to that of Au/(TBEA + NP) (FIG. 2c and f); however, a considerably decreased background, virtually coinciding with the baseline, in FIG. 2d and g, indicates a clear improvement of the barrier properties for the mixed monolayer membrane. Thus the selective complexation of Cu^{2+} enables its penetration into the monolayer and electron exchange with the underlying electrode, whereas hydrated Fe^{3+} remains in the bulk solution at considerably greater distance from the electrode, which precludes its electrochemical reduction in the applied voltage range. Fe^{3+} forms a red complex with dissolved TBEA, possibly an oligomeric octahedral complex. For steric reasons, this should be prevented when the ligand is bound to the surface in an oriented monolayer. Total suppression of voltammetric response is also observed with other ions, which are either trivalent (for instance, Ce^{3+}) or sterically incompatible (for instance, VO^{2+}). The monolayers on gold were characterized by contact-angle measurements, reflection-absorption Fourier transform infrared (RA-FTIR) spectroscopy, and various electrochemical measurements. Indirect electrochemical evidence indicates $\sim 50\%$ ligand coverage in the present (TBEA+OM) mixed monolayers. Surprisingly high contact angles for Au/(TBEA + OM), indicative of a rather unusual mode of film packing (typical values: 108° , 59° and 57° for water, bicyclohexyl and n-hexadecane, respectively, with no hysteresis) and significant contact angle variations are observed after Cu^{2+} uptake and removal. FIG. 3 shows selected infrared spectra for the Au/(TBEA+OM) system, from which a number of general conclusions can be drawn: (1) complexed TBEA (enol form) can be detected spectroscopically in the monolayer on gold, (2) the enol form is preserved upon electrochemical removal of the Cu^{2+} ; (3) differences in the relative intensities of the various C-H stretch peaks in FIG. 3a, b and c are indicative of non-random orientation of TBEA on the surface; (4) the system appears stable towards electrochemical treatment. Common prominent features in FIG. 2f and g, which may be correlated with structural characteristics of an ordered Cu^{2+} -selective monolayer barrier, are: (1) the complete absence of $Fe^{3+/2+}$ peaks; (2) the absence of Cu UPD peaks; (3) the negative shift of the bulk Cu deposition peak by ~ 0.25 V; (4) the existence of a loop when the voltammetric scan direction is reversed. The absence of Cu UPD peaks may indicate that Cu atoms are deposited inside the organized monolayer at some distance from the surface, not in direct contact with the gold substrate. The shift in the bulk Cu deposition potential and the voltammetric loop are indicative of the preferred perpendicular orientation of the ligand. In a monolayer where TBEA molecules are oriented normal to the substrate plane (as in FIG. 1), the complexed Cu^{2+} ions are held at a distance of ~ 7 Å from the Au surface, which introduces a tunnelling barrier for electron transfer with the underlying electrode (assuming that quantum-mechanical tunnelling governs electron transfer over distances of this order of magnitude). However, reduced Cu atoms are not complexed and