Crown thioethers and 1,4-dithiacyclanes immobilized on silica carrier: preparation and studies of complexation affinity towards metal ions

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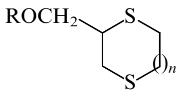
Crown thioethers and their non-macrocyclic analogues have been immobilized on a silica matrix coated with ω-(triethoxysilyl)-undecanoic acid. Thiacrown modified silica carriers were found to be highly suitable as complex-forming adsorbents for silver(I) and gold(III) ions under dynamic conditions, and application of their complexation affinity for preparation of solid-state electrochemical sensors based on composite carbon-paste electrodes has been demonstrated.

The widespread development of crown thioether chemistry during the past two decades has been encouraged by their importance as ligands which provide unexpected properties and the behaviour of their metal complexes in biological[1–3] and chemical systems.[3–7] Crown thioethers are considered to be substances of fundamental interest for application in medicine.[8–10] They are also widely used as selective extraction agents, ionophores for ion-selective electrodes and modifiers for chromatographic sorbents in various fields of analytical chemistry.[11]

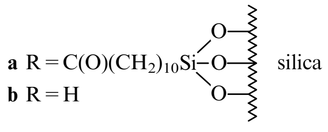
Reagent-modified silica gel seems to be a highly powerful tool for the complete, selective and fast removal of metal traces from water.[12] Water insolubility, stability in solutions of low pH and rapid formation of insoluble complexes with metal ions can be listed among the desirable properties of an immobilized reagent. Analytical properties of macrocyclic compounds might be significantly improved by their immobilization on the surface of suitable organic or inorganic polymeric supports.[11,13–15] In contrast to quite intensively studied immobilized oxygen- and nitrogen-containing crown ethers, only a few data on the synthesis and chemical properties of immobilized crown thioethers have been published.[16]

Recently, the universal strategy of crown thioether synthesis based on homolytic macrocyclisation–cycloaddition of α,ω-dithiols with alkynes was developed,[17] which allowed us to synthesize 12-,[18a] 14-,[18b] 16-,[18c] and 18-membered crown thioethers[18d,e] containing only sulfur or both sulfur and oxygen heteroatoms. This approach is especially useful for the synthesis of crown thioethers with modified functional groups suitable for further modification and covalent binding to any support.

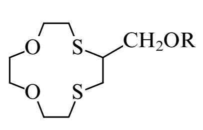
In this paper we report our studies on the preparation and analytical properties of 12-, 16- and 18-membered crown thioethers **3a**–**5a,** as well as their 6- and 7-membered non-macrocyclic analogues **1a**, **2a,** immobilized *via* covalent binding on silica matrix ‘coated’ with COOH groups on treatment with trimethylsilyl 11-(triethoxysilyl)undecanoate.†



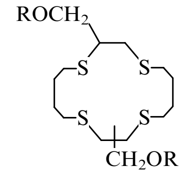
1a,b $n = 1$
2a,b $n = 2$



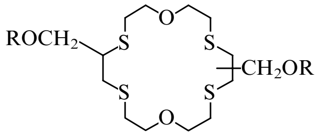
a $R = C(O)(CH_2)_{10}Si(O-)_3$ silica
b $R = H$



3a,b



4a,b



5a,b

The choice of thiaheterocycles was determined by the capabilities of the synthetic approach used.

Two sets of experiments were performed to investigate the behaviour of thiaheterocycle-modified silica carriers **1a**–**5a** as complex-forming materials for the binding of redox metal ions: (i) a study of adsorption capacity and (ii) voltammetric sensing of metal ions at a carbon-paste electrode (CPE).

To evaluate the adsorption capacity of these newly prepared materials, 50 mg of each dry material was packed into a micro column and incorporated into the injector manifold of a flow-injection (FI) system with spectrophotometric detection (see ref. 19 for experimental details). A given volume of a standard metal solution was pumped through the column and collected in a measuring flask. The metal concentration in each solution before and after the column was measured by injection into the above-mentioned FI

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† *Typical procedure for the preparation of thiaheterocycle-modified silica carriers* **1a**–**5a**. On treatment of pure silica carrier with trimethylsilyl 11-(triethoxysilyl)undecanoate and subsequent acidic work-up procedure (*cf.* ref. 21), modified phase SC containing 0.49 mg equiv. of COOH group per 1 g of carrier (titration data) was obtained.

Alcohols **1b**, **2b**[22] and **4b**[18c] were synthesized according to recently published procedures. Homolytic cycloaddition–macrocyclization of prop-2-yn-1-ol with 3,6-dioxaoctane-1,8-dithiol[18a] and 3-oxapentane-1,5-dithiol[18d] led to newly synthesized **3b** and **5b**, respectively. **3b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.50 (broad s, 1H, OH), 2.60–2.90 (m, 7H), 3.50–3.70 (m, 6H), 3.80–4.10 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 31.78, 31.89, 35.46, 49.89, 63.50, 70.22, 70.65, 73.80, 74.05 ppm; MS (EI) *m/z* 238 (I^+, 100), 86 (98), 73 (98), 123 (97), 117 (97), 87 (93), 89 (92), 45 (88), 220 (67), 150 (67), 178 (60), 179 (50), 119 (47), 149 (40), 182 (38), 134 (33), 132 (23). **5b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.40–2.50 (broad s, 2H, OH), 2.60–3.00 (m, 14H), 3.65–4.10 (m, 12H); MS (EI) *m/z* 370 ($M^+ - H_2O$, 100%), 135 (98), 91 (98), 59 (94), 136 (75), 87 (68), 75 (69), 61 (63), 60 (58), 103 (56), 194 (50), 265 (45), 117 (44), 104 (43), 102 (40), 57 (38), 331 (38).

Esterification of SC with **1b**–**5b** in the presence of DCC and DMAP[23] led to modified silica carriers **1a**–**5a**, which contained, respectively, 0.08, 0.12, 0.18, 0.18 and 0.13 mg equiv. of the corresponding immobilized crown thioether and thiaheterocycle per 1 g of a resulting material (elemental analysis data).

Table 1 The degree of adsorption capacity Q(%) of the thiaheterocycle-immobilized SC towards redox metal ions (flow rate 1.2 ml min^{-1}, metal concentration 1 μg ml^{-1}, matrix solution 0.2 mol dm^{-3} NaCl, fixed amounts of each sorbent 50 mg and of each metal 10 μg).

Entry	Material	Cu^{II}	Pd^{II}	Ag^{Ia}	Au^{III}	Hg^{IIa}
1	Silica matrix	14	1	22	25	21
2	SC	64	7	44	34	49
3	**1a**	47	10	56	68	49
4	**2a**	45	12	57	72	53
5	**3a**	55	16	78	80	82
6	**4a**	48	19	86	87	84
7	**5a**	46	13	94	97	75

[a] Matrix solution 0.2 mol dm^{-3} $NaClO_4$.

Table 2 The cathodic peak currents (μA) of the cyclic voltammograms for some metal ions at the CPE modified with 25 mass% of thia- heterocycle-immobilized SC (concentration of each metal ion solution 5×10^{-4} mol dm^{-3}; supporting electrolyte 0.2 mol dm^{-3} NaCl; scan rate 50 mV s^{-1}).

Entry	Modifier	Cu^{II}	Ag^{Ia}	Au^{III}	Hg^{IIa}	Pd^{II}
1	Silica matrix	34.0	7.0	47.0	24.0	40.0
2	SC	110.0	11.0	92.5	40.0	192.5
3	**1a**	80.0	12.0	105.0	41.0	197.0
4	**2a**	76.0	12.5	107.5	47.5	200.0
5	**3a**	85.0	25.0	110.0	51.0	207.0
6	**4a**	82.0	28.0	131.0	52.5	212.0
7	**5a**	78.0	34.0	148.0	49.0	202.0

[a] Supporting electrolyte 0.2 mol dm^{-3} $NaClO_4$.

system. Data on the recovery of several redox metal ions from a sodium chloride (or perchlorate) matrix solution obtained under the fixed flow and chemical conditions are presented in Table 1.

Clearly, almost all of the immobilized crown thioethers possess a significant adsorption capacity towards Ag^{I}, Au^{III} and Hg^{II} ions. In contrast, the supporting silica carrier (SC) itself shows good adsorption capacity only for Cu^{II} and Hg^{II} ions. All these metals were also recovered on application of SC-immobilized 1,4-dithiacyclanes **1a**, **2a.** No significant affinity was observed for Ni^{II}, Co^{II}, Cd^{II}, Fe^{III}, Mg^{II} and Ca^{II} ions. Some of the results obtained revealed the binding effect of residual carboxylic groups of SC upon the overall adsorption ability of the materials prepared. For example, recovery of Cu^{II} and Zn^{II} cations scarcely depended on the nature of the immobilized thiacompounds and was less effective than in the case of free SC.

Among the materials studied, **5a** containing an 18-membered crown thioether moiety was found to be highly suitable for the removal and preconcentration of Ag^{I} and Au^{III} ions, *e.g.* more than 90% of Au^{III} ions was removed from the matrix solutions. These results enable us to consider **5a** (as well as **3a**, **4a**) as promising reagents for the preconcentration of gold from sea water. A dynamic recovery system of this type could be especially useful in FI analysis due to the favourable kinetics of the sorption and elution processes.

In order to obtain more information about the nature and selectivity of the interaction between immobilized molecules of thiaheterocycles on silica carrier and redox metal ions, electrochemical studies have been carried out. Chemically-modified CPEs were prepared by incorporation of the appropriate quantity (20 mg) of each tested material into the paste mixture.[20] The prepared bulk-modified CPEs were tested for their response to metal ions by a cyclic voltammetry method using a three-electrode arrangement with a saturated calomel reference electrode and platinum foil counter electrode. *I-E* characteristics for all redox ions were found to be strongly dependent on the nature of the immobilized ligand. Values of cathodic peak currents on cyclic voltammograms recorded for 5×10^{-4} mol dm^{-3} solutons are given in Table 2. It was found that CPEs modified with crown thioethers exhibit much better sensitivity towards Ag^{I} and Au^{III} ions than pure CPE and CPEs modified with SC as well as SC-containing containing 6- and 7-membered 1,4-dithiacyclanes (**1a** and **2a**). Both the peak current (I_p) and peak potential (E_p) depended strongly on the nature of functional groups fixed onto the electrode surface. Figure 1 demonstrates the variations of I_p and E_p values for redox processes of Ag^{I} ion in 0.2 mol dm^{-3} $NaClO_4$. It is clear that the peak current grows with an increase in the ring size as well as of the number of heteroatoms in the heterocycle. The increase in cathodic peak current was accompanied by a negative shift of the cathodic peak potential, while the anodic peak potential did not change along with an increase in the anodic peak current. The reduction potential for Ag^{I} ions at the thiacrown-modified CPEs is at a more negative potential than that obtained with pure and SC-modified CPE. In the case of Au^{III}, the cathodic (reduction) peak potential depended only slightly on the nature of the modifier, while the oxidation (anodic) potential changed significantly.

The remarkable effect observed for Ag^{I} and Au^{III} ions through modification of the CPE with crown thioether-

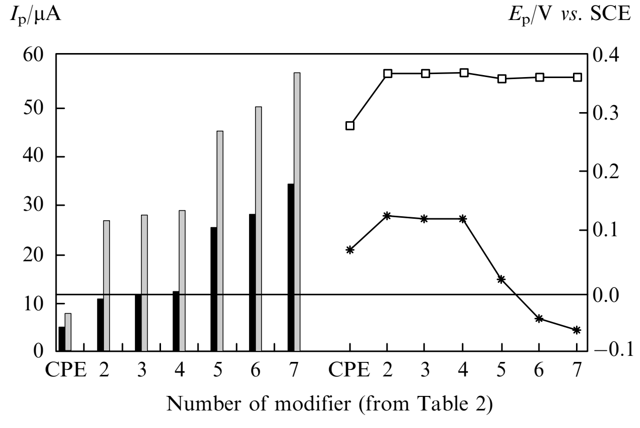

Figure 1 Peak current and peak potential of cyclic voltammograms for 5×10^{-4} mol dm^{-3} Ag^{I} in 0.2 mol dm^{-3} $NaClO_4$ at unmodified CPE and CPE modified with silica carriers (SC/CPE). Scan rate 50 mV s^{-1}.

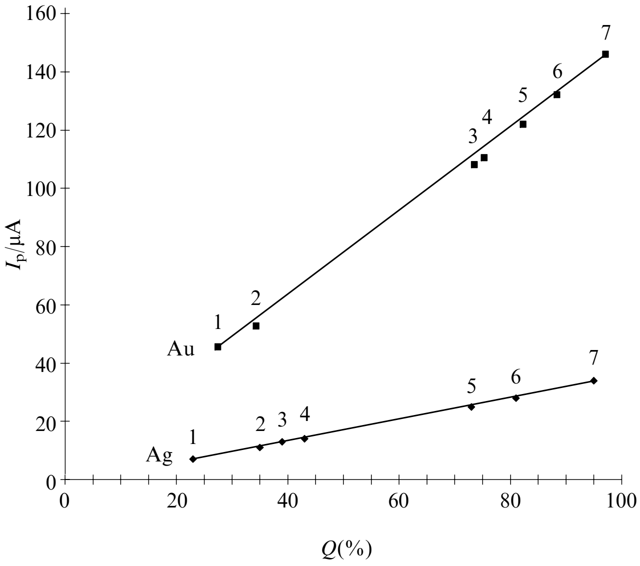

Figure 2 Plot of cathodic peak current I_p at the SC/CPE *vs.* corresponding Q values for Au^{III} and Ag^{I} ions. (Numbers correspond to the entries in Table 1).

containing silica carriers could be caused by the formation of complexes between fixed macrocyclic ligand and metal cations. One could assume that these species are accumulated in the form of ion associates between the positively charged complexes on the electrode and counter anions in the solution.

The peak current increased linearly with increase of the corresponding degree of adsorption capacity Q (Figure 2).

In conclusion, the results obtained demonstrate that the crown thioether-immobilized silica carrier materials studied are promising both for the preconcentration of trace amounts of silver and gold ions and for the preparation of electrochemical sensors for the determination of the above-mentioned redox ions.

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