Mendeleev Commun., 2004, 14(1), 24–25

Interaction between gold(III) and mercapto and disulfide groups covalently bound to a silica gel surface

Vladimir N. Losev,*[a] Eugenie V. Elsuf'ev,[a] Elena V. Buiko,[a] Anatoly K. Trofimtchuk[b] and Elena V. Andrianova[b]

[a] *Research Engineering Centre 'Kristall', 660041 Krasnoyarsk, Russian Federation.*
Fax: +7 3912 44 5659; e-mail: scien_kristall@lan.krasu.ru
[b] *Department of Chemistry, T. G. Shevchenko Kiev National University, 01033 Kiev, Ukraine. E-mail: aktrof@svitonline.com*

DOI: 10.1070/MC2004v014n01ABEH001738

The interaction between gold(III) and mercapto and disulfide groups covalently bound to a silica gel surface in hydrochloric acid solutions was studied.

A special emphasis was placed on the study of the interaction between extractable ions and functional groups covalently bound to the surfaces of solid bodies, particularly, silicon dioxide surfaces, in order to substitute extraction preconcentration for sorption preconcentration. Studies on mechanisms of interaction of gold(III) with *N*-allyl-*N'*-propylthiourea covalently bound to a silica gel surface were used for the sorption and preconcentration of gold from natural water[1] and solutions obtained after the decomposition of minerals.[2]

We report the interaction of gold(III) with mercaptopropyl and arched-structure dipropyldisulfide groups covalently bound to a silica gel surface.

Silica gel chemically modified with mercaptopropyl groups (MPS) was prepared using the reaction of silica gel 60 Merck (100–230 mesh, pore diameter of 150 Å, and surface area of 370 m^2 g^{-1}) with γ-mercaptopropyltriethoxysilane in toluene. Silica gel chemically modified with dipropyldisulfide groups (DPDSS) was derived from MPS using iodine oxidation.

The thiol group surface concentration was determined using back thiolometric titration of an excess of a silver nitrate standard solution. The disulfide group surface concentration was calculated to be half that of the SH group surface concentration of MPS. The concentrations were 1.32±0.03 and 0.52±0.03 mmol g^{-1} for MPS and DPDSS, respectively.

The standard solution of Au$^{\text{III}}$ was prepared using thermal dissolution of a weighed portion of gold (ZlA-1, 99.9%) in a mixture of concentrated hydrochloric and nitric acids (3:1) and then afterwards converting it to a hydrochloric medium (2 M HCl).

A batch equilibrium technique was used to study the sorption of gold(III). Typically, 20 μg of gold (as a solution in 2 M HCl), NaOH or HCl (to adjust the required pH) and distilled water (up to a total volume of 10 ml) were mechanically equilibrated with 0.1 g of each of the modified silica gels by shaking well. The analysis of metal distribution was carried out by flame (acetylene–air) atomic absorption spectrometry (AAS) using a Saturn-2M spectrometer (λ = 242.8 nm).

The spectra and intensities of the luminescence were measured using a spectrofluorimeter with a MDR-4 monochromator, an SVD-120A mercury quartz lamp and a UFS-2 light filter at a low temperature.

The pH of the solutions was measured using an I-130 ion meter.

The equilibration time for the sorption of gold(III) using MPS is 2 min. The extraction runs to 99.9% over a wide range of acidity (4 M HCl – pH 8) (Figure 1).

Wet MPS sorbates exhibited a yellow-orange luminescence under UV irradiation at 77 K. The luminescence spectrum has a wide structureless band with maximum at 575 nm. The luminescence is caused by electron transitions inside the complexing Au$^{\text{I}}$ ion, and this radiation can be attributed to *dd** phosphorescence.[3] The radiation is evidence of the reduction Au$^{\text{III}}$–Au$^{\text{I}}$ caused by thiol groups covalently bound to the silica gel surface during sorption

$$4\,\text{R–SH} + \text{H[AuCl}_4] = [\text{Au(S–R)}_2]^- + \text{RS–SR} + 4\text{HCl} \qquad (1)$$

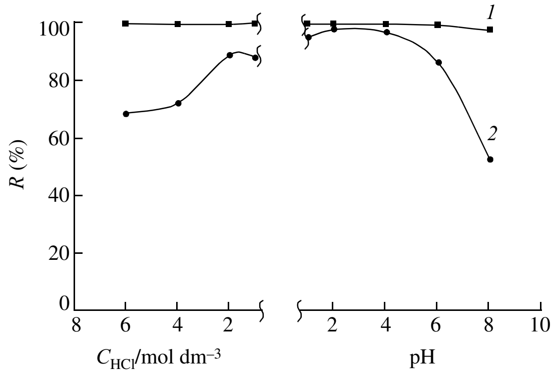


Figure 1 Batch equilibration of gold with (*1*) MPS and (*2*) DPDSS as a function of pH or hydrochloric acid concentration (C_{Au} = 10 μg ml^{-1}; V = 10 ml; sorbent weight of 0.1 g; equilibration time of 10 min).

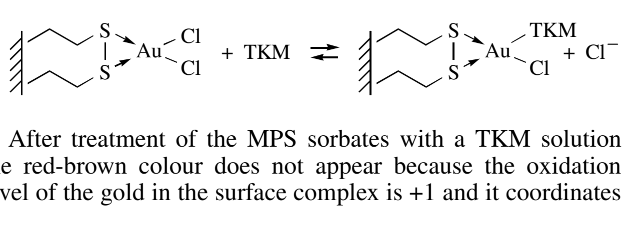
The reactions between gold(III) and mercaptans in solution proceed in a similar manner.[4] Furthermore, the reduction of gold(III) to gold(I) comprises the coordination of sulfur-containing ligands with gold(III) and the subsequent reduction of Au$^{\text{III}}$ to Au$^{\text{I}}$ within the coordination compound.[5]

In case of Au$^{\text{III}}$ sorption by DPDSS, the equilibration time is shorter than 10 min. Thus, metal uptake depends on the acidity of the solution: it rises from 69 to 98.5% when passing from 4 M HCl to pH 2; a further increase in pH up to 8 leads to a decrease of metal uptake to 54% (Figure 1).

The pH effect on gold uptake provides evidence for the lower coordination affinity of disulfide groups compared with that of mercapto groups. This phenomenon is typical of processes involving gold(III) complexation with thiol sulfur-containing ligands and their oxidised disulfide form in aqueous solutions.[4]

Wet DPDSS sorbates have no yellow-orange luminescence under UV irradiation at 77 K. This fact indicates that gold remains in the oxidation state +3.

The treatment of DPDSS sorbates using an aqueous alcoholic solution of Meckler thioketone (TKM) leads to red-brown sorbates. The colour of the gold complex with TKM is the same; 1 μg of gold on the surface gives a quite intense colour. This absence of luminescence and the interaction with TKM lead to the conclusion that gold remains surface complexed at an oxidation level of +3. The surface processes are represented in the following scheme:



After treatment of the MPS sorbates with a TKM solution the red-brown colour does not appear because the oxidation level of the gold in the surface complex is +1 and it coordinates only two mercapto groups as is shown in reaction (1). Thus, gold(I) has occupied both coordination sites and the addition of an external ligand (Meckler thioketone) does not lead to sorbent colouration.

The MPS sorbates become slightly coloured when the gold content of the surface is more than 400 μg per 0.1 g of MPS. Insular filling of the silica gel surface with functional groups leads to a gold complex with the ratio Au:S = 1:1 with rising surface gold content. In this case, the molecule of TKM replaced one chloride ligand.

The yellow-orange luminescence under UV irradiation at 77 K appears during long-term (more than 10 days) storage of DPDSS sorbates. The position of the maximum in the luminescence spectrum ($\lambda_{\max} = 575$ nm) is the same as the maximum in the luminescence spectra of MPS sorbates. However, the luminescence intensity remains less than half even after being stored for a relatively long period (more than 10 days). These findings are evidence of the primary surface complex formation of Au^{III} with the disulfide groups of DPDSS. Then, as time goes by, the reduction of gold(III) to gold(I) proceeds in the surface complex, as the oxidation of disulfide groups occurs simultaneously. Decomposition of the disulfide groups into mercapto and sulfoxide groups occurs in the presence of heavy metals.[6] It is likely that similar processes take place in this case. Mercapto groups, which appeared during decomposition of disulfide groups, remain associated with gold(I) because there are no significant interactions between the chloro complexes of noble metals and sulfoxide groups in hydrochloric acid solutions at room temperature.[7]

The oxidation of mercapto groups by gold(III) goes through the stages of formation of disulfide and sulfoxide groups until they are sulfo acids.[6] The oxidation of disulfide groups to sulfo acids proceeds analogously. An analogous mechanisms of oxidation leads to roughly equal sorptive capacities, which are determined from the horizontal lengths of isotherms and amount to 0.28 and 0.23 mmol g^{-1} for MPS and DPDSS, respectively.

In the case of the reaction between MPS sorbent and concentrated (more than 1 mg ml^{-1}) gold-containing solutions, the sorbates become yellow. However, MPS sorbates became colourless after several minutes, while DPDSS sorbates remained unchanged over at least two days.

Solutions isolated from the sorbents become lighter in colour. In case of MPS sorbates the solution discolouration is more rapid and intense in comparison with solutions from DPDSS sorbates. Elemental gold precipitates from these solutions with time:

$$3Au^{I} \rightarrow Au^{III} + 2Au^{0} \qquad (2)$$

It is necessary to take into account these time-dependent processes at the surface of the modified silica gels and in solution, in the practical application of sorbents studied and of other sorbents with thiol functional groups.

References

1 A. K. Trofimtchuk, N. I. Makarenko, A. I. Yarmoluk and V. N. Losev, *Khimiya i Tekhnologiya Vody*, 1999, **21**, 617 (in Russian).

2 V. N. Losev, S. V. Kuzenko and A. K. Trofimtchuk, *Zh. Anal. Khim*., 1997, **52**, 11 [*J. Anal. Chem.* (*Engl. Transl.*), 1997, **52**, 6].

3 V. N. Losev, E. V. Elsuf'ev, Yu. V. Alennikova and A. K. Trofimtchuk, *Zh. Anal. Khim*., 2003, **58**, 269 [*J. Anal. Chem.* (*Engl. Transl.*), 2003, **58**, 236].

4 V. A. Pronin, M. V. Usol'tsev, V. A. Trofimov, E. P. Vyalikh and Z. N. Shastina, *Zh. Prikl. Khim*., 1973, **46**, 2602 [*J. Appl. Chem. USSR* (*Engl. Transl.*), 1973, **46**, 2758].

5 R. G. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, Oxford, New York, 1978.

6 G. F. Bolshakova, *Seraorganicheskie soedineniya nefti* (*Organosulfur Compounds of Oil*), Nauka, Novosibirsk, 1986, p. 90 (in Russian).

7 V. S. Tchekushin and V. F. Borbat, *Ekstraktsiya blagorodnykh metallov sul'fidami i sul'foksidami* (*Extraction of Noble Metals with Sulfides and Sulfoxides*), Nauka, Moscow, 1984 (in Russian).

Received: 14th March 2003; Com. 03/2064