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Reactions of osmium in various oxidation states with mercaptopropyl and aminopropyl groups simultaneously attached to a silica gel surface

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The sorption characteristics and diffuse reflectance and EPR spectra of osmium surface complexes showed that Os^{8+} and Os^{6+} in OsO_4 and $K_2[OsO_2Cl_4]$, respectively, react with mercaptopropyl groups, whereas Os^{4+} in $K_2[OsCl_6]$ reacts with aminopropyl groups covalently bound to a silica gel surface.

Sorption belongs to the most efficient separation and concentration methods. Platinum group metals are generally concentrated using sorbents that contain electron-donating nitrogen and sulfur atoms, such as chemically modified silica gels. Osmium(VI) and osimum(VIII) compounds are labile, whereas the osmium(IV) chloride complex is among the most kinetically inert compounds.

We studied the sorption of osmium in various oxidation states (Os^{8+}, Os^{6+} and Os^{4+}) on silica gels chemically modified by both mercapropropyl and aminopropyl groups with various surface concentrations.† These sorbents are multiphase sorbents[1] with two or more different functional groups attached to the surface. To synthesize such sorbents, we treated silica gels with 3-aminopropyltriethoxysilane and 3-mercaptopropyltriethoxysilane modifiers, which are widely used to obtain aminopropyl and mercaptopropyl silica gels.[2,3]

These sorbents have two centres where metal ions can react by complexation or anion-exchange mechanisms. The mercaptopropyl group acts as a complexing group, whereas aminopropyl acts as an anion exchange group due to protonation in acidic media.

Sorbents I and II quantitatively extract osmium(VIII) from 0.1–3 M H_2SO_4 and osmium(VI) from 0.1–4 M HCl at room temperature (the extraction ratio is 98.0–99.9%). The equilibration time is less than 5 min for osmium(VIII) or 1 min for osmium(VI). The chloride complex of osmium(IV) is not extracted by sorbents I and II from 1–4 M HCl solutions. The maximum extraction ratio of this compound (60–80%) is attained at pH > 4 (Figure 1).

Similar results were observed for the sorption of osmium(VIII) and osmium(VI) with silica gels chemically modified with mercaptopropyl groups,[7] as well as for that of osmium(IV) with silica gels chemically modified with aminopropyl groups.[8] The decrease in the extraction ratio of the osmium(IV) chloride complex at smaller concentrations of aminopropyl groups and higher concentrations of mercaptopropyl groups (sorbent II) is due to differences in the surface arrangement of the groups. Aminopropyl groups are arranged parallel to the silica gel surface owing to the formation of hydrogen bonds with the surface hydroxy groups,

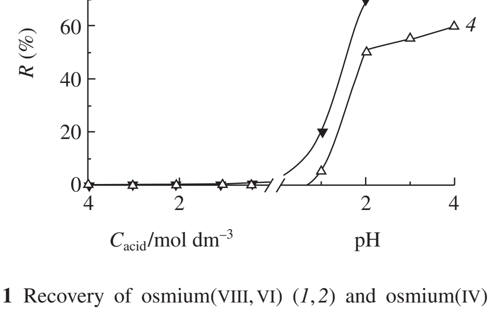

Figure 1 Recovery of osmium(VIII, VI) (*1*,*2*) and osmium(IV) (*3*,*4*) by sorbent I (*1*,*4*) and sorbent II (*2*,*3*) *vs*. the concentration of sulfuric or hydrochloric acid (*1*,*2*) and pH (*3*,*4*) (C_{Os} = 10 μg cm^{-3}, V = 10 ml, 0.1 g of a sorbent, equilibration time of 10 min, 20 °C).

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† The sorbents were synthesized from silica gel 60 (Merck, 100–230 mesh, specific surface area of 260 m^2 g^{-1}, mean pore diameter of 12 nm) in accordance with a published procedure[4] using 3-aminopropyltriethoxysilane and 3-mercaptopropyltriethoxysilane (Merck) as modifiers. For this purpose, 20 g of silica gel calcined at 400 °C was placed in a reactor equipped with a stirrer and a reflux condenser; then, dry toluene (80 ml) and a mixture of the modifiers in a required molar ratio (total amount of 0.05 mol) were added. The mixture was boiled with stirring for 6 h. The resulting sorbent was washed for 48 h with toluene in a Soxhlet apparatus and dried *in vacuo* (2×10^3 Pa) at 95 °C. The concentration of grafted amino groups was determined by potentiometric titration, and that of mercaptopropyl groups was determined by back complexometric titration of excess standard solution of silver nitrate in 1 M HNO_3 with unithiol in the presence of di(*p*-sulfophenyl)thiocarbazone as a metallochrome indicator. The concentrations were as follows: 0.81 (–SH) and 0.17 mmol g^{-1} (–NH_2) for sorbent I; 0.33 (–SH) and 0.66 mmol g^{-1} (–NH_2) for sorbent II.

The solution of osmium(VIII) was prepared by dissolving an accurately weighed portion of commercial OsO_4 in 0.5 M sulfuric acid. Osmium(VI) and osmium(IV) solutions were prepared by dissolving $K_2[OsO_2Cl_4]$ and $K_2[OsCl_6]$ salts (synthesized as described elsewhere[5]), respectively, in 2 M hydrochloric acid.

A batch equilibrium technique was used to study the sorption of osmium. Typically, 10 μg of osmium(VIII) (as a solution in sulfuric acid) or osmium(VI, IV) (as a solution in hydrochloric acid), H_2SO_4 (HCl) or NaOH (to adjust pH), and distilled water (to a total volume of 10 ml) were put in a tube with a ground glass stopper and mechanically equilibrated for 1–30 min with 0.1 g of each of the modified silica gels by shaking well. The sorption at 95 °C was studied in temperature-controlled cells. After sorption, the sorbents were separated from solutions by decantation and placed in a fluoroplastic cell, and the diffuse reflectance spectra were measured.

Osmium distribution was monitored by the spectrophotometric analysis (Perkin-Elmer Lambda 35 spectrophotometer, USA) of an aqueous phase using the reaction with thiourea.[6] The diffuse reflectance spectra were recorded with a Pulsar spectrophotocolorimeter (Khimavtomatika, Russia). The EPR spectra were recorded with an Elexsys E-580 instrument (Bruker, Germany).

whereas the arrangement of mercapropropyl groups is perpendicular to the surface due to the mutual repulsion with hydroxy groups.[9] Therefore, as the number of amino groups decreases, the shielding effect of mercaptopropyl groups increases and amino groups become less accessible for osmium(IV) chloride complexes.

As osmium(VIII) is sorbed on sorbents I and II, the surfaces acquire a yellowish brown colour. The diffuse reflectance spectra of the surface complexes are downward curves with slightly expressed maxima at the UV-visual boundary. They are similar to the spectra obtained for the sorption of osmium(VIII) and osmium(VI) on silica gels chemically modified with mercaptopropyl groups.[7]

Osmium(VIII) and osmium(VI) are not sorbed from sulfuric and hydrochloric acid solutions with silica gel modified by aminopropyl groups; this fact confirms that they react with the mercaptopropyl groups of the sorbents in acidic media.

As osmium(IV) is sorbed, the sorbent surface acquires a yellow colour typical of the $[OsCl_6]^{2-}$ complex, which suggests that sorption occurs by the anion exchange mechanism

$$SiO_2–NH_2 + H^+ = SiO_2–NH_3^+;$$
$$2(SiO_2–NH_3^+) + [OsCl_6]^{2-} = (SiO_2–NH_3^+)_2[OsCl_6].$$

Reactions of Os^{VIII} and Os^{VI} with the mercaptopropyl groups of sorbents result in two types of surface paramagnetic centres (Figure 2). These centres can be attributed to Os^{III} low-spin complexes (type I and II). An asymmetric shape of the EPR signal line in lower fields (Figure 2, curve *4*) attributed to type I complexes is typical of powder samples in case of perpendicular orientation of magnetic field to the axis of symmetry. In this case, $g_\perp = 2.58$. Isoelectronic cations of Ir^{4+}, Ru^{3+}, and Os^{3+} in various coordination environments were studied previously using EPR spectroscopy.[10–12] It was found that $g_\parallel$ is closer to zero for values of $g_\perp$ greater than 2.5. Perhaps for this reason, in this case, transition corresponding to $g_\parallel < 0.5$ is not observed in EPR spectra. A similar parameter ($g_\perp = 2.580$) was obtained for the osmium(III) compound that is formed on silica gel surfaces chemically modified with mercaptopropyl groups; it was attributed to the $[OsLCl_5]^{3-}$ complex.[7] The EPR signal of type II from Os^{III} centres has a complex nonuniform line shape. It is evidenced by the presence of a number of breaks as a result of superposition of signals with close parameters. The most intense signals have a rhombic anisotropy of *g*-tensor with the following parameters: $g_x = 2.35$, $g_y = 2.23$, $g_z = 1.84$ (Figure 2, curve 2).

The formation of complexes with axial symmetry can be attributed to the existence of one sulfur atom in the coordination environment of Os^{3+}, since the absence of a coordinated ligand in the *trans*-position should be assumed to explain the weakening of axial bonds. Furthermore, the short spacer (propyl group) and the octahedral structure of the complex prevent the coordination of the ligand at the *trans*-position. Therefore, judging by the axial type of the EPR signal, an octahedron with a sulfur atom at its vertex is the most suitable configuration for the Os^{VIII} surface complex.

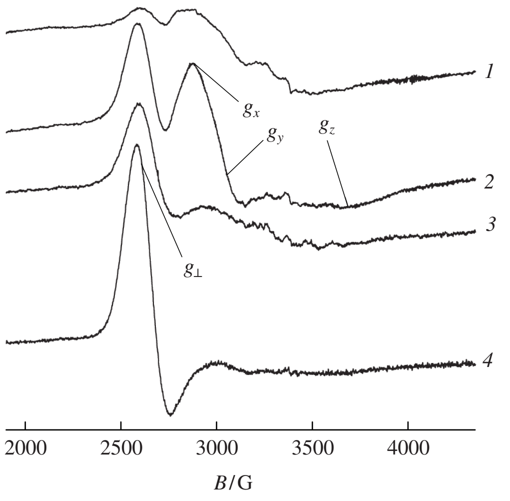

Figure 2 EPR spectra of osmium(III) surface complexes formed on the surface of sorbent I (*1*,*2*) and sorbent II (*3*,*4*) during the sorption of osmium(VIII) (*1*,*3*) and osmium(VI) (*2*,*4*).

The surface complexes of osmium(III) characterized by centres of rhombic anisotropy manifest smaller deviations of their *g*-factors from the purely spin-based value (g_s) in comparison with the deviations of the *g*-factors of complexes with axial symmetry, which suggests a considerable increase in t_{2g}^5-configuration splitting. This is possible if strong bonds are formed in an octahedron plane upon the coordination of osmium(III) with at least two mercapropropyl groups to give various complexes, *e.g.* *cis*-$[OsL_2Cl_4]^{3-}$, face- and edge-located isomers of $[OsL_3Cl_3]^{3-}$. The presence of different complexes in these samples is consistent with EPR data (EPR spectra have type II complex signals of Os^{III} centres).

As the concentration of mercaptopropyl groups decreases and that of aminopropyl groups increases, the probability of formation of osmium(III) *cis*-complexes diminishes and that of complexes with one coordinated mercapto group grows. The latter occurs in the case of sorbent II, which predominantly forms $[OsLCl_5]^{3-}$ complexes, where L is a mercaptopropyl group attached to the silica gel surface.

The more intense transitions in EPR spectra observed for surface complexes after sorption of osmium(VI) suggest that a much larger amount of osmium is included in surface complexes with osmium in the oxidation state 3+.

The similar EPR parameters and spectroscopic characteristics of complexes obtained during the sorption of osmium in various oxidation states on sorbents I and II and on silica gels modified by only mercaptopropyl groups[7] suggest that identical processes occur at the sorbent surfaces.

The absence of EPR signals from sorbents after sorption of osmium(IV) suggests that osmium exists in the oxidation state 4+ on sorbent surfaces.

Thus, sorption involves the reactions of Os^{VIII} and Os^{VI} with mercaptopropyl groups, whereas Os^{IV} reacts with aminopropyl groups covalently bound to the silica gel surface. By changing the solution pH, it is possible to use silica chemically modified with both mercaptopropyl and aminopropyl groups for the concentration and separation of osmium in various oxidation states.

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