Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Pilśniak, Magdalena , Trochimczuk, Andrzej W. and Apostoluk, Wiesław(2009) 'The Uptake of Gold(I) from Ammonia Leaching Solution by Imidazole Containing Polymeric Resins', Separation Science and Technology, 44: 5, 1099 — 1119

To link to this Article: DOI: 10.1080/01496390902729007

URL: http://dx.doi.org/10.1080/01496390902729007

Separation Science and Technology, 44: 1099–1119, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390902729007

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The Uptake of Gold(I) from Ammonia Leaching Solution by Imidazole Containing Polymeric Resins

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Abstract: The polymeric resins containing guanylthiourea, 1-methylimidazole, 2-mercapto-1-methylimidazole ligands have been synthesized from vinylbenzyl chloride-divinylbenzene copolymers and used in the removal of Au(I) from ammonium buffer and ammoniacal thiosulphate solutions. The best gold sorption from ammonium buffer that contains 100 g/dm^3 $NH_3 \cdot H_2O$ and 5 g/dm^3 $(NH_4)_2SO_4$, is reached in the case of 1-methylimidazole resin (**2**) (27.9 mg/g) and all three resins do not have a measurable sorption of copper(II) ammine complexes. The resins display a higher affinity towards gold(I) from ammoniacal thiosulphate solutions than from the ammonium buffer solution. The XPS analysis of gold loaded resins suggests the presence of gold at Au(I) oxidation state, most likely in the form of ionic pair $Au(NH_3)_2{}^+OH^-$ or neutral complex $AuNH_3OH$ and as highly-dispersed metallic gold. The degree of gold desorption is about 50% using 1% potassium cyanide solution in 0.3% hydrogen peroxide solution. Resins retain their capacity towards gold in five consecutive sorption/desorption cycles.

Keywords: Desorption, gold(I), imidazole complexes, polymeric resins, sorption

Received 8 March 2008; accepted 3 November 2008.

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INTRODUCTION

The recovery of precious metals, including gold, attracted the attention of many researches over last several years. This noble metal, although sometimes present in its native state, is often extracted from complex ores such as sulphide and carbonaceous refractory ores, waste recycled materials, e.g. electronic and jewellery scraps (1). The majority of gold is obtained from ores using alkaline cyanide leaching but this process is not an ideal one on account of its toxicity, low leaching rate, and its inefficiency in the treatment of certain classes of refractory ores. The kinetics of gold leaching with cyanide is very slow (2–4 days). In addition, this process is not selective enough for gold because of the extremely high complexation ability of the cyanide anion. Most of the cyanide used in gold metallurgy is consumed by the accompanying metals such as Fe, Cu, Zn, and Hg. As a consequence, the complexed heavy metals strongly affect public health and influence all the elements of the environment (1). Other leaching processes utilizing thiosulphate, acidified thiourea, hydrochloric acid, and ammonia solution have been also studied and some of these processes have found applications in the industry.

The leaching of gold from ores using thiosulphate has been studied in the last two decades. Leaching of gold in thiosulphate-based systems is promoted by ammonia and copper (2–3). In ammoniacal-thiosulphate solutions gold is oxidized by the action of Cu^{2+} ions, in the form of the ammine complex, $Cu(NH_3)_4{}^{2+}$, according to the following equation:

$$2Au^0 + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} \longrightarrow Au(S_2O_3)_2^{3-} + Cu(S_2O_3)_3^{5-} + 4NH_3 \quad (1)$$

Oxygen or some other oxidant is required to convert Cu^+ to Cu^{2+} to keep the oxidative capacity of the leaching solution with the oxidation reaction proceeding according to the equation:

$$2Cu(S_2O_3)_3^{5-} + 8NH_3 + 1/2O_2 + H_2O \rightarrow Cu(NH_3)_4^{2+} + 2OH^- + 6S_2O_3^{2-} \quad (2)$$

The efficiency of leaching depends on many factors including pH, Eh, ammonia to thiosulphate ratio, temperature, and solution stability.

The use of thiourea in noble metal leaching has been discussed for long time. For example, several disadvantages have been reported for thiourea leaching (4). During gold oxidation, thiourea decomposes through formamidine disulphide to cyanamide and sulphur, which is sticky and prevents the attack of the reagent on gold. The use of SO_2 to reduce such irreversible decomposition of thiourea also inversely affects the gold dissolution. Thus, thioureation conditions are still the main objects of many studies.

The recovery of gold from hydrochloric acid solutions is gaining more attention because of the considerable interest in developing a safe alternative to cyanide leaching and since an increasing amount of this metal is recovered from secondary sources and waste material (5). Gold plated electronic parts are being stripped of this metal with acid and the resulting solution contains a high amount of copper (ca. 600 mg/dm^3), whereas gold is usually present at the concentration of ca. 20 mg/dm^3.

Ammonia is a particularly attractive alternative to cyanide as a lixiviant for gold. Ammonia is less toxic than cyanide, relatively inexpensive, and easily regenerated by evaporation techniques (6–7). Thus, the process of leaching with ammonia solution has been developed in recent years. The dissolution of gold in ammonia solution under certain conditions of temperature, pressure, and oxidants is favorable. More than thirty years ago Skibsted and Bjerrum (8–9) showed that gold is soluble in ammonia solution even at room temperature. Although the stability of gold ammine complexes indicates that gold should be soluble in ammonia solutions at room temperature, kinetic experiments showed that gold is essentially not leached unless the temperature is raised to at least 80°C, but more practically to above 120°C. Researchers at the South Dakota School of Mines and Technology proved that it is possible to dissolve gold in ammonia solution at relatively high temperature in an autoclave (10–11). The recovery of gold in solutions containing ammonia, ammonium salts, and proper oxidants at 160-200°C is better than 95% within 1–2 h of reaction (6). In the presence of oxidants, ammonia leaching of gold is a redox reaction. Gold is oxidized to the form the ammine complexes, $Au(NH_3)_2{}^+$, according to the following reaction:

$$Au + 2NH_3 = Au(NH_3)_2^+ + e \qquad (3)$$

If cupric tetra-ammine complex is used as an oxidant, the cathodic reaction can be written as:

$$Cu(NH_3)_4^{2+} + e = Cu(NH_3)_2^+ + 2NH_3 \qquad (4)$$

The reaction of cupric tetra-ammine to cuprous di-ammine is the most effective cathodic reaction for dissolution, except the case when iodine was used as an oxidant. The complexes of copper are used both as an oxidant and as catalyst. However, the application of these complexes has serious disadvantage because large quantities of copper (10–15 g/dm^3) appear in the leachate compared with concentration of gold (4 mg/dm^3), which makes the recovery of Au from the obtained solution difficult.

There is little information concerning the removal of gold from ammonia solutions. The active carbons have been used for $Au(NH_3)_2{}^+$ uptake from such solution (12). The maximum gold adsorption on activated carbon was about 10 kg/t of carbon and the adsorption efficiency was 98%. The increased free-ammonia concentration reduced the percent recovery of gold. The initial adsorption rate was relatively fast, when compared to the entire adsorption period. The apparent activation energy for the adsorption was determined to be 15.8 kJ/mol. This value suggested chemisorption of $Au(NH_3)_2{}^+$ on activated carbon. Desorption of gold was carried out using ammonium buffer (50 g/dm^3 $(NH_4)_2SO_4$, 100 g/dm^3 $NH_3 \cdot H_2O$) under nitrogen atmosphere (20 atm) and high temperature (180°C). The degree of gold desorption was about 50%.

In the case of application of polymeric resins in $Au(NH_3)_2{}^+$ recovery there are two reports (13–14). In the recent work we synthesized polymeric materials containing amino ligands and investigated their sorptive properties towards gold from ammonium buffer (50 g/dm^3 $(NH_4)_2SO_4$, 100 g/dm^3 $NH_3 \cdot H_2O$) and selectivity of sorption in the presence of copper (14).

In this work we would like to present the detailed investigations of the influence of factors like ammonia, ammonium sulphate, and sodium thiosulphate concentration on gold sorption on the polymeric resins and suggest the mechanism of gold uptake by the resins. Sorption kinetics and gold desorption have been also studied.

EXPERIMENTAL

Chemical Reagents

The chemicals were Sigma-Aldrich products. The solution of gold in ammonium buffer was prepared by dissolving metallic gold in aqua regia. The solution of $[AuCl_4]^-$ was introduced into ammonium buffer solution (50 g/dm^3 $(NH_4)_2SO_4$, 100 g/dm^3 $NH_3 \cdot H_2O$). An experiment was carried out in autoclave under oxygen atmosphere (10–15 atm) and high temperature (120°C). The preparation of gold solution can be described using the following reactions:

$$Au^0 + HNO_3 + 4HCl \longrightarrow [AuCl_4^-] + H^+ + NO + 2H_2O \qquad (5)$$

$$2[AuCl_4^-] + 8NH_3 \cdot H_2O = 2Au(NH_3)_2^+ + O_2 + 8Cl^- + 4NH_4^+ + 6H_2O \qquad (6)$$

$$Au^{3+} = Au^+ - 2e/2 \qquad (7)$$

$$2O^{2-} = O_2 + 4e \qquad (8)$$

The initial gold concentration was 431.40 mg Au/dm^3. This solution was diluted twenty times with ammonium buffer (0.1–100 g/dm^3 $NH_3 \cdot H_2O$, 0.05–50 g/dm^3 $(NH_4)_2SO_4$) in order to obtain the concentration of 21.57 mg Au/dm^3 and various concentrations of ammonia and ammonium sulphate.

The solutions of $Au(NH_3)_2{}^+$ containing each time 21.57 mg /dm^3 of gold and 0.1-100 g/dm^3 $NH_3 \cdot H_2O$ and 0.05–50 g/dm^3 $(NH_4)_2SO_4$ were used in the sorption experiments.

The solutions of $Au(S_2O_3)_2{}^{3-}$ were prepared by dissolving various amounts of sodium thiosulphate (19.7-3190 mg/dm^3) in ammonium buffer (100 g/dm^3 $NH_3 \cdot H_2O$, 50 g/dm^3 $(NH_4)_2SO_4$) containing 21.57 mg/dm^3 of gold.

The polymeric resins used in the course of this work have been prepared from the starting material: vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer. The chloromethyl groups present in its structure serve as a reactive place for the immobilization of a ligand. The prepared resins are characterized by an expanded gel structure.

Methods of Analysis

The sorption capacity of resins towards gold from ammonium buffer and thiosulphate containing ammonium buffer solutions was determined by contacting the resin samples with 10 cm^3 of metal ions solution. Metal ions solution containing Au(I) (21.57 mg/dm^3) is used in the sorption experiments. The ratio of ligands in the resin to metal ions in the solution has been set to 10:1. After 24 h the polymers are separated by filtration and the concentration of Au is measured using an atomic absorption method on a Perkin-Elmer Analyst 100 with the wavelength set at 242.8 nm.

The sorption isotherms were determined by contacting various amount of resins with 10 cm^3 of solution containing 21.57 mg/dm^3 of Au(I), 100 g/dm^3 $NH_3 \cdot H_2O$, 5 g/dm^3 $(NH_4)_2SO_4$ for 24 h and plotting the sorption as a function of the equilibrium concentration.

For the kinetics of sorption, the identical samples of resin were shaken with 10 cm^3 of solution containing 21.57 mg/dm^3 of Au(I) in an ammonium buffer (100 g/dm^3 $NH_3 \cdot H_2O$, 5 g/dm^3 $(NH_4)_2SO_4$). Samples were taken at different intervals of time, resin, and solution separated and the concentration of gold was determined by AAS.

Desorption of gold was determined by contacting an amount of resin, loaded with the known amount of gold, with 10 cm^3 of an eluent at room temperature (24°C) and at 50°C for 24 h. After that time the concentration of gold was determined by AAS and the percentage of Au eluted was calculated.

X-ray photoelectron spectroscopy (XPS) was performed using equipment designed by Vacuum Systems Workshop Ltd. England. X-rays were generated using anode operating at 200 W. The energy scale was calibrated using C-C and C-H binding energy at 284.6 eV. C_{1s}, N_{1s}, O_{1s}, S_{2p} and Au_{4f} peaks of 1-methylimidazole and 2-mercapto-1-methylimidazole resins gold loaded from $Au(NH_3)_2^+$ or $Au(S_2O_3)_2^{3-}$ solutions in ammonium buffer were fitted and derived by XPSPEAK 4.1 program using the Gaussian-Lorenzion curve profile.

Three samples of gold loaded resins were studied using XPS analysis:

D_1: 1-methylimidazole resin (**2**) gold loaded from $Au(NH_3)_2^+$ solution in ammonium buffer,
D_2: 1-methylimidazole resin (**2**) gold loaded from $Au(S_2O_3)_2^{3-}$ solution in ammonium buffer,
D_3: 2-mercapto-1-methylimidazole resin (**3**) gold loaded from $Au(NH_3)_2^+$ solution in ammonium buffer.

The sorption of gold on the above samples was carried out from solution containing 21.57 mg/dm^3 of Au(I), 100 g/dm^3 $NH_3 \cdot H_2O$, 50 g/dm^3 $(NH_4)_2SO_4$ (samples D_1) and 21.57 mg/dm^3 of Au(I), 100 g/dm^3 $NH_3 \cdot H_2O$, 50 g/dm^3 $(NH_4)_2SO_4$, 1.6 g/dm^3 $Na_2S_2O_3$ (samples D_2).

RESULTS AND DISCUSSION

In our recent work we synthesized polymeric resins that exhibited very good affinity towards $Au(NH_3)_2^+$(14). The best sorption towards $Au(NH_3)_2^+$ is displayed by the following polymeric resins: guanylthiourea resin (**1**), 1-methylimidazole resin (**2**) and 2-mercapto-1-methylimidazole resin (**3**) and their affinity towards gold are studied in details in this work.

The basic characteristic of these resins is placed in Table 1.

Influence of $NH_3 \cdot H_2O$, $(NH_4)_2SO_4$ and $NA_2S_2O_3$ Concentration on Gold(I) Sorption

The polymeric resins (**1**–**3**) were used for the removal of gold from ammonium buffer (0.1–100 g/dm^3 $NH_3 \cdot H_2O$, 0.05–50 g/dm^3 $(NH_4)_2SO_4$). The metal uptake as the function of concentration of ammonia solution and ammonium sulphate is presented in Fig. 2.

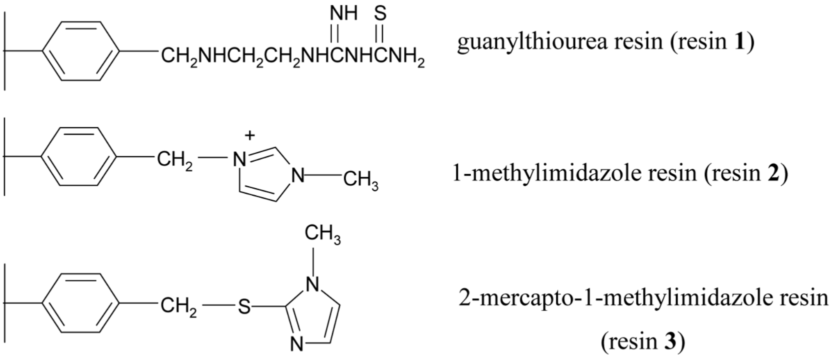

Figure 1. Structure of investigated resins.

The presented above plots show that the concentration of $(NH_4)_2SO_4$ (Fig. 2b) has a significant effect on the uptake of Au. In the case of resins **1** and **2** the sorption decreases sharply in the presence of $(NH_4)_2SO_4$, whereas resin **3** shows much more stable sorption of Au(I) complex, at least up to the 30 g of ammonium sulphate per dm^3. The relatively strong effect caused by ammonium sulphate can be ascribed to its complete dissociation, whereas $NH_3 \cdot H_2O$ ($pK_b = 4.40$) affects the sorption to much smaller extend (see Fig. 2a). The negative effect of the ammonium sulphate concentration on the sorption of gold can be attributed to the competition of ammonium and sulphate ions with gold ammine species on the polymeric resins. Both NH_4^+ and SO_4^{2-} ions are sorbed by resins what is confirmed by XPS analysis. The details of XPS analysis are presented in the next section.

The higher $(NH_4)_2SO_4$ concentration leads also to an increase of solution density which additionally may create some difficulties in the diffusion of $Au(NH_3)_2^+$ to polymeric resins and leads to the decrease in the gold recovery.

Figure 2a presents the effect of $NH_3 \cdot H_2O$ concentration on the sorption of gold on the studied resins. It appears that the sorption of Au on resin **1** decreases with increasing ammonia solution concentration. Resin **3** displays the best sorption of Au at $NH_3 \cdot H_2O$ concentration of 70 g/dm^3. The sorption of gold decreases when the concentration of ammonia solution is greater or smaller than 70 g/dm^3.

In the case of resin **2** the sorption of gold is stable and then increases with increasing $NH_3 \cdot H_2O$ concentration above 70 g/dm^3. It can be suggested that resin **2** as anion exchanger displays no affinity towards ammonium cations, but prefers sulphate anions, which are present in ammonium sulphate solution (Fig. 2b).

Table 1. Characteristics of the polymeric resins

Resin No	Water regain [g/g]	Nitrogen content [mmol/g]	Sulfur content [mmol/g]	Chlorine content [mmol/g]	Ligand concentration [mmol/g]	Yield of modification [%]	Sorption Au [mg Au/g_{resin}]/ ([mmol Au/ g resin])	Sorption Au [mmol Au/ mmol ligand]
1	0.64	8.07	2.87	0.00	1.61	41	12.5 (0.064)	0.390
2	4.00	6.20		0.00	3.10	63	15.5 (0.079)	0.025
3	0.51	4.20	2.19	2.05	2.10	50	7.12 (0.036)	0.017

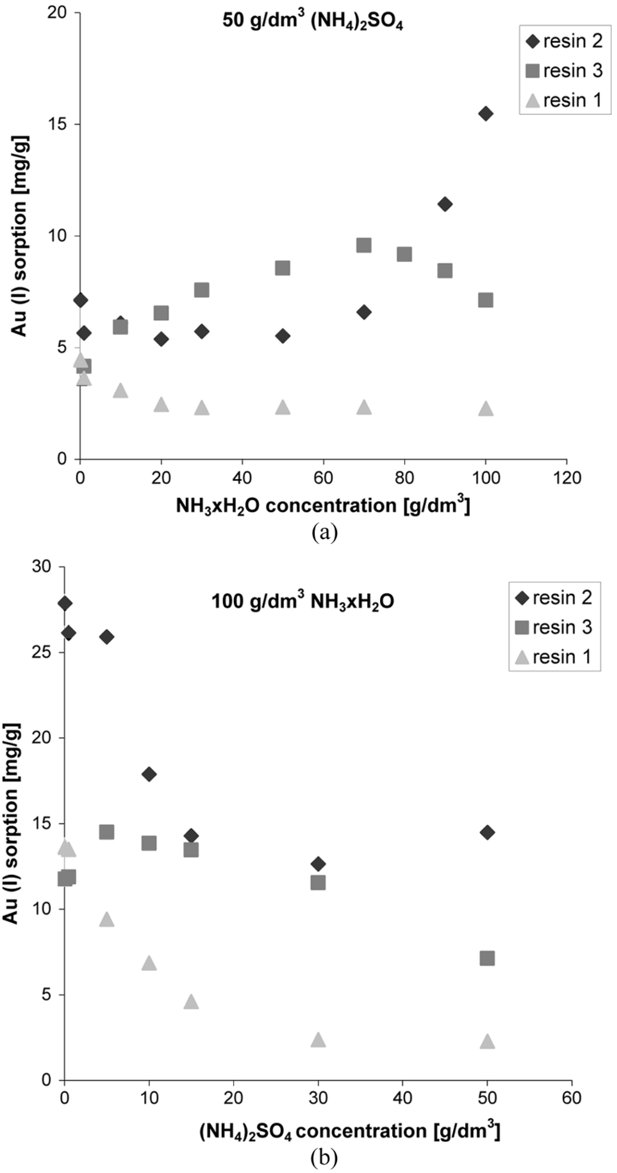

Figure 2. Au(I) sorption as a function of $NH_3 \cdot H_2O$ and $(NH_4)_2SO_4$ concentration.

The best Au(I) sorption can be observed from solution containing 100 g/dm^3 $NH_3 \cdot H_2O$, 5 g/dm^3 $(NH_4)_2SO_4$. For resin **1** it reaches 9.41, for resin **2** 27.9, and for resin **3** 14.5 mg Au/g. All subsequent experiments, including sorption isotherms obtaining and kinetics studies were carried out using this solution.

Effect of Thiosulphate Addition

An addition of sodium thiosulphate to the studied system was used in an attempt to eliminate the strong competition of the cationic species such as NH_4^+ and $Cu(NH_3)_4^{2+}$, which are present in the solution at the concentrations much higher than the targeted $Au(NH_3)_2^+$.

Figure 3 shows the dependence of the sorption of gold(I) on the sodium thiosulphate concentration. Logarithm of stability constant of $Au(NH_3)_2^+$ is $\beta_2 = 26.5$ and in the case of $Au(S_2O_3)_2^{3-}$ equals $\beta_2 = 26.0$ (15). These almost even values suggest that during dissolution of $Na_2S_2O_3$ in ammonium buffer containing gold ammine complexes, $Au(NH_3)_2^+$, the formation of gold thiosulphate anionic complexes takes place to some extend. The presence of these coordination compounds in the solution is observed as an increased sorption of gold on resins (**1**–**3**), especially on resin **2**. It can be explained by the preferential sorption of anionic $Au(S_2O_3)_2^{3-}$ complexes on the anion exchange resins. The 1-methylimidazole resin showed the highest sorption, ca. 95–100 mg Au/g g of resin, at $Na_2S_2O_3$ concentration of 267 mg/dm^3. The gold sorption on resin **2** from ammoniacal-thiosulphate solutions was 7 times higher

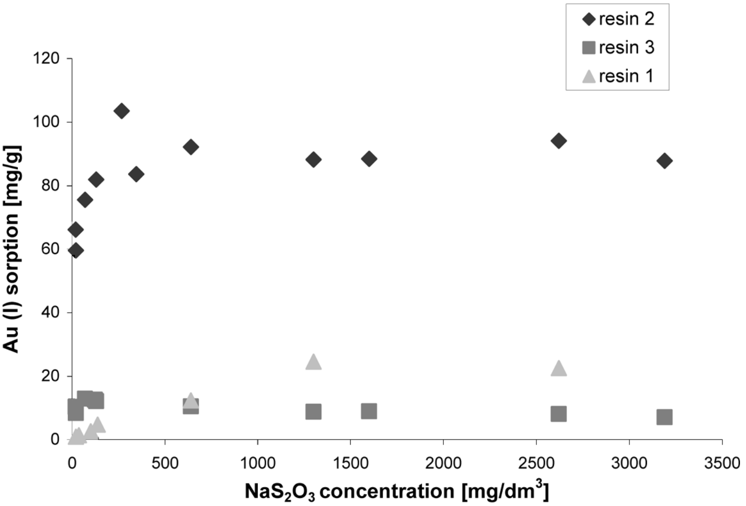

Figure 3. Au(I) sorption as a function of $Na_2S_2O_3$ concentration.

than the sorption from ammonium buffer (100 g/dm^3 $NH_3 \cdot H_2O$, 50 g/dm^3 $(NH_4)_2SO_4$) (14). The resins **1** and **3** displayed twice higher affinity towards gold from solution containing $Na_2S_2O_3$ compared to Au sorption from ammonium buffer (14).

XPS Analysis of Gold Loaded Resins

The XPS analysis suggests that gold is present on the surface of 1-methylimidazole resin (**2**) in the Au(I) oxidation state as two peaks are present: at 85.4 eV and at 87.8 eV (Fig. 4). Both of them can be attributed to the Au(I) complexes and the latter one has the binding energy of Au_{4f} suggesting the presence of neutral and anionic complexes of gold(I). So, the most probable are complexes like $Au(NH_3)(OH)$, $Au(OH)_2^-$. These complexes of Au(I) can exist in ammonium buffer (16). Very interestingly, the comparable results of XPS analysis were obtained in the case of samples D_1 (resin **2** gold loaded from $Au(NH_3)_2^+$ solution in ammonium buffer) and D_2 (resin **2** gold loaded from $Au(S_2O_3)_2^{3-}$ solution in ammonium buffer), despite the fact that the sorption of gold was carried out from two different solution (section 2.2). Sulphur is present in the spectra of D_1 and D_2 and the values of binding energy are 167.9 and 168.2 eV, respectively (Fig. 4). Proximity of binding energy in both cases suggests that sulphur on the resin surface has the same origin. These energy peaks suggests the presence of sulphate ions on the polymeric surface. Very significant is that the characteristic peak for $(S_2O_3)_2^{3-}$ at 162.5 eV is absent in the XPS spectra of the studied D_2 resin. The high-energy peak, which appeared at 532.0 eV can be related to oxygen (O_{1s}). This binding energy of oxygen is typical of many oxygen forms, among them those in sulphate groups. This peak is also characteristic for oxygen of OH^- ions, which are present in ammonium buffer and probably appeared on the polymeric surface as a ligand in $Au(NH_3)(OH)$, $Au(OH)_2^-$ gold complexes.

The XPS spectra for 1-methylimidazole resin (samples D_1 and D_2) showed two peaks that are ascribed to N_{1s} nitrogen atoms. The first one, at 401.3 eV, can be attributed to the aromatic nitrogen. The presence of this peak confirms that 1-methylimidazole groups are attached to the polymeric matrix. The next peak at 399.4 eV can be related to amina ligands, which are present in $Au(NH_3)_2^+(OH^-)$ and $Au(NH_3)(OH)$ species. The XPS spectra indicate that in both samples D_1 and D_2 the same energy peaks appeared for nitrogen and gold.

In order to provide a rational explanation for this fact it is necessary to keep in mind few basic facts about the resin and the solutions. First of all, the resin with 1-methylimidazolium ligands is a medium strength

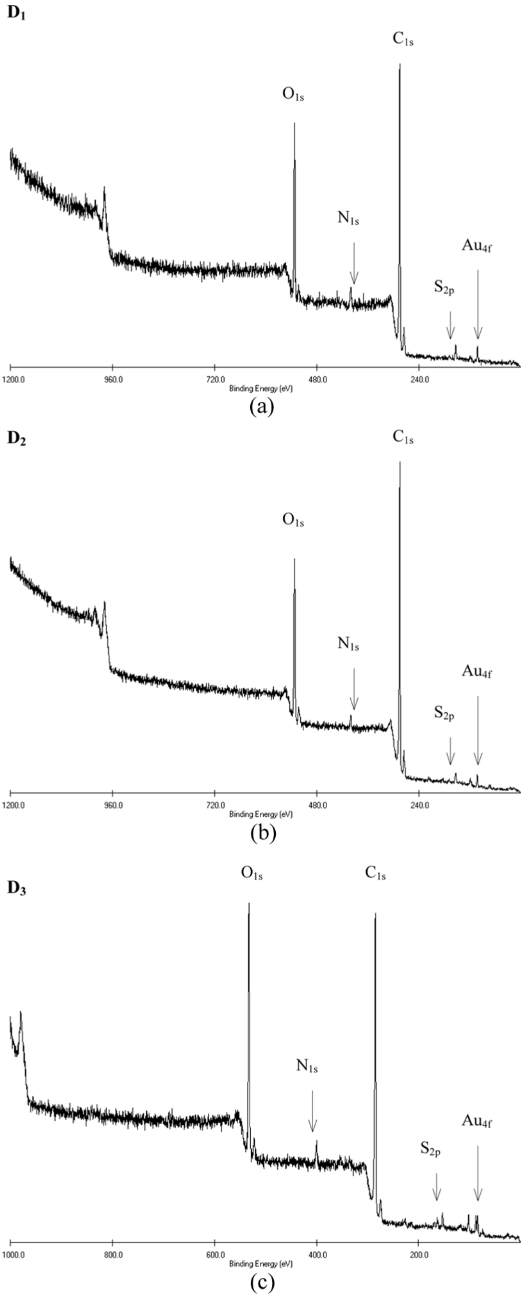

Figure 4. XPS spectra of samples D_1, D_2 and D_3.

anion–exchanger, which means that the main polymeric backbone has a positive charge and is surrounded by the exchangeable anions. Therefore, the binding energy of Au_{4f} at 85.3 suggests that gold is sorbed by resin (samples D_1) in the form of Au(I) but definitely not as $Au(NH_3)_2^+$, as these cations can not enter the resin phase due to the electrostatic repulsion. Peak at 87.3 eV indicates the presence of complexes of gold(I) such as $Au(NH_3)(OH)$, $Au(OH)_2^-$ or ion pair $Au(NH_3)_2^+(OH^-)$. Secondly, the observed marked increase of the gold uptake from the solution that contains thiosulphate must be driven by the presence of $Au(S_2O_3)_2^{3-}$, which is not unexpected because $Au(S_2O_3)_2^{3-}$ as trivalent anions are strongly attracted by an anion-exchanger. But, after reaching the resin phase these complex anions must exchange ligands for OH^- forming $Au(OH)_2^-$, which remain in the resin as a counterion to the imidazolium groups, whereas thiosulphate anions must return to the external solution and thus are not detected by XPS of the resin.

The XPS spectrum for 2-mercapto-1-methylimidazole resin (sample D_3) showed two peaks that are ascribed to N_{1s} nitrogen atoms (Fig. 4). The high-energy peak, at 401.9 eV, can be attributed to the aromatic nitrogen. It clearly shows that 2-mercapto-1-methylimidazole groups are attached to polymeric matrix. The low-energy peak, which appeared at 400.0 eV, can be related to ammonium cations, which are derived from $(NH_4)_2SO_4$. Sulphur is present in D_3 in two forms, what is confirmed by the peaks at 162.9 and 168.9 eV. The first one can be attributed to the organic compounds of sulphur and indicates on the presence 2-mercapto-1-methylimidazole groups in polymer. The second peak suggests the presence of sulphate ions on the polymeric surface. This is supported by a characteristic peak for oxygen in sulphate groups that appears at 532.2 eV. The binding energy of gold (Au_{4f}) is 84.3 eV and suggests the presence of Au on the resin surface as high-dispersed metallic gold but not as gold complexes e.g. $Au(NH_3)_2^+$, $Au(NH_3)(OH)$, $Au(OH)_2^-$ or specific complexes of gold(I) with imidazole ligands.

Sorption Isotherms and Kinetics Studies

For the resins **1**–**3** displaying high affinity towards gold(I) from ammonium buffer solution, sorption isotherms were obtained and plotted in Fig. 5.

The highest sorption of Au(I), 55 mg/g, is reached in the case of 1-methylimidazole resin (**2**). Sorption on guanylthiourea (**1**) and 2-mercapto-1-methylimidazole resin (**3**) is smaller and reaches 20 and 18 mg/g, g, respectively. When the sorption is expressed in terms of mmol of gold per mmol of the ligand, the sorption equals 0.09, 0.04 and 0.06 mmol

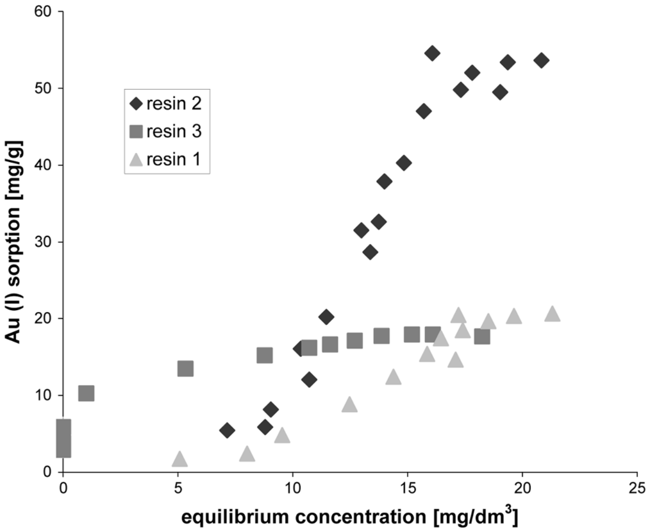

Figure 5. Au(I) sorption isotherms for resins **1**–**3**. Samples of resin containing 0.1–10x molar excess of ligand were shaken with 10 cm^3 of solution containing 21.57 mg/dm^3 of Au(I) in ammonium buffer (pH 11.10) at 23 ± 2°C.

Au(I)/mmol of ligand in the resin **2**, **3,** and **1**, respectively (Table 2). It can be seen that only ca. 5 to 9% of ligand can be utilized in the removal of gold. Resin **3** shows the classical sorption isotherms, i.e. Langmuir isotherm or isotherm of class L. The isotherm of class L describes a horizontal (level) arrangement of adsorbate on surface of adsorbent.

Resins **1** and **2** exhibit some uptake of Au(I) only at the equilibrium concentrations higher than ca. 5 mg/dm^3. These polymeric resins show sorption isotherms of class S. The isotherm of class S describes a vertical orientation of adsorbate molecule in surface of the adsorbent.

The resin with 1-methylimidazole ligands has no free pair of electrons on nitrogen atoms of imidazole rings, which suggested that coordination

Table 2. The characteristic parameters of the sorption isotherms

Resin no	Maximum gold uptake [mg Au/g resin]	Maximum gold uptake [mmol Au/mmol ligand]	Equilibrium concentration [mg/dm^3]
1	20	0.06	17.2
2	55	0.09	16.1
3	18	0.04	15.2

of Au(I) is not the mechanism of gold uptake. This positively charged resin **2** has negatively charged species e.g. OH^-, SO_4^{2-} present as counterions. These species can be exchanged for the anionic complexes of gold, $Au(OH)_2^-$. Alternatively, gold(I) can be sorbed on this polymeric resin as a neutral ion pair, $Au(NH_3)_2^+(OH)^-$ or as neutral complex, Au $(NH_3)(OH)$. The sorption of the ion pair on imidazole resins was suggested by Green (17) in the case of gold(I) uptake from cyanide solutions. He also noticed that the sorption of $Au(CN)_2^-$ Na^+ caused poor elution of gold(I) with 0.1 M NaOH and that the aromatic structure of ligands favoured the sorption of ion pairs.

It seems probable that during the sorption of $Au(NH_3)_2^+$ on resins **3**, the imidazole ligands, having in this case a free electron pair, formed specific complexes of Au(I) by ligand exchange mechanism. Gold(I) can be then coordinated to two nitrogen donor-ligands and has a linear coordination geometry (Fig. 6).

The formation of these complexes might be the reason of a small sorption of gold, because two bulky imidazole groups take part in the formation of one $Au(Im)_2^+$ complex.

The coordination chemistry of gold(I) is studied due to the applications of these metal complexes in medicine, specifically as potential anti-tumor agents (17–21), in bioinorganic chemistry (22, 23) and in

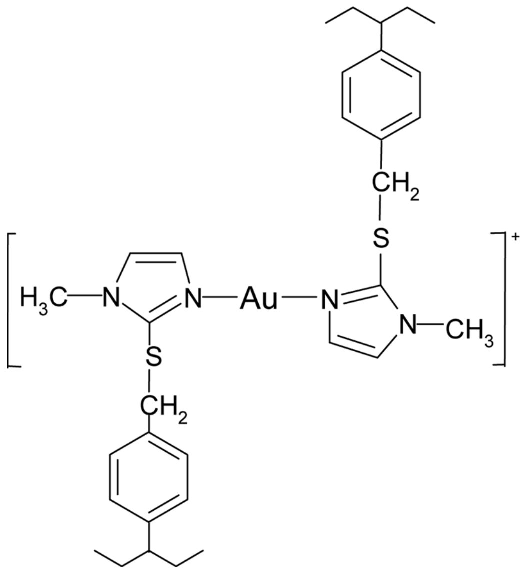

Figure 6. The proposed structure of 2-mercapto-1-methylimidazole resin (**3**) with sorbed gold(I).

catalytic processes (24, 25). So far, numerous works indicate that imidazole forms with transition metals some of the most stable complexes of all heterocyclic-N ligands (26–29). This is caused by the high acid association constant of imidazole. Unfortunately, there is no data concerning the stability constants (log β) of gold(I) imidazole complex. In such case we have to compare the stability constants of metals such as silver(I) and copper(II), which in many respects are similar to gold. For silver(I), the values of log β_2 of $Ag(NH_3)_2^+$ and $Ag(Im)_2^+$ (Im = imidazole) are similar (7.23 and 6.98, respectively); for $Cu(NH_3)_4^{2+}$ and $Cu(Im)_4^{2+}$ the values correspond to 12.95 and 12.78, respectively (15). Comparable values of log β for these metals ammine and imidazole complexes may suggest that $Au(Im)_2^+$ may be as stable complex as $Au(NH_3)_2^+$, what is the necessary condition for the formation of gold complexes on the resin with imidazole groups.

High uptake of gold and the fact that resins do not adsorb $Cu(NH_3)_4^{2+}$ from ammonium buffer (14) makes them potentially useful in the recovery of gold from various sources such as sulphidic and carbonaceous ores and jewellery scrap.

The application of polymeric materials is promising for gold (I) sorption due to a small concentration of gold (4 mg/dm^3) and large quantities of copper (15 g/dm^3) present in solution obtained by ammonia leaching of gold-bearing raw material.

Figure 7 shows the sorption of gold(I) as a function of time. The maximum uptake of gold is reached within 120 hours (Table 3). Gold(I) is sorbed faster at the beginning of the process (50% of maximum uptake is reached after 25–48 h), but later the rate of uptake decreases and 100% of uptake is reached within 5 days.

The resins **1** and **3** showed a similar retention behaviour but for resin **2** is different. It can be explained that resins **1** and **3** have a free pair of electrons on nitrogen and on sulfur atoms. Such electron pairs should be able to coordinate with the gold in ammine complexes, which suggests that the main mechanism of $Au(NH_3)_2^+$ uptake is coordination of metal ions.

In the case of resin (**2**), the absence of a free pair of electrons on nitrogen atoms of imidazole rings suggests that coordination of Au(I) is not the mechanism of gold sorption. The mechanism of gold sorption on 1-methylimidazole resin is explained in the previous section.

In relation to activated carbon, the adsorption rate of gold complexes on this material is relatively fast during the initial stage (compared to the entire adsorption period). The maximum gold adsorption (10 kg Au/t of carbon) was obtained after 120 hours, and the adsorption efficiency was 98% (12). It can be stated that the kinetics of gold(I) adsorption on activated carbon is similar to the sorption kinetics on polymeric resins.

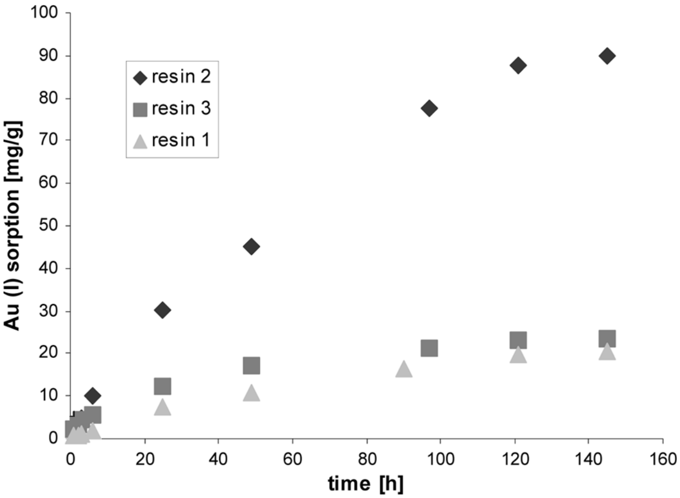

Figure 7. Kinetics of gold(I) sorption on polymeric resins. Samples of resin containing 0.01 mmol of ligand were contacted with solutions containing 10x molar excess of gold ion in ammonium buffer (pH 11.10) at 23 ± 2°C and the concentration was checked at specified time intervals.

Desorption of Gold(I) from the Resins

Desorption of the sorbed gold from the polymeric resins (**2** and **3**) was tried with different eluents: HCl at different concentration, 2 M HCl + 0.3% H_2O_2, 0.16% $Na_2S_2O_3$, ammonium buffer (50 g/dm^3 $(NH_4)_2SO_4$, 100 g/dm^3 $NH_3 \cdot H_2O$), KCN at different concentration, 1% KCN + 0.3% % H_2O_2. This process was carried out at room temperature (24°C) and at 50°C. It was found that each of the eluents was used for desorption of a similar amount of gold on resin. The results are given in Table 4.

It was observed that eluents more effectively desorbed gold from resin at elevated temperature, but the process efficiency is not satisfactory. It

Table 3. The characteristic parameters of the kinetic of gold sorption

Resin no	Maximum gold sorption (S_{max}) [mg Au/g resin]	Maximum gold sorption (S_{max}) [mmol Au/mmol ligand]	Time of S_{max} [h]
1	20	0.06	120
2	88	0.14	120
3	23	0.06	120

Table 4. Elution of gold(I) from resin **2** using different eluent

	Temp. 24°C		Temp. 50°C	
Eluent	Amount of gold on resin [mg]	% Elution	Amount of gold on resin [mg]	% Elution
1 M HCl	0.2087	2.60	0.2118	4.52
2 M HCl	0.2106	1.52	0.2099	3.34
2 M HCl + 0.3% H_2O_2	0.2208	2.74	0.2203	3.81
0.16% $Na_2S_2O_3$	0.2144	6.10	0.2114	13.5
Ammonium buffer	0.2163	0.00	0.2145	4.43
0.2% KCN	0.2098	4.36	0.2157	6.95
1% KCN	0.2156	9.47	0.2154	23.3
1%KCN + 0.3% H_2O_2	0.2151	13.5	0.2156	32.4

can be caused by the formation of anionic complexes of gold during elution and their preferential sorption on polymeric material. Depending on the type of eluent the following reactions can take place:

1. *1–2 M HCl*

$$Au^+ + 2Cl^- = \mathbf{AuCl_2^-} \tag{9}$$

2. *2 M HCl* + 0.3% *H_2O_2*

$$Au^+ + 4Cl^- = \mathbf{AuCl_4^-} + 2e \tag{10}$$

$$H_2O_2 + 2H^+ + 2e = 2H_2O$$

3. *0.16% $Na_2S_2O_3$*

$$Au^+ + 2S_2O_3^{2-} = \mathbf{Au(S_2O_3)_2^{3-}} \tag{11}$$

4. *0.2–1% KCN*

$$Au^+ + 2CN^- = \mathbf{Au(CN)_2^-} \tag{12}$$

5. 1% *KCN* + 0.3% *H_2O_2*

$$Au^+ + 4CN^- = \mathbf{Au(CN)_4^-} + 2e \tag{13}$$

$$H_2O_2 + 2e = 2OH^-$$

The 1-methylimidazolium resin (**2**) is an anion-exchanger and shows preferential sorption of negatively charged complexes of Au. The attempts to elute this metal in the form of anionic complexes are therefore inefficient.

In the case of 2-mercapto-1-methylimidazole resin (**3**), sorbed gold was eluted by 1%KCN + 0.3% H_2O_2 at room temperature (24°C) and 50°C. The result of desorption was comparable in both cases: 47.6% (24°C) and 54% (50°C) and is better compared to the results of Au desorption from resin **2**. It can be explained that gold bonded to resin **3** is bonded to less basic ligands (an imidazole ring is not attached to the polymer backbone directly through the nitrogen atom but indirectly through the sulfur). On the other hand, the XPS analysis showed that Au is present on the surface of 2-mercapto-1-methylimidazole resin as highly-disintegrated metallic gold, which is weakly connected to the resin and can be better eluted by 1% KCN under oxidizing conditions.

CONCLUSIONS

- Polymeric resins (**1**–**3**) are useful for the sorption of Au(I) from ammonium buffer solutions and show preferential sorption of gold from solution containing 100 g/dm^3 $NH_3 \cdot H_2O$ and 5 g/dm^3 $(NH_4)_2SO_4$,
- The presence of large excess of ammonium cations, NH_4^+, and sulphate anions, SO_4^{2-}, in the studied solutions caused a substantial decrease in the gold recovery,
- The resins display higher affinity towards gold(I) from ammoniacal thiosulphate solutions (19.7–3190 mg/dm^3 $Na_2S_2O_3$, 100 g/dm^3 $NH_3 \cdot H_2O$, 50 g/dm^3 $(NH_4)_2SO_4$) than from ammonium buffer solution (100 g/dm^3 $NH_3 \cdot H_2O$, 50 g/dm^3 $(NH_4)_2SO_4$),
- The XPS analysis of 1-methylimidazolium resin gold loaded suggests the presence of gold at Au(I) oxidation state as Au^+ and as complexes: $Au(NH_3)(OH)$, $Au(OH)_2^-$, in the case of 2-mercapto-1-methylimidazole resin gold loaded as highly-disintegrated metallic gold,
- The loaded resins can be regenerated with 1% potassium cyanide solution in 0.3 % hydrogen peroxide solution at elevated temperature (50°C).

ACKNOWLEDGEMENT

We thank Polish Committee for Scientific Research for supporting this work through grant 1 T09B 101 30.

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