Multifunctional Effect of the Polymer Extractant
Thiomethylbenzoxazoyl-α-Methylstyrene on the Extraction of Au(III)

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(Received January 14, 2019; Accepted February 22, 2019)

In this study, we synthesized a polymer extractant and its monomer analogue, and the multifunctional effect was investigated by comparing their extraction behavior for Au(III). To increase the affinity for gold ions, we introduced a sulfur atom into the molecular structure of the extractant as a soft donor. The extraction ability of the new extractants for gold ions was influenced by the HCl concentration in the aqueous feed solution. The multifunctional effect appeared when using the polymer extractant in the liquid–liquid extraction of gold ions. Selectivity of the extractants toward Au(III) was evaluated using a model solution generated from leaching of waste cellphones. Selectivity for Au(III) was found to be enhanced by the multifunctional effect of the polymer extractant.

1. Introduction

Solvent extraction (SX) is one of the most useful methods for the separation of metal ions in industrial processes [1]. The recovery of critical metals from spent wastes has also been conducted using the SX process [2]. To obtain high-purity metals, various extractants have been used for the separation of common and precious metals. Waste materials, when used as secondary resources, often contain a variety of different metals, therefore more efficient extractants are required to provide selective and efficient SX processes. For the selective extraction of metals, size recognition is known to be effective when using macrocyclic ligands, such as calixarenes and crown ethers [3–5]. These cyclic ligands have some advantages of high selectivity for a specific metal ion, utilizing the size-recognition effect [6]; however, such ligands tend to be costly. Such specific characteristics also appear when integrating functional groups or using the chelate or conformation effects [7]. A self-assembly approach for the selective separation of rare-earth metals using multivalent cooperativity was recently reported [8]. It is important to create a novel concept for the development of various types of advanced extractants. Of these, polymer extractants are one of the lesser-known extractant types that present a similar effect to that of macrocyclic compounds. Kubota et al. reported that a polymerized Schiff base ligand showed faster extraction of copper and nickel than that of its monomer analogue [9].

A few polymer extractants have been synthesized and applied to SX [10,11]. In general, a unique
property is induced by the multifunctional groups, known as the “polymer effect” [12]. To our knowledge, some researchers have reported the extraction of precious metals using macrocyclic ligands, such as calixarene derivatives and crown ethers [13–16]; however, so far, no study has been made of the polymer effect on the extraction of precious metals and its selectivity compared with that of the monomer analogue. To investigate the polymer effect on the extraction of Au(III), we synthesized a novel polymer extractant, thiomethylbenzoxazoyl-α-methylstyrene (TBMS), and its monomer analogue, 2-ethylhexyl thiobenzoxazole (EHTO). The extraction behavior of gold ions using both TBMS and EHTO was compared, and the multifunctional effect was discussed with respect to extraction ability and selectivity for Au(III).

2. Experimental

2.1 Synthesis of thiobenzoxazoyl-α-methylstyrene and 2-ethylhexylthiobenzoxazole

The novel TBMS polymer extractant was synthesized by introducing the thiobenzoxazoyl group into the 4-chloromethyl-α-methylstyrene polymer. This polymer was synthesized in our laboratory by free radical polymerization of 4-chloromethyl-α-methylstyrene. 4-Chloromethyl-α-methylstyrene (5 g, 30 mmol) was added to tetrahydrofuran in a round-bottomed flask and mechanically stirred under a nitrogen atmosphere. Azobisisobutyronitrile was added to the solution and reacted at 333 K for 24 h. The solution was added dropwise into methanol. The white precipitates obtained were washed several times with methanol and the 4-chloromethyl-α-methylstyrene polymer was obtained with a yield of 81%. The synthesis scheme of TBMS is shown in Figure 1. First, 4-chloromethyl-α-methylstyrene polymer (5 g, 30 mmol) and potassium carbonate (16 g, 120 mmol) were added to dimethylformamide and mechanically stirred in a round-bottomed flask. Mercaptobenzoxazole (9 g, 60 mmol) was then dropped into the solution, and allowed to react at 333 K for 24 h. The product was dissolved in chloroform and washed once with water and then several times with 0.1 mol dm\(^{-3}\) NaOH. After dehydration of the solution using calcium sulfate, the solvent was evaporated. A yellowish powdery product was obtained with a yield of 84%. The average molecular mass of the polymer extractant TBMS was determined by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry and found to be around 60 000 (degree of polymerization = 215).

The monomer analogue, 2-ethylhexyl thiobenzoxazole (EHTO), was synthesized as a monomer extractant by the same reaction pathway. The synthesis scheme of EHTO is shown in Figure 2. 2-Ethylhexyl bromide (5 g, 26 mmol) and potassium carbonate (14 g, 104 mmol) were added to dimethylformamide and mechanically stirred in a round-bottomed flask. Mercaptobenzoxazole (8 g, 52 mmol) was then added to the solution. A yellowish liquid was obtained with a yield of 90%.

The purified products were identified using proton nuclear magnetic resonance (\(^1\)H-NMR) as follows: thiobenzoxazoyl-α-methylstyrene polymer (TBMS): \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.9\text{--}1.3 \text{ (m, 3H, CCH}_3\text{)}, 2.8\text{--}3.0 \text{ (m, 2H, C–CH}_2\text{–C)}, 4.44 \text{ (brs, 2H, Ar–CH}_2\text{–S)}, 6.1\text{--}7.1 \text{ (m, 4H, C–ArH–C)}, 7.1\text{--}8.1 \text{ (m, 4H, S–ArH)}. 2-ethylhexylthiobenzoxazole (EHTO): \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.82\text{--}0.98 \text{ (m, 6H, CCH}_3\text{)}, 1.19\text{--}1.81 \text{ (m, 9H, C–CH}_2\text{–CH}_2\text{–CH}_2\text{–CH–CH}_2\text{–C)}, 3.35 \text{ (d, 2H, C–CH}_2\text{–S)}, 7.2\text{--}7.6 \text{ (m, 4H, S–ArH)}.}
2.2 Solvent-extraction experiments

All extraction and stripping experiments were carried out using the conventional batch method. The organic phase was prepared by dissolving the extractant, TBMS or EHTO, in chloroform to ensure that the concentration based on the thiobenzoxazoyl group was 10 mmol dm$^{-3}$. The aqueous phase was prepared as 0.1 mmol dm$^{-3}$ Au(III) in hydrochloric acid of a specified concentration. Equal volumes (5 cm$^3$) of the aqueous and organic phase were vigorously mixed using a vortex mixer. Extraction was carried out in a water bath held at 298 K. The concentration of Au(III) in the aqueous feed phase was measured by inductively coupled plasma optical emission spectroscopy (PerkinElmer Optima 8300, USA). The percentage extraction $E$ [%], percentage stripping $S$ [%], distribution ratio $D$ [–], and separation factor $SF$ [–] were calculated using the following equations:

\[ E = \frac{C_0 - C_{aq}}{C_0} \times 100; \quad S = \frac{C_{strip}}{C_{org}} \times 100; \quad D = \frac{C_{org}}{C_{aq}}; \quad SF = \frac{D_{Au}}{D_{M}}, \]

where $C_0$ is the initial metal concentration in the aqueous phase, $C_{aq}$ is the metal concentration in the aqueous phase after extraction, $C_{org}$ is the metal concentration in the organic phase after extraction (calculated by $C_0 - C_{aq}$), and $C_{strip}$ is the metal concentration in the stripping phase after stripping.

3. Results and Discussion

3.1 Effect of contact time on extraction of Au(III)

The effect of contact time on the extraction of Au(III) with TBMS was compared with that of the monomer analogue EHTO. Two different HCl concentrations were prepared: 0.1 mol dm$^{-3}$ and 8 mol dm$^{-3}$, because the protonation of the extractants would change depending on the HCl concentration. The rates of the extraction of Au(III) from aqueous HCl concentrations of (a) 0.1 mol dm$^{-3}$ and (b) 8 mol dm$^{-3}$ are shown in Figure 3. The plots at 0 h indicate the extraction immediately after vigorously mixing by the vortex mixer.
In the case of 0.1 mol dm\(^{-3}\) HCl, the polymer extractant TBMS showed much faster kinetics for Au(III) extraction than that of EHTO. The amount of extraction of Au(III) using TBMS was also greater than that of EHTO. In the case of 8 mol dm\(^{-3}\) HCl, the rate of the extraction of Au(III) with the polymer extractant TBMS was similar to that of the monomer analogue EHTO; however, the extraction amount of Au(III) was higher using TBMS. The polymer extractant showed much better extraction ability for Au(III) compared with that of the monomer extractant. It was thought that the faster extraction rate was caused by the higher surface activity of the polymer extractant: surface activity of a monomer is known to be enhanced by polymerization [17]. Further, the different extraction kinetics between the low and high HCl concentrations in the aqueous phase were probably caused by a change in the extraction mechanism. In general, extraction by coordination of ligands and metals is relatively slow, while extraction via the formation of an ion-pair complex is fast. These results suggested that Au(III) extraction proceeded by a coordination mechanism under low HCl concentration and by ion-pair formation under high HCl concentration.

3.2 Effect of HCl concentration on the extraction of Au(III) using TBMS or EHTO

The effect of HCl concentration on the extraction of Au(III) was studied. The aqueous HCl concentration was changed from 0.01 to 8 mol dm\(^{-3}\). The shaking time was fixed at 72 h. Figure 4 shows the extraction behavior of Au(III) from the different HCl concentrations using TBMS or EHTO. The extraction of Au(III) using TBMS was twice as high as that using the monomer analogue, while the extraction tendency for both the extractants was similar. The degree of extraction of Au(III) decreased with an increase in the HCl concentration to 3 mol dm\(^{-3}\), and then increased again with an increase in the HCl concentration to 8 mol dm\(^{-3}\).

Sulfur is a soft element that has a high affinity for soft metals like Au and other precious metals [18]. Oxazole is a weak base and the \(pK_a\) of its conjugate acid is known to be 0.8 [19]. At low HCl concentrations, Au(III) was considered to be extracted by coordination with the S atom in the extractant; at high HCl concentrations, it would be extracted through the formation of an ion pair with the protonated N atom in the
benzoxazoyl group. We confirmed the cationic nature of the polymer extractant by the fact that a N–H stretching vibration at 3500 cm$^{-1}$ appeared in its infrared spectrum after contacting it with 8 mol dm$^{-3}$ HCl. The higher extraction ability of TBMS is thought to be obtained by the multifunctional effect of the polymer extractant that is caused by the adjacent group effect which holds the metal complex by the long polymer chains.

Based on these results, it can be said that the polymer extractant exerted a strong influence on the formation of an inner-sphere complex. In other words, the newly synthesized polymer extractant increased the coordination ability for gold ions.

### 3.3 Selectivity study

To investigate the polymer effect on the metal extraction selectivity, a model solution representing that generated by the leaching of waste cellphones was used as the aqueous feed solution. The composition referred to our previous study on cellphone leachate and was prepared using 10 mg dm$^{-3}$ each of Au(III), Pd(II), Pt(IV), Ni(II), Cu(II), Zn(II), Fe(III), Al(III), and Pb(II) in 0.1 mol dm$^{-3}$ HCl [20]. The extraction behavior of these metals using TBMS or EHTO is shown in Figure 5.

The extraction of Au(III) using TBMS was three times higher than that of EHTO, while the other metals were not effectively extracted. In contrast, the monomer analogue extractant EHTO did not show effective extraction for any of these metals. In particular, Pt(IV) was not extracted at all due to steric hindrance between the bulky aromatic ring in the extractant and the octahedral structure of Pt(IV). In a preliminary experiment using a Pt(IV) single-metal solution, Pt(IV) was confirmed to be very poorly extracted under
these experimental conditions. Comparison with the behavior of Au(III) using a single-metal solution, extraction of Au(III) in the mixed-metal system was inhibited by the presence of other metals using both TBMS and EHTO; however, the polymer extractant TBMS still showed a higher extraction ability for Au(III), even in the mixed-metal solution. The separation factors for Au(III) over the other metals are listed in Table 1. All separation factors for the polymer extractant TBMS were higher than those of the monomer analogue, EHTO. We confirmed that the polymer effect is useful for enhancing selectivity.

3.4 Stripping study

Stripping experiments were carried out using 3 mol dm\(^{-3}\) HCl, 1 mol dm\(^{-3}\) HNO\(_3\), 1 mol dm\(^{-3}\) H\(_2\)SO\(_4\), and 0.1 mol dm\(^{-3}\) thiourea in 1 mol dm\(^{-3}\) HCl as stripping solutions [21]. After extraction of Au(III) with TBMS, the organic and stripping phases were contacted at equal volumes (5 cm\(^3\)) and shaken at 298 K. The degree of stripping of Au(III) using each solution is summarized in Table 2. Au(III) was found to be effectively stripped using 0.1 mol dm\(^{-3}\) thiourea in 1 mol dm\(^{-3}\) HCl aqueous solution within 24 h, while Au(III) was hardly stripped at all by conventional acidic solutions, such as 3 mol dm\(^{-3}\) HCl, 1 mol dm\(^{-3}\) HNO\(_3\), or 1 mol dm\(^{-3}\) H\(_2\)SO\(_4\). Such effective stripping of Au(III) with thiourea is due to the high affinity of thiourea for gold ions: it is known to form a stable cationic complex [22].

| time[h] | 3M-HCl | 1M-HNO\(_3\) | 1M-H\(_2\)SO\(_4\) | 0.1M-thiourea (1M-HCl) |
|---------|--------|--------------|-----------------|------------------------|
| 24      | 9.1    | 0            | 0               | 94.5                   |
| 48      | 5.0    | 0            | 0               | 95.8                   |
| 72      | 3.8    | 0            | 0               | 94.1                   |

(“M” is defined as “mol dm\(^{-3}\)”)

4. Conclusions

A novel polymer extractant, thiomethylbenzoxazoyl-\(\alpha\)-methylstylene polymer (TBMS), and its monomer analogue extractant, 2-ethylhexylthiobenzoxazole (EHTO), were synthesized. The polymer extractant TBMS showed faster extraction kinetics and higher extraction ability toward Au(III) compared with that of the monomer analogue. In the selective extraction from a simulated waste cellphone leaching solution, the polymer extractant TBMS showed high extraction selectivity for Au(III) and other common base metals were not extracted. In the stripping study, Au(III) was effectively stripped using 0.1 mol dm\(^{-3}\) thiourea in 1 mol dm\(^{-3}\) HCl.

Based on these results, it was confirmed that the multifunctional effect of the polymer extractant on the extraction of Au(III) was influenced by the formation of an inner-sphere complex that is stabilized due to the adjacent group effect. The polymer effect was also effective for ion-pair extraction. Further investigation of surface interaction and the spectroscopic analysis of extracted complexes would provide more details of
the multifunctional effect of the polymer extractant.

Acknowledgement

This work was supported by the Environment Research and Technology Development Fund (Grant No. 3-1710) of the Ministry of the Environment, Japan. We thank Kathryn Sole, PhD, from Edanz Group (www.edanzediting.com/ac) for editing a draft of this manuscript.

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