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REVIEW ARTICLE

Progress in gold solvent extraction*

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Abstract Gold solvent extraction has been used to recover gold by analytical chemists for about one century. Due to the potential advantages of solvent extraction technology over present zinc-dust cementation and carbon-adsorption procedures in gold recovery, metallurgists have paid much attention to the study of gold solvent extraction in recent years. Some promising extraction systems were proposed and studied. Recently some new progress in gold solvent extraction have been achieved in our research group. In the mechanism study on quaternary amine extraction system, a supramolecular structure model based on hydrogen bonding between modifier and $Au(CN)_2^-$ was proposed. For the stripping of quaternary amine extraction system, a procedure based on $NaClO_4$ solution and saturated KCl solution was reported.

Keywords: gold, solvent extraction, IR spectrum, stripping.

The recovery of metals by solvent extraction processes has been widely used in industry. In the case of gold, the potential advantages of solvent extraction technology over present zinc-dust cementation and carbon-adsorption procedures have prompted metallurgists to pay much attention to the study of gold solvent extraction in recent years. This method has been used to recover gold by analytical chemists for about one century.

In the present paper, the studies of gold solvent extraction is reviewed comprehensively. The new progress made by our research group are reported.

1 History of gold solvent extraction

Gold solvent extraction was first reported in 1911, when Mylius used ether to extract $HAuCl_4$ from hydrochloride medium by solvation extraction[1]. Later, in 1926 Lenher and Kao investigated the extraction behavior of about twenty ester compounds for $HAuCl_4$ and found that ethyl acetate had the highest loading capacity among the examined extractants[2]. After that, more and more extractants

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were found to be suitable for gold solvent extraction. These extractants covered a wide variety of organic compounds, including organic phosphorus oxide compounds[3], amines[4—7], some sulphureous compounds[8—10], etc. Generally, the gold solvent extraction by oxygenous compounds follows a special solvation extraction mechanism. Amine extractants extract gold by an ion-association mechanism. Some sulphureous compounds such as dialkyl sulphide, dialkyl phosphorodithioate and diethyldithiocarbamate (DDC) can coordinate with gold during extractions, therefore, these extraction systems follow some coordination mechanism.

Some special types of extractants have also been studied for gold solvent extraction. For example, Murphy et al. used tetraphenyl arsonium to extract $AuCl_4^-$ into chloroform. And the extracted species was supposed to be an ion pair of $[(C_6H_5)_4As]^+[AuCl_4]^-$[11]. Cotton and his coworker described a method for the micro-determination of gold, in which *p*-dimethylaminobenzylidene rhodanine was used to extract $HAuCl_4$[12].

2 Classification of gold solvent extractions

According to their difference in extraction mechanisms, gold solvent extraction systems can be classified into three types: solvation extraction, ion-association extraction and coordination extraction.

Gold solvent extraction can also be classified into univalent gold (Au(I)) extraction and trivalent gold (Au(III)) extraction according to the gold valence in aqueous phase. In the analytical chemistry of gold, most extraction systems belong to Au(III) extraction, in which Au(III) is extracted from acidic solutions to organic phases. For industrial application, the Au(I) extraction systems are the commonest ones because in gold recovery gold exists as $Au(CN)_2^-$ anion in alkaline cyanide solutions.

3 Studies of gold solvent extraction for gold recovery

In recent years, more and more studies on this subject have been carried out by metallurgists[13]. The long-term objective of metallurgists is to develop a selective extraction procedure for $Au(CN)_2^-$ from alkaline($pH > 9.4$) cyanide solution in place of the well-established zinc-dust cementation and carbon-adsorption procedures. So far six extraction systems have been proposed i.e. amine system[14—23], organic phosphorus oxide compound system[24—26], guanidine system[27], sulfoxide and sulfone system[24], imidazoline system[28] and crown ether extraction system[29], among which, amine extraction system is the most promising system from the viewpoint of practical applications.

Quaternary ammonium salts are the earliest used extractants for gold recovery from alkaline cyanide liquor[14]. Recent investigations have further revealed that quaternary ammonium salts such as Aliquat 336 possess a good selectivity for gold over basic metals and a high loading capacity. It was also found that gold could either be stripped by acidic thiourea and air sparging or be recovered in metallic form by incinerating the organic solvent. A small pilot plant demonstrated the feasibility of the extraction system in industry[16].

Simple amines including primary, secondary and tertiary amines are also prospective extractants for gold recovery. Generally, the affinity of simple amines for $Au(CN)_2^-$ is very low at a higher pH value and no simple amine can extract gold from alkaline ($pH > 9.4$) cyanide solutions efficiently. This extraction property of simple amines greatly hampered their use in $Au(CN)_2^-$ extraction from real cyanide solution. In 1983, Mooiman et al. published their significant finding that the addition of some organic phosphorus oxide compounds could greatly increase the affinity of simple amines for $Au(CN)_2^-$ at a higher pH value[18]. This finding means that it is possible to use simple amines to extract $Au(CN)_2^-$ from alkaline cyanide solutions. Afterwards, investigations on various aspects of these modified extraction systems were made by Miller and his coworkers[17, 19].

In a mechanism study, Miller assumed that the extraction mechanism was ion-association plus solvation, which can be represented by the following equation:

$$[Am]_o + [H^+]_a + [Au(CN)_2^-]_a + n[M]_o = [Am\ H^+\ Au(CN)_2^- \cdot nM]_o$$

where Am stands for amine; M, modifier; subscript a, aqueous phase; subscript o, oil phase.

Further IR studies showed that CN stretching vibration did not change after extraction. Based on the spectroscopic results, Miller deduced that there was no special interaction between modifiers and $Au(CN)_2^-$.

Alguacil et al. also conducted extensive studies on extraction mechanism for amine extraction system[20—23]. Based on the IR studies on loaded organic phases, they drew the same conclusion as Miller's that there was no special interaction between $Au(CN)_2^-$ and its surroundings.

4 New progress in gold solvent extraction

At present, a joint project sponsored by Peking University and Yunnan Province on gold(I) extraction from alkaline cyanide liquor is underway in our research group. Our research focuses on two aspects of gold solvent extraction, i.e. the microscopic extraction mechanism and the development of a solvent-in-pulp procedure for industrial application. Here we report our new progress in these two aspects. Due to some practical consideration, our work mainly focused on the extraction system based on quaternary ammonium salts.

4.1 Supramolecular microstructure models

In the past, the commonest approach to extraction mechanism was through equilibrium distribution study, where the data were fitted into an extraction equation, in order to determine species stoichiometry. The drawback of the traditional method is that both the aqueous phase and organic phase were considered as homogeneous solutions (or real solutions) and the differences in microstructure among different extraction systems were ignored. In our opinion, the complex chemistry occurring in extraction procedures may lead to complex microstructures in organic and aqueous phases, which means that in many cases both phases are heterogeneous. Therefore, the microstructure should be an important aspect in the study on extraction mechanism, otherwise the understanding of extraction mechanism will be incomplete. Based on this consideration, the microstructure has been the major subject in the study on extraction mechanism in our group for decades.

In 1980 we reported our significant finding that saponified extractants could form reverse micelle (or water/oil microemulsion) in organic phases in some rare earth extraction systems[30]. Further FT-IR studies revealed that the polar head of saponified extractants were hydrated[31, 32]. It was also found by dynamic light scattering (DLS) that oil/water microemulsion could be formed in the aqueous phase in these rare earth extraction systems[33].

Besides micelle microstructure model, aggregate is another type of microstructure model found in the study of extraction mechanism. For example, it has been found that linear aggregates would be formed in some extraction systems under appropriate conditions[34—36].

In our previous studies, a variety of physicochemical techniques including FT-IR, nuclear magnetic resonance, dynamic light scattering, fluorescence and transmission electron microscopy have been successfully used to investigate the microstructures of extraction systems. Among these techniques, FT-IR was found to be a powerful tool for microstructure studies. In many cases, some characteristic frequencies of the loaded organic phases can be used as the microstructure probes to help us to understand the extraction mechanism on a molecular level.

Figure 1 shows the CN stretching vibrations of loaded organic phases in three extraction systems: N263/xylene, N263/tributyl phosphate(TBP)/*n*-dodecane and N263/2-ethyl hexanol(*iso*-octanol)/*n*-dodecane (N263 is a commercial quaternary ammonium salt similar to Aliquat 336).

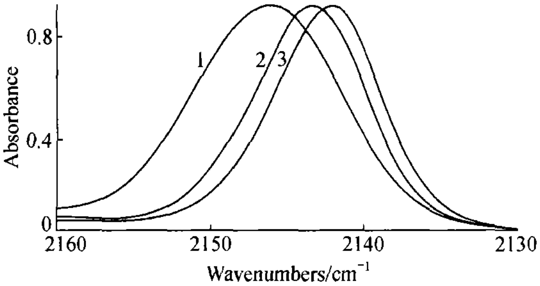

Fig. 1. $C\equiv N$ stretching vibrations in loaded organic phases 1, N263/isooctanol/dodecane; 2, N263/TBP/dodecane; 3, N263/xylene.

It can be seen that the CN stretching vibrations of loaded organic phases in these three cases are different not only in peak frequency but also in bandwidth. This significant finding conflicts with the results obtained in both Miller[24] and Alguacil's work[25, 26], in which the CN stretching vibrations were found unchanged in extraction. Further improvement of resolution reveals that the fine structures of CN stretching modes in these three systems are also different. Fig. 2 shows the second and fourth derivative spectra of CN stretching modes in loaded organic phases of the three extraction systems. It can be inferred from these findings that the microstructures of the loaded organic phases in the three systems should be different and there must be some special interactions between modifier and

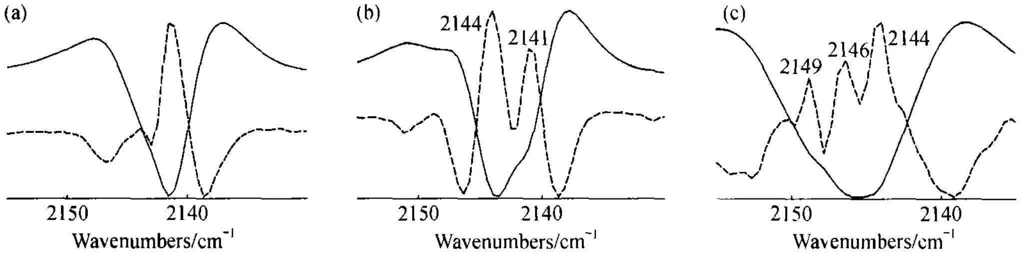

Fig. 2. Second and fourth derivatives of $C\equiv N$ stretching band (a) N263/xylene; (b) N263/TBP/dodecane; (c) N263/isooctanol/dodecane. ——, the 2nd derivative; -----, the 4th derivative.

$Au(CN)_2^-$ anion. In order to explain the IR difference in CN stretch of different extraction systems, three microstructure models including two supramolecular structures for the loaded organic phases have been proposed, which are schematically illustrated in figure 3.

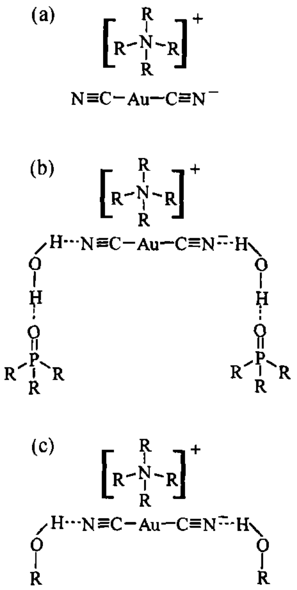

Fig. 3. Probable microstructure models in loaded organic phases (a) N263/xylene; (b) N263/TBP/dodecane; (c) N263/isooctanol/dodecane.

4.2 Stripping of gold from quaternary ammonium salt extraction system

It is well known that because of their high affinity for gold(I) cyanide complexes, quaternary ammonium salts are not readily stripped. Although acidic-thiourea solution can elute gold efficiently, the formation of high toxic HCN during stripping makes this procedure unsuitable for industrial application. In fact, the industrial application of quaternary amines for gold recovery from cyanide solutions has been hampered by this stripping procedure for many years. Herein we propose a new stripping procedure using $NaClO_4$ solution and saturated KCl solution. The principle of this new procedure can simply be depicted by the following two equations:

Stripping of gold

$$[R_4NAu(CN)_2] + [NaClO_4]_a \rightleftharpoons [R_4NClO_4]_o + [NaAu(CN)_2]_a \quad (1)$$

$$\downarrow$$

a: aqueous phase o: oil phase

Regeneration of organic phase

$$[R_4NClO_4]_o + [KCl]_a \rightleftharpoons [R_4NCl]_o + KClO_4\downarrow \quad (2)$$

a: aqueous phase o: oil phase

It can be seen that $Au(CN)_2^-$ can be stripped by ClO_4^- first and then N263 regenerated by KCl.

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