

Investigation on the Extraction Mechanism of Au (I) from Cyanide Solution with Quaternary Ammonium System

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Abstract: The mechanism of Au (I) extraction has been characterized using ^{198}Au radiometry, thermodynamic equilibrium, Karl-Fischer titration and FT-IR spectroscopy techniques. The results indicate that the extraction follows ionic combination and solvent interaction mechanism. The stoichiometry of the extracted species is 1:1:4:4 for $\text{TDMBA}^+ : \text{Au}(\text{CN})_2^- : \text{TBP} : \text{H}_2\text{O}$. The microstructure model of the extracted complex is a supramolecular structure *via* hydrogen bonding, ion dipole interaction and ionic combination. The extraction process can be described as micelles in the aqueous phase transfer into the organic phase and reversed micelles or microemulsion (W/O) form in the organic phase.

Keywords: Solvent extraction, $\text{Au}(\text{CN})_2^-$, FT-IR, tetradecyldimethylbenzylammonium chloride (TDMBAC).

During the past decades, there has been a renewed interest in the application of solvent extraction to the recovery of Au (I) from cyanide solutions^{1,2}. Among those various extractants, the amine extractants with the addition of organic phosphorus oxide as cosolvent have been widely investigated^{3,4}. Various diluents and modifiers have been selected to optimize the extraction system so as to increase the loading capacity, improve the selectivity and/or reduce emulsification⁵. Quaternary ammonium salts have also been used to partition gold and regarded as excellent extractants due to their high loading capacity over a broad range of pH values. However, the extracted Au (I) is not readily stripped from the quaternary ammonium-diluent solutions because of their high affinity to the aurocyanide complex.

Tetradecyldimethylbenzyl chloride (TDMBAC) is a comparatively weak-base. We found that TDMBAC was an excellent extractant for the separation of Au (I) from cyanide solution if a modifier such as tri-*n*-butyl phosphate (TBP) or long-chain alcohol was added. Furthermore, the stripping was much easier with diglylenethioether, glycol or ammonium thiocyanate. The experiments indicate that the extraction of Au (I) follows the ion-combination and solvent interaction mechanism. The extraction process can be described by microemulsion mechanism.

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Results and Discussion

Au(CN)₂⁻ Extraction and Stripping

The extraction percentage of Au (I) depends upon the concentrations of TDMBAC, TBP and Au(CN)₂⁻. Initially, the extraction percentage (*E*) linearly increases with the increase of the molar ratio of TDMBAC to aurocyanide, *n_r*, and then approaches to its saturation value 100% when *n_r* reaches 1. This indicates that the molar ratio of TDMBA⁺ to Au(CN)₂⁻ in the extracted complex is 1:1.

The modifier TBP also plays an important role. Almost all of the Au (I) remains in the aqueous phase without the addition of TBP. As the content of TBP increases, the extraction percentage increases markedly. When TBP content reaches 15%, most of Au (I) is extracted into the organic phase. When ϕ is less than 10%, $\log D$ is a linear function of $\log \phi$ with a slope $k=4.2\pm 0.2$, where *D* and ϕ represent the distribution ratio of Au(CN)₂⁻ and the volume percentage of TBP, respectively. The results suggest that four TBP molecules can be proposed to participate in the formation of extracted species.

When the Au (I) concentration is extremely low, such as 0.4 mg/L, the extraction percentage can reach 95% when *n_r* is bigger than 1. Both the extraction at normal Au (I) concentration and low concentration suggest that TDMBAC is an efficient extractant for the Au (I) separation.

Au (I) can be efficiently transferred from the loaded organic phase to the aqueous phase with certain concentration of diglylenethioether (DGTE), glycol (GLY) or ammonium thiocyanate. When the concentration of NH₄SCN is 2.0 mol/L, the stripping percentage reaches 97%.

FT-IR Spectroscopy of the Au (I) Loaded Organic Phase

The water content in the organic phase at different Au (I) concentrations was determined by Karl-Fischer titration. The results indicate that the water concentration in the organic phase increased with the increase of Au concentration. FT-IR spectroscopy was used to analyze the microstructure of water in the organic phase. There are at least three types of P=O group around 1286 cm⁻¹, 1272 cm⁻¹ and 1234 cm⁻¹, which are assigned to the unhydrated, weakly hydrated and hydrated P=O stretching vibration, respectively. The intensity of the peak around 1286 cm⁻¹ decreases, while that of 1272 cm⁻¹ increases with the increase of Au (I) concentration. This means that the interaction of water with TBP increases with the increase of gold concentration.

In order to investigate the water component and its roles in the organic phase, the bands of O-H stretching vibration in the range from 3270 to 3720 cm⁻¹ with different gold concentration were analyzed by the Fourier self-deconvolution technique. The Fourier self-deconvolution spectra of O-H bands for the organic phase with 8 g/L gold shows that there are six subpeaks of O-H stretching vibration, around 3689, 3631, 3561, 3500, 3451 and 3389 cm⁻¹, respectively. The subpeak around 3689 cm⁻¹ is assigned to free water trapped by alkyl chains of heptanes or surfactants. Its intensity does not change much as the gold concentration increases. The peaks around 3631 and 3561 cm⁻¹

are attributed to O-H stretching vibration of water binding to Lewis bases such as P=O in the organic phase. The peak around 3500 cm^{-1} is due to the bulk-like water, while IR bands of the bounded water by interaction with Lewis acids such as the head group of quaternary ammonium salt, are located around 3451 and 3389 cm^{-1} .

The curve-fitting method can also be used to provide an estimation of the fraction of each water component. The results show that the fraction of water binding to the comparatively weak Lewis base or Lewis acid, represented by subpeaks around 3560 and 3450 cm^{-1} , increases with the increase of gold concentration ranging from 1 to 10 g/L , while the fraction of bulk-like water decreases. Then, the possible number of water participating in the formation of extracted species is estimated to be 4 according to the fractions of water binding to the comparatively weak Lewis base and Lewis acid, which are regarded as the interaction of water with the headgroup of TBP and TDMBA⁺ cation.

Extraction Mechanism and Extraction Process of Au (I)

The thermodynamic equilibrium and FT-IR measurements above suggest that the extraction follows the ion-combination and solvent interaction mechanism. The species in the organic phase is $[\text{TDMBA}^+]\cdot[\text{Au}(\text{CN})_2^-]\cdot 4\text{TBP}\cdot 4\text{H}_2\text{O}$. The microstructure model is a supramolecular structure based on the hydrogen-bonding of water with TBP and $\text{Au}(\text{CN})_2^-$, the ion-dipole interaction of hydrated TBP molecules with TDMBA⁺ and the ionic combination between such two large supramolecular anion and cation.

Similar to CTMAB, TDMBAC also has a long hydrophobic chain and a hydrophilic head group. Micelles form when the concentration reaches its critical micelle concentration (CMC). When $\text{KAu}(\text{CN})_2$ aqueous solution is added into a TDMBAC-rich solution, emulsion is formed. After agitation, the aqueous phase turns into transparent. This means that micelles exist either before or after the addition of aurocyanide solution. When an organic phase containing TBP or long-chain alcohol is added into an aqueous gold-rich solution, micelles in the aqueous phase transfer into the organic phase and turn into oil-wrapped water (W/O) microemulsion or reversed micelles. Dynamic laser scattering (DLS) method testified its possibility. When gold concentration in the organic phase reaches 9.8 g/L , aggregations form in the organic phase. The average radii of micelles are 5.3 and 8.5 nm when gold concentrations are 9.82 and 10.87 g/L , respectively. With the further increase of gold concentration, the organic phase splits into two layers. Au (I) and water are mainly located at the lower layer. The results demonstrate that the extraction process can be described by microemulsion mechanism.

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References

1. A. H. Schwellnus, B. R. Green, *Solvent Extraction and Ion Exchange*, **1990**, 8, 223.
2. A. M. Sastre, A. Madi, F. J. Alguacil, *J. Chem. Technol. Biotechnol.*, **1999**, 74, 310.
3. G. Ma, W. F. Yan, T. D. Hu, J. Chen, C. H. Yan, H. C. Gao, J. G. Wu, G. X. Xu, *Phys. Chem. Chem. Phys.*, **1999**, 1, 5215.
4. J. Z. Jiang, W. J. Zhou, H. C. Gao, J. G. Wu, G. X. Xu, J. Chen, *Chinese J. Inorg. Chem.*, **2001**, 17 (3), 343.
5. R. Y. Wan, J. D. Miller, *Mineral Processing and Extractive Metallurgy Review*, **1990**, 6, 143.

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