RESEARCH ON THE INTERFACIAL PROPERTIES,
EXTRACTION EQUILIBRIA, AND KINETICS OF VARIOUS
TYPES CALIX[4]ARENE DERIVATIVES FOR EXTRACTIVE
SEPARATION OF PRECIOUS METALS

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RESEARCH ON THE INTERFACIAL PROPERTIES, EXTRACTION EQUILIBRIA, AND KINETICS OF VARIOUS TYPES CALIX[4]ARENE DERIVATIVES FOR EXTRACTIVE SEPARATION OF PRECIOUS METALS

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Abstract of the Thesis

Having a wide range of applications in mind, the growing economic impact of precious metals can be understood quite easily. Precious metals and their compounds have been widely used in the automobile, electroplating, chemical, and petroleum fields. Precious metals are also used as conductors in the electrical and electronic industries, in extrusion devices, in dental and medical prostheses, and in jewelry. Due to characteristics such as the resistance to corrosion and oxidation, high melting points, electrical conductivity, and catalytic activity, precious metals are extremely useful in various fields. However, the separation and purification of these metals are usually difficult because of their similar properties and chemical behavior. It is essential that efficient approaches for the separation and purification of precious metals have been developed. Solvent extraction is one of major separating operation technology in hydrometallurgical processes. The preparation of selective and useful extractants with property of the extractants which affect efficiency of extraction process for the separation of precious metals is necessary, because predominantly and mutual separations in some metal media are still poor. Macrocyclic ligands, in using as the extractant are fascinating which provide rigid and three-dimensionally arranged cyclic structure. They have been designed with the principle of ion recognition, synthesized and examined in their capability to extract precious metals. A recent development in the complexant field is the recognition that calixarenes may be useful extractants for precious metals, and possibly make a contribution toward alleviating some of the problems associated with the application of the traditional macrocyclic crown ethers and cryptands for extraction purposes. Thus, in this research work, three types p-tert-octylcalix[4]arene derivatives such as ketonic- (methyl
ketonic and phenyl ketonic), amido- (dibenylamido and diethylamido), and heterocyclic- (2-quinolyl and 2-pyridyl) types derivatives have been prepared as the hydrophobic extractants for precious metals. The property of three types $p$-tert-octylcalix[4]arene derivatives based on the different chemical structure is extremely different such as natural (ketonic-), high polarity of amide group (amido-), and high electron density of nitrogen atom with lone pair electrons (heterocyclic-types) derivatives. For Ag extraction was conducted in nitric acid media because silver was precipitated as silver chloride for the hydrochloric acid concentration less than 3 M. Therefore, it can be expected that different extraction equilibria and kinetics by using three types $p$-tert-octylcalix[4]arene derivatives with the different chemical structure are observed.

First, extraction behavior with ketonic- and amido- types $p$-tert-octylcalix[4]arene derivatives was investigated for the separation of precious metals by the batch-wise method in nitric acid media. Both of them exhibited extremely high extraction ability and selectivity towards Ag and Pd. However, the solvent extraction rate for Ag and Pd between two derivatives showed large difference at 0.1 and 1.0 M nitric acid concentrations. Slight differences on their chemical structures cause such significant difference on the extraction rate for Ag and Pd. In order to determine the stoichiometry of Pd extraction with both derivatives and to understand the difference in extraction behavior based on the structural effect, the effects of the extractant concentrations on the distribution ratio were also investigated.

Second, the solvent extraction kinetics were investigated with three types $p$-tert-octylcalix[4]arene derivatives such as ketonic- (methyl ketonic and phenyl ketonic), amido- (dibenylamido and diethylamido), and heterocyclic- (2-quinolyl and 2-pyridyl) types derivatives. Researches on the solvent extraction kinetics are necessary and very important to reveal mechanism of the extraction process. It is interesting to find ways for improvement of
the extraction rate via the investigation on kinetics in nitric acid media.

In more detail, in framing the mass transfer mechanism of the solvent extraction, the key is how the interface-active species, their molecular forms and interfacial concentrations are known. Since such properties related to interface-active species directly reflect on the interfacial tension, it is meaningful to investigate more clearly the interfacial phenomena in the solvent extraction process. Thus, the interfacial phenomena of various types \( p\text{-}\text{tert-octylcalix}[4]\text{arene derivatives} \) were investigated. From the obtained results, it was found that the Ag extraction rate directly corresponded to the interfacial activity of extractants. Then, it was proposed mass transfer mechanism and rate determining step in nitric acid media.

As the advanced study, exact information about extraction kinetics and mechanism is necessary. The modified Lewis cell was used to perform the solvent extraction kinetics of Ag extraction with methyl ketonic \( p\text{-}\text{tert-octylcalix}[4]\text{arene derivative} \) in nitric acid media. From these results, the extraction rate equations and mechanism of Ag extraction with methyl ketonic \( p\text{-}\text{tert-octylcalix}[4]\text{arene derivative} \) were proposed in nitric acid media. Besides, the study of thermodynamic parameters indicated an exothermic nature of adsorption and a spontaneous process in the modified Lewis cell system.

Consequently, based on the results, the differences in specific solvent extraction ability, extraction rate, the interfacial activity, and adsorption effectiveness were discussed with the different functional groups of various types \( p\text{-}\text{tert-octylcalix}[4]\text{arenes} \). Finally, mass transfer mechanism and rate determining step were proposed in the liquid-liquid system.
Summary

By the survey of the literature, it is well known that precious metals which possess special physical and chemical properties are important materials and have been applied widely in industry and technology [1]. However, the separation and purification of precious metals are usually full of difficulties, mainly due to their chemically similar behaviors or synergistic extraction actions in an acidic medium. So it is necessary and urgent to develop applicable extraction and separation processes of precious metals [2].

Solvent extraction has been proved to be a very efficient and practicable approach for extraction and recovery of the precious metals leached from their low-grade sources or spent chemicals electronic devices such as catalysts [3]. Then, for decades, many efforts have been made in seeking for highly selective extractants used to effectively extract and separate precious metals.

Calixarenes are a major category of building blocks for supramolecular chemistry research. It is well known that the calixarenes and their derivatives were taken as a family of receptors to bind selectively the inorganic/organic ions or molecules forming the host-guest complexes, which have been applied successfully to separate science and technology [4].

On the other hand, some functional calixarene derivatives can form the nanometer structure supramolecular assemblies and/or molecular devices through the cooperative working of several weak intermolecular interactions. Various types $p$-tert-octylcalix[4]arene derivatives with different functionalities are reported to perform the solvent extraction equilibria and kinetics.
To develop and optimize the operating conditions for this research work, the thesis entitled “Research on the Interfacial Properties, Extraction Equilibria, and Kinetics of Various Types Calix[4]arene Derivatives for Extractive Separation of Precious Metals” is organized into the following chapters. There are mainly two parts of the entire thesis.

Hence, solvent extraction equilibria and kinetics together with the definition of precious metals as target metals and calix[4]arene derivatives as the solvent extraction reagent investigated in this research work were described, and raised problems and objectives of this research work are represented in Chapter 1.

In PART I (Chapters 2 and 3), ketonic- and amido-types $p$-tert-octylcalix[4]arene derivatives were prepared for the separation of precious metals in nitric acid media by the conventional technique such as batch-wise method.


Phenyl and methyl ketonic-type derivatives were prepared to investigate. Then, the research on the distribution ratio of Pd was performed to determine the stoichiometry for Pd with both ketonic-type derivatives.


Dibenzylamido and diethylamido-type derivatives were prepared to examine extraction ability and selectivity towards precious metals by the batch-wise method in nitric acid media. Then, the study on the distribution ratio of Pd was conducted in order to determine the stoichiometry for Pd.
From the observed results in **Chapters 2 and 3**, it was found that slightly structural difference caused the significant difference in Ag and Pd extraction and separation, while the stoichiometry of Pd extraction with various types $p$-tert-octylcalix[4]arene derivatives exhibited dependency on the type of functional group.

Although there have successfully showed specific extraction ability and high selectivity towards Ag and Pd with various types $p$-tert-octylcalix[4]arene derivatives containing phenyl ketonic, methyl ketonic, dibenzylamido, and diethylamido functional groups by the batch-wise method in nitric acid media, such experiments have some limitation on the solvent extraction system. That is, in the conventional system, the rate regularity and transfer mechanism of precious metals with the extractants are not clear and should be studied further. Thus, recently, researches on the solvent extraction kinetics are important to clarify the mechanism of the extraction process. In addition, it is interesting to find ways for improvement of the extraction rate *via* the investigation on the kinetics. Detailed and exact information about the solvent extraction kinetics and mechanism is necessary for the optimization of the solvent extraction process. Then, the interfacial chemistry of hydrometallurgical liquid-liquid extraction system is still very incompletely understood. In such processes the liquid-liquid interface plays a key role since the metal transport occurs across the interface. Moreover, as the solvent extraction reaction in many cases occurs at the interface, the activities of the interface can kinetically influence the performance of the extractor rather than significantly influence the equilibrium properties. In other words, the interfacial activities control not only the hydrodynamics in a liquid dispersion but also the rate of the solvent extraction. Thus, study on the interfacial tension which is the most easily measured for the interfacial property of the liquid-liquid extraction system, is required, because the kinetics of the metal extraction process depends upon the concentration of the extractants species at the reaction sites.
Hence, in **PART II (Chapters 4 and 5)**, the interfacial activity and interfacial phenomena of various types $p$-**tert**-octylcalix[4]arene derivatives in the liquid-liquid extraction system were focused for the investigation of the solvent extraction kinetics.

In **Chapter 4, “Liquid-Liquid Interfacial Phenomena for Various Types Calix[4]arene Derivatives”**, the research at the liquid-liquid interface phenomena of the derivatives was conducted by the drop volume method in nitric acid media. The drop volume method is one of the preferred ones for the interfacial tension measurement due to its simplicity of handling, easy temperature control, small sample size, good reproducibility and its applicability for the liquid-liquid extraction system. The Ag extraction rate and interfacial activity of various types $p$-**tert**-octylcalix[4]arene derivatives in nitric acid media were investigated. Based on the results, it was found that Ag extraction rate and interfacial activity of a certain type of $p$-**tert**-octylcalix[4]arene derivative corresponded each other, while the difference in different type of derivatives was observed. Thus, it is evident that the difference in Ag extraction rate and in the interfacial activity is also caused dependent on the chemical structures of the extractants. Additionally, mass transfer mechanism and rate determining step on the liquid-liquid interface were proposed briefly in nitric acid media.

As the further study in **Chapter 5, “Solvent Extraction Kinetics of Ag with Methyl Ketonic Derivative by Using the Modified Lewis Cell System”**, solvent extraction kinetics with methyl ketonic $p$-**tert**-octylcalix[4]arene derivative was conducted in the modified Lewis cell system in nitric acid media. The different parameters affecting Ag extraction rate such as stirring speed, temperature, and extractant concentrations were considered, respectively.
From the obtained results in Chapter 5, it can be concluded that Ag extraction with methyl ketonic \( p\text{-} \) tert-octylcalix[4]arene derivative was governed by mixed regime (diffusion and chemical reaction) in the liquid-liquid interface system. It is supported clearly by the suggestion of Chapter 4 on the mass transfer mechanism. It can be also identified to be rate determining step in the solvent extraction system briefly.

Finally, the overall concluding remarks are summarized in Chapter 6. At last part of this thesis, a list of publications and manuscripts in preparation corresponded to author’s works, a list of presentations are described in appendices.

References


