Solvent Extraction of Silver(I) and Palladium(II) Ions with Ketone Derivative of Calix[4]arene from Highly Acidic Nitrate Media

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(Received November 13, 1995)

The solvent extraction of silver (I) and palladium (II) ions with 25,26,27, 28-tetrakis(acetomethoxy)-5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene (1) in chloroform from nitric acid solution was investigated. The compound 1 was capable of highly selectively extracting silver over palladium from about 1 mol dm^{-3} nitric acid solution and was effective in removing trace amounts of silver from a large excess of palladium. The coordination site of silver ion on 1 was also determined from the chemical shift in the ^{1}H-NMR spectra.

In previous work, we investigated the extraction behavior of carboxylate derivatives of calixarenes for rare earth (III) ions.[1] In the stripping of rare earth ions, we found that this was completely achieved with dilute hydrochloric acid, whereas an increase of the acid concentration lowered the stripping efficiency. This result suggested that the extraction with carboxylate derivatives of calixarenes did not take place according to the simple ion-exchange mechanism with carboxyl groups, but also via a solvation mechanism with carbonyl groups ion-paired with the chloride anion. This means, therefore, that the carbonyl compound was capable of extracting some metal ions from such a highly acidic solution. In our recent study, we have found that silver (I) ion was extracted with tetrameric calixarene carboxylic acid from highly acidic nitrate media.[2]

In the present work, the ketone derivative of calix[4]arene was synthesized as the carbonyl compound for investigation of its solvent extraction behavior towards silver (I) and palladium (II) ions under conditions of high nitric acid concentration. Although both silver and palladium are classified as soft Lewis acids, it is well-known that the latter is selectively extracted over the former at equilibrium with conventional extractants, not only those of soft Lewis bases but also those of hard Lewis bases. There have been some reports of the extraction (or the complexation) of silver (I) with calixarene derivatives[3-6] and their analogs,[7-9] and palladium (II) also with calixarene derivatives,[3,9] but no papers have reported on the extraction from highly acidic solution. From a practical point of view, large amounts of palladium are now being used for manufacturing various electronic devices in Japan, for which purpose highly purified palladium, free from contamination of other metals, is required. Since the major contaminating metal contained in commercially available palladium ingot is silver, the selective removal of trace amounts of silver from a large excess of palladium would contribute to producing highly purified palladium suitable for the manufacture of advanced electronic devices.

The extractant 1 was synthesized according to the reaction reported by Neu et al.,[10] i.e., 5,11,17,23-tetrakis(1,1,3,3-tetramethylbutyl)calix[4]arene-25,26,27,28-tetrol, 2 was reacted with chloroacetone in the presence of potassium carbonate and sodium iodide in acetone. Compound 1 was identified by IR and ^{1}H-NMR spectra, and elemental analysis. Extraction experiments were carried out by the conventional batch-method at 30 °C in chloroform. Concentrations of hydrogen and metal ions in the aqueous phase were determined by titration with sodium hydroxide solution and atomic absorption spectrophotometry, respectively.

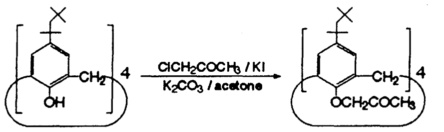

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Figure 1 shows the relation between % extraction of silver (I) and palladium (II) ions and shaking time of organic and aqueous phases. From this figure, it is obvious that the extractant 1 is capable of extracting silver and palladium ions from 6.23 mol dm^{-3} nitric acid. The times necessary for silver and palladium to reach equilibrium were about 72 h and 6 h, respectively.

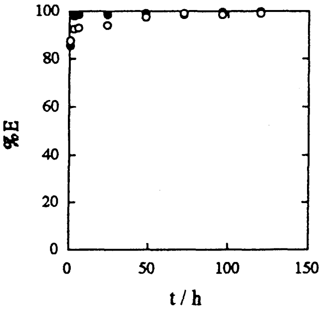

Figure 1. Effect of shaking time on % extraction of silver (I) and palladium (II) ions. open symbol: silver, filled symbol: palladium, $[HNO_3]$=6.23 mol dm^{-3}, $[Ag^+]=[Pd^{2+}]=1\times10^{-4}$ mol dm^{-3}, diluent: chloroform, [1]=3.3 mmol dm^{-3}.

Figure 2(a) shows the effect of the concentration of nitric acid on % extraction of silver and palladium ions with the extractant 1. In the concentration region of nitric acid below 0.23 mol dm^{-3}, palladium was precipitated as a black solid in the aqueous phase during the extraction. Although silver was almost quantitatively extracted over the whole concentration range of nitric acid, palladium was hardly extracted at all of low acidities while extraction increased with increasing acid concentration. From this result, it is apparent that selective extraction of silver over palladium is satisfactorily achieved at about 1 mol dm^{-3} of nitric acid solution. Although, as mentioned earlier, it is well-known that palladium ion is preferentially extracted over silver ion with conventional extractants, the ketone-type calixarene compound 1, employed in the present work exhibits the opposite extraction behavior to the conventional extractants. This peculiar behavior suggested that the extractant **1** can be a candidate for the removal of trace amounts of silver from high concentrations of palladium. In order to confirm this point, a small amount of silver was extracted from a solution containing 100 times as much palladium.

Figure 2(b) shows also the effect of the concentration of nitric acid on the % extraction of silver and palladium ions with **1**. In spite of the large concentration difference between palladium and silver (a factor of 100), silver was selectively extracted over palladium and, consequently, the selective removal of trace amounts of silver from a large excess of palladium appears to be possible with this reagent.

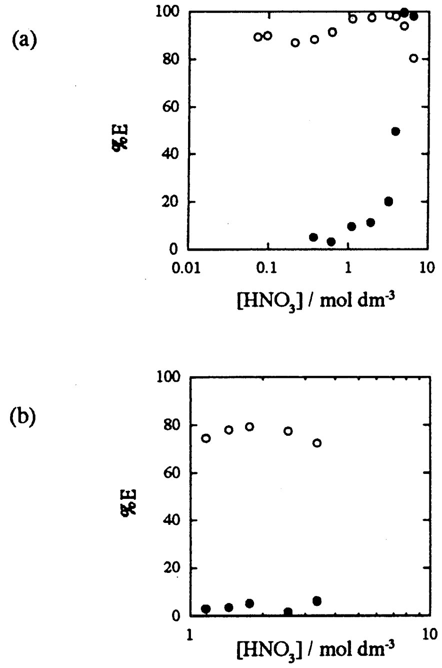

Figure 2. Effect of the concentration of nitric acid on % extraction of silver (I) and palladium (II) ions. open symbol: silver, filled symbol: palladium, diluent: chloroform, shaking time: 72h, [$\underline{1}$]=3.3x10^{-3} mol dm^{-3}. (a) [Ag$^+$]=[Pd^{2+}]=1x10^{-4}mol dm^{-3}, (b) [Ag$^+$]=2.5x10^{-5} mol dm^{-3}, [Pd^{2+}]=2.5x10^{-3} mol dm^{-3}.

Since the extractant **1** is a neutral extracting reagent, the participation of carbonyl groups in the extraction of silver ion with **1** from highly acidic nitrate media must be considered. However, it has been reported that the uptake of silver ion with 1,3-alternate calix[4]arene takes place by π-cation interaction, i.e. by the interaction between the π-electrons of the benzene rings and the silver ion.[4,6] The above concept may be applied also to the present extractant. In order to determine the coordination site of the silver ion with **1**, the chemical shift of the ^{1}H-NMR spectrum was observed. For comparison, a similar observation was carried out for sodium ion. Figure 3 shows the partial ^{1}H-NMR spectra of **1**. Based on x-ray diffraction,[10] the encapsulation of sodium ion with tetrameric calixarene ketone has been reported to take place with four phenoxy oxygens and four carbonyl oxygens. In the extraction of both silver and sodium ions with **1**, chemical shifts were observed and the position of the shifted peaks for silver ion was completely in agreement with that for sodium. Therefore, it can be concluded that the silver ion is coordinated by phenoxy and carbonyl oxygens in a similar manner to sodium.

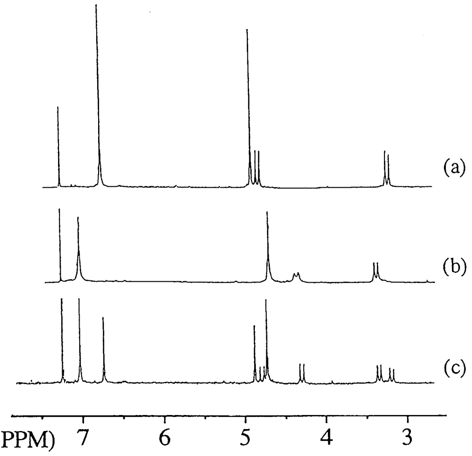

Figure 3. Partial ^{1}H-NMR spectra of $\underline{1}$. (a) original, ^{1}H NMR (CDCl$_3$, 270MHz) δ 6.76 (s, 2H, ArH), 4.87 (s, 2H, OCH$_2$CO$_2$), 4.78 (d, 1H, ArCH$_2$Ar (*endo*)), 3.16 (d, 1H, ArCH$_2$Ar (*exo*)); (b) in the system containing silver ion, δ 7.04 (s, 2H, shifted ArH), 4.67 (s, 2H, shifted OCH$_2$CO$_2$), 4.34 (d, 1H, shifted ArCH$_2$Ar (*endo*)), 3.34 (d, 1H, shifted ArCH$_2$Ar (*exo*)); and (c) sodium ion, δ 7.05 (shifted ArH), 6.76 (ArH), 4.87 (OCH$_2$CO$_2$), 4.78 (ArCH$_2$Ar (*endo*)), 4.72 (shifted OCH$_2$CO$_2$), 4.29 (shifted ArCH$_2$Ar (*endo*)), 3.32 (shifted ArCH$_2$Ar (*exo*)), 3.16 (ArCH$_2$Ar (*exo*)), [Ag$^+$]=[Na$^+$]=0.4 mol dm^{-3}, [$\underline{1}$] = 2x10^{-3} mol dm^{-3}, D$_2$O / CDCl$_3$ = 1 / 1.6 (cm^3), shaking time: 72 h, 30 °C.

In conclusion, it was found that the ketone derivative of calix[4]arene can extract silver (I) and palladium (II) ions from highly acidic nitrate solution into chloroform. Furthermore, at about 1 mol dm^{-3} nitric acid, silver was selectively extracted over palladium, and the removal of traces of silver from a large amount of palladium was accomplished.

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