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# High Selective Solvent Extraction of Palladium(II), Rhodium(III), and Platinum(IV) with 2-Ethylhexylaminomethylpyridine from Hydrochloric Acid

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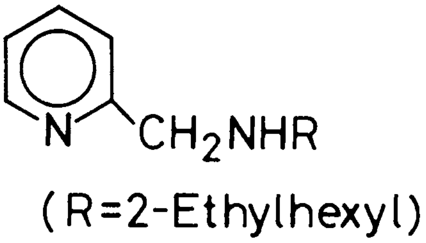
2-Ethylhexylaminomethylpyridine can extract Pd(II), Rh(III) and Pt(IV) with excellent selectivity over Cu(II), Ni(II), Co(II), Cd(II), Zn(II), and Ir(III) from the aqueous hydrochloric acid solution. It forms 1:1 complexes with palladium(II), rhodium(III), and platinum(IV) ions accompanied by chloride ions.

The platinum group metals, especially, palladium(II), rhodium(III), and platinum(IV) are very important metals in industry. The high prices of these metals have stimulated investigations of their separation, concentration and purification by solvent extraction techniqes.[1,2] These metals occur in the nature associated with the major base metals, copper, nickel and cobalt. Both technical and commercial considerations demand that the individual platinum group metals are separated not only from the other metals but also from each other to a high purity, with a high yield and with a high percentage of recovery. From such point of view, it is desired to develop new extracting reagents with high selectivity for these metals. Thus far, a number of extractants for platinum group metals have been developed, however, the majority of them are those of the sulfur atom donating ligand type.[3-10] Few studies on extractants which contain plural nitrogen atoms as ligating ones have been reported on the solvent extraction of platinum group metals.

In the present paper, we report on a novel type of pyridine derivative, 2-ethylhexylaminomethylpyridine(EHAP), which can exhibit the specific extraction behavior for platinum group metals.



EHAP

EHAP was synthesized from 2-ethylhexylamine and chloromethyl pyridine by using a conventional method.[11] Identification of the purified product was carried out by using NMR spectra and elemental analysis. The purity was verified to be 98.3% by gas chromatography. An analytical grade of toluene was used as a diluent.

Equal volumes of aqueous and organic phases were shaken in a flask immersed in a thermostated water bath maintained at 30 °C overnight to attain equilibrium. The equilibration had been confirmed to be attained within 5 hours in a preliminary experiment for platinum group metals. The initial concentration of each metal was about 5 mmol $dm^{-3}$. The initial and equilibrium concentrations of the metal in the aqueous phase were determined by using a Nippon Jarrell-Ash model AA-782 atomic absorption spectrophotometer. The metal concentration in the organic phase was calculated from the mass balance of the metal contents in the aqueous phase before and after equilibrium. In the range of the low loading ratio, the concentration was determined by the method described above after stripping with 2 mol $dm^{-3}$ hydrochloric acid.

Figure 1 shows the percent extracted of metal ions with EHAP from hydrochloric acid. EHAP can extract only platinum group metals such as

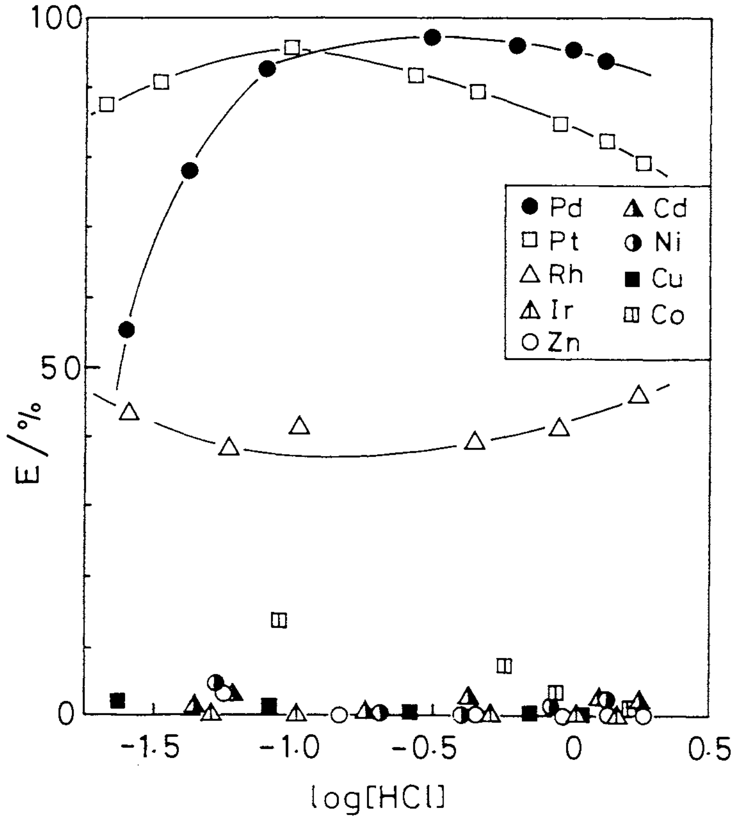


Fig.1. Effect of the concentration of hydrochloric acid on the percent extracted of various metal ions([EHAP]=0.01 mol $dm^{-3}$).

palladium(II), rhodium(III), and platinum(IV) from the aqueous hydrochloric acid solution. Base metals such as copper(II), nickel(II), cobalt(II), zinc(II), and cadmium(II) can not be extracted from hydrochloric acid with EHAP. Thus, EHAP is considered to be a highly selective extractant for palladium(II), rhodium(III), and platinum(IV) from the hydrochloric acid solution containing the base metal ions as mentioned above.

The composition of the Pd(II)-EHAP, Rh(III)-EHAP, and Pt(IV)-EHAP complexes formed in the organic phase was studied by the standard mole ratio method as applied to a two-phase extraction system. Two phases of equal volumes were brought into equilibrium according to the extraction procedures described above. The concentration of metal ions in the aqueous phase was determined by atomic absorption spectrophotometry in the usual manner. The mole ratios of the extractant to metal ions extracted in the organic phase were plotted as a function of the concentration of metal ions.

The results of the mole ratio study are shown in Fig.2 for Pd(II), Rh(III), and Pt(IV). This indicates that the molar ratio of EHAP to palladium(II), rhodium(III), and platinum(IV) in the organic phase asymptotically approaches unity, respectively. The results suggest that Pd(II), Rh(III) and Pt(IV) are extracted as 1:1 complexes.

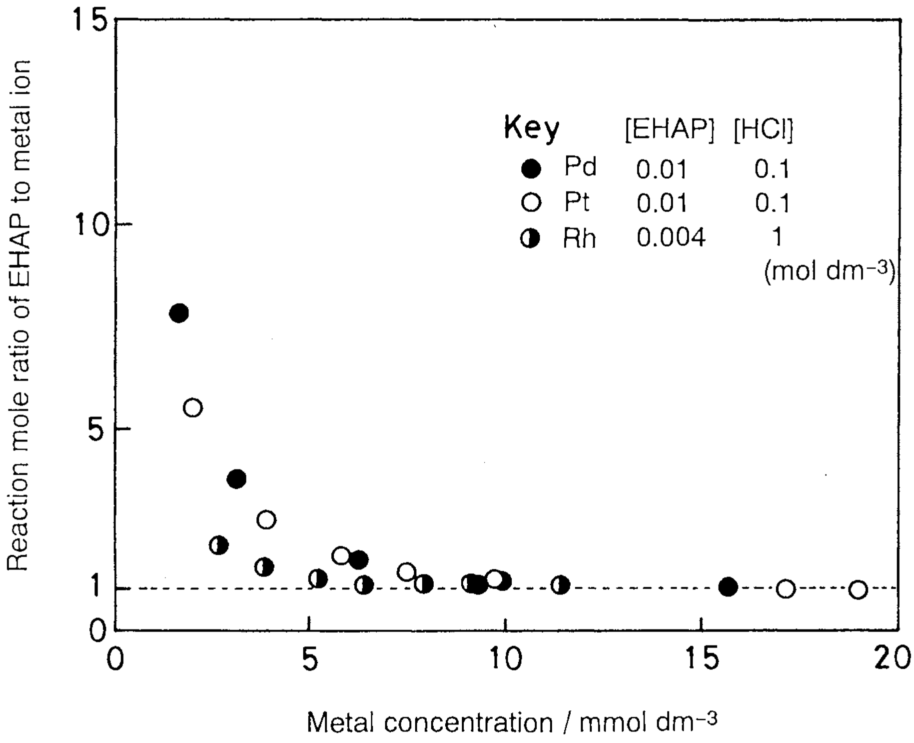


Fig.2. Determination of the reaction mole ratio by molar ratio method.

Since palladium(II) and platinum(IV) are so strongly extracted by EHAP, it is expected that these metals are hard to strip with a conventional stripping solution, such as hydrochloric acid or ammonia. Actually, aqueous ammonia solution( 1 or 2 mol $dm^{-3}$), which is usually used for palladium(II) stripping, could strip neither palladium(II) nor platinum(IV) from the solvent containing 4 mmol $dm^{-3}$ of palladium(II) or platinum(IV). Only 16.7% or 35.6% palladium(II) could be stripped with 1 or 2 mol $dm^{-3}$ aqueous ammonium thiocyanate solutions, respectively, from the solvent containing 4 mmol $dm^{-3}$ of palladium(II) and 20 mmol $dm^{-3}$ of EHAP. The 99.3% of palladium(II) could be stripped using 1 mol $dm^{-3}$ aqueous thiourea solution from the solvent containing about the same concentrations of palladium(II) and reagent.

In conclusion, it was found that EHAP has excellent selectivity to palladium(II), rhodium(III), and platinum(IV) over base metals, such as Cu(II), Ni(II), Co(II), Cd(II), and Zn(II), and Ir(III) which is a member of the platinum group metals in the extraction from hydrochloric acid.

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