—Communication—

Voltammetric Behavior of Cadmium(II) Iodide with a Hanging Mercury Drop Electrode Modified with Trioctylphosphine Oxide

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1 Introduction

Chemically modified electrodes with trioctylphosphine oxide (TOPO-modified electrode) can be easily prepared¹⁾. This TOPO-modified electrode was applied to the uranyl ion system. Preconcentration of uranyl ion was observed in the TOPO layer. Subsequently, trace amounts of uranyl ion were determined by using the TOPO-modified electrode^{2,3)}. However, there was no detailed investigation except for the application of the TOPO-modified electrode to the uranyl ion system but some other metal ions were studied briefly⁴⁾. Recently, the equilibria of Cd(II) halogeno complexes have been studied in solvent extraction systems of TOPO/hexane and the extraction constants of Cd(II) halogeno complexes were estimated⁵⁾. As the extraction constant of Cd(II) iodide was greater than those of chloro- and bromo-complexes, we now have dealt with the study on the electrochemical behavior of Cd(II) iodide preconcentrated on the TOPO-modified electrode. In this communication, application of a TOPO-modified hanging mercury drop electrode (HMDE) is described for the voltammetric measurements of Cd(II) iodide and ability of electroanalytical probe of Cd(II) ion.

2 Experimental

The TOPO was a Dotite reagent (Dojindo Co.). Other reagents used were of analytical reagent grade. The TOPO-modified electrode was prepared by immersing in a 5×10^{-2} mol dm⁻³ TOPO ethanolic solution for a few seconds. A stock solution of 1.0×10^{-3} mol dm⁻³ Cd(II) ion was prepared by dissolving pure cadmium metal in a

small amount of concentrated nitric acid. As described by Lubert et al²⁾, preconcentration of Cd(II) ion was carried out by immersing the TOPO-modified electrode in Cd(II) ion solution under open circuit.

Cyclic and differential pulse voltammograms were measured by using a polarograph model 312 (Fuso Seisakusho Co., Kawasaki) with a function generator HB-104 (Hokuto Denko Ltd., Tokyo). A hanging mercury electrode (0.017 cm²) was model AS-01 (Mitsubishi Chemical Industries Ltd., Kanagawa). All the potentials were referred to a saturated calomel electrode (SCE); and all the electrochemical measurements with the TOPO-modified electrode were carried out in a phosphate buffer solution containing 0.5 mol dm⁻³ sodium sulfate as supporting electrolyte in a nitrogen atmosphere.

3 Results and Discussion

The TOPO-modified electrode was dipped for 30 s in a 10^{-5} mol dm⁻³ Cd(II) solution which was free from iodide ions. The cyclic voltammogram showed no wave corresponding to the reduction or oxidation of cadmium (curve A in Fig. 1), indicating that no Cd(II) ion was preconcentrated in the TOPO layer. When the TOPO-modified electrode was dipped in the 10^{-5} mol dm⁻³ Cd(II) solution containing 0.1 mol dm⁻³ iodide ion, the cyclic voltammogram showed two peaks, whose peak potentials for cathodic and anodic processes were $E_{pc} = -0.65$ and $E_{pa} = -0.58$ V, respectively (curve B of Fig. 1). This result showed that Cd(II) iodide was preconcentrated in the TOPO layer.

From the results of Fig. 2, this electrode system is considered to take part in both the adsorption and diffusion in the cathodic and anodic processes. At multi-sweep cyclic voltam-

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Fig. 1 Cyclic voltammograms of cadmium (II) with TOPO-modified electrode

Scan rate : 0.1 V/s,

Curve A : iodide-free pre-concentration solution

Curve B : 0.1 mol dm⁻³ sodium iodide pre-concentration solution

Fig. 2 The relation between (scan rate)^{1/2} and peak height of cyclic voltammograms

(○) : anodic peak height,

(●) : cathodic peak height

metry, cathodic and anodic peak heights obtained by repeating potential sweeps were kept constant by using a scan rate more than 100 mV/s.

From the analytical aspect, differential pulse polarography was applied to the cadmium TOPO-

Fig. 3 The relation between concentration of Cd (II) and peak height of differential pulse polarograms

Scan rate : 0.02 V/s

Modulation amplitude : 20 mV,

Preconcentration time : 5 min,

(○) : cathodic peak height,

(●) : anodic peak height

modified electrode system, because this technique provides much higher sensitivity than cyclic voltammetry and most suitable peak shapes for measuring signals⁶). The relationships between the concentration of Cd (II) ion (10⁻⁶~5×10⁻⁸ mol dm⁻³) and the heights of cathodic and anodic peak were obtained as shown in Fig. 3. These two curves show linear relations, respectively as follows.

$$I_{pa}(\mu A) = 0.57 \times 10^7 [Cd(II)] + 0.76 \quad (\text{curve A}) \quad (1)$$

$$I_{pc}(\mu A) = 0.29 \times 10^7 [Cd(II)] + 0.56 \quad (\text{curve B}) \quad (2)$$

where [Cd (II)] represents the molar concentration of Cd (II) ion. It can be concluded that trace amounts of Cd (II) ion can be determined by using this preconcentration technique.

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