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Application of a Mercury-Coated Platinum Electrode to the A.C. Stripping Analysis of a Trace Amount of Metal Ions

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Previously,[1,2] we have studied the characteristics of a hanging mercury-drop electrode (HMDE) in alternating current (a.c.) polarography and have used this electrode for the a.c. stripping analysis of thallium(I). Although the HMDE has the advantages of a mercury electrode (high hydrogen overvoltage, reproducible surface, and suitability for multicomponent analysis), the loss of deposited metals by diffusion into the bulk of the electrode limits the application of HMDE to the stripping analysis of trace amounts of metals. In this connection, we tried to use the mercury-coated platinum electrode, which has been established not to have the above-mentioned disadvantage of a mercury-drop electrode. The preparation of mercury-coated platinum electrodes suitable for anodic stripping analysis has been reported by several authors.[3-5] In this work, we followed the continuous and simultaneous depositon procedure proposed by Bruckenstein and Nagai;[6] that is, mercury was plated by electrolysis on a platinum electrode, plated continuously and simultaneously with the deposition of the metals to be determined.

Experimental

Reagents. The way of preparing standard solutions of thallium(I), cadmium(II), lead(II), and copper(II) ions has been described in previous papers.[7,8] The standard solution of mercuric nitrate was prepared by dissolving a known amount of metallic mercury in dilute nitric acid (1+1) and by then removing the excess nitric acid by distillation under reduced pressure. All the other chemicals were of an analytical reagent grade and were used without further purification.

Apparatus and Procedure. The apparatus and the experimental procedures used were the same as those which have been described previously.[2] The platinum-base electrode to be coated with merculy was constructed by sealing a platinum wire 0.4 mm in diameter and 6 mm in length one end of a 6 mm soft-glass tube and by then bending it at right angles to the glass tube. Before use, the platinum base was treated with warm nitric acid (1+1) for 20 min and was then cathodized for 5 min in a sodium perchlorate solution containing 0.01 M $HClO_4$.

Results and Discussion

Mercury Plating. In order to prepare a mercury-coated platinum electrode suitable for a.c. anodic stripping analysis by the continuous simultaneous deposition of mercury, we first studied the current-voltage behavior of a platinum base in stirred solutions of constant pH values and ionic strengths (pH=2.0, 0.5M $NaClO_4$) but with varying concentrations of mercuric ion. Each solution was stirred by a magnetic stirring bar driven by a synchronous motor. Throughout the experiment an alternating-current potential (15 mV) was superposed on the d.c. potential; this superposition had little effect on the mercury plating or on the analysis. The a.c. base current was measured by scanning the potential of the platinum base in the anodic direction at a constnt rate (2.78 mV/sec) from the limiting-current region of the mercuric ion (−1.50 V *vs.* SCE). As the concentration of mercuric ions is increased, the a.c. base current, especially at negative potentials, decreases, whereas the a.c. peak-height due to the anodic dissolution of mercury at about +0.40 V *vs.* SCE increases. These facts clearly indicate that with an increase in the mercury-film thickness and the coverage of the platinum base with mercury, the overvoltage for the hydrogen evolution reaction is increased. At the mercuric ion concentration of 1.0×10^{-4}M, the hydrogen overvoltage almost approaches the limiting value, and in the concentration range from 1.0×10^{-4} to 1.0×10^{-3}M, a reproducible low base current could be obtained. At mercuric ion concentrations higher than 1.0×10^{-3}M, a droplet of mercury was formed.

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As long as the potential scanning in the anodic direction is stopped at +0.50 V *vs.* SCE, the hydrogen overvoltage increases with the number of plating-stripping cycles of mercury. At mercuric ion concentrations higher than 1×10^{-4}M, reproducible a.c. base currents were obtained on repeated runs of the plating-stripping process. On the other hand, if the electrode is oxidized at potentials more positive than +1.0 V *vs.* SCE, the electrode gives a higher base current than that at a nude platinum base. These findings agree well with those by Hartley *et al.*[5] Thus, all the above examples of current-voltage behavior can be explained in the following manner. The mercury deposited on the platinum base interacts with the platinum base and can not be removed completely by anodizing the electrode at +0.50 V *vs.* SCE. However, by anodizing the electrode at potentials more positive than +1.0 V *vs.* SCE, the mercury on the platinum base is completely removed; the resulting platinum surface behaves much as a platinized platinum. It may also be concluded that the formation of intermetallic compounds between mercury and platinum[6] is essential for the formation of mercury film with the desirable properties. Mercury plating was also studied by varying the initial potential from which the potential of platinum base was scanned in the anodic direction. Initial potentials more negative than −1.50 V *vs.* SCE resulted in vigorous hydrogen evolution and gave only the mercury-coated platinum electrode, which behaves in a less reproducible fashion.

A.C. Stripping Analysis of Metal Ions. A.c. polarograms of thallium(I), lead(II), and cadmium-(II) ions in solution containing 1.5×10^{-4}M mercuric ions were measured by scanning the potential of a platinum base in the anodic direction from −1.50 to +0.50 V *vs.* SCE. Reproducible, well-developed a.c. polarograms were obtained on repeated potential excursions. Typical polarograms of thallium(I) are given in Fig. 1. As in the case of HMDE,[2] by stopping the stirring at potentials 70 mV negative with respect to the summit potential, a remarkable increase in sensitivity could be obtained. The a.c. peak-height of the metal was a linear function of the effective pre-electrolysis time and increased exactly with the time according to the relation (1) in Ref. (2). As Table 1 shows, the a.c. summit potentials of a metal at a mercury-coated platinum electrode are located at potentials more positive than those at a nude platinum electrode. This may

Table 1. Summit-potential of metal
0.50M sodium perchlorate
pH=2.00

Electrode	Sumitm-potential, V *vs.* SCE			
	Tl(I)	Cu(II)	Pb(II)	Cd(II)
Bright platinium electrode	−0.76	+0.05	−0.53	−0.72
Mercury-coated platinum electrode	−0.57	+0.00	−0.42	−0.64

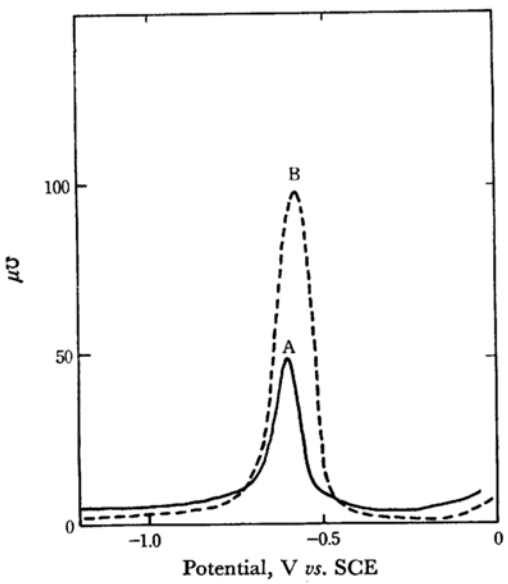

Fig. 1. A.c. polarograms of thallium(I) at a mercury-coated platinum electrode.
Concentration of mercuric ion=1.5×10^{-4}M
Concentration of thallium(I)=2.0×10^{-7}M
0.50M $NaClO_4$, pH=2.0
Scanned anodically from −1.50 V *vs.* SCE
A: Not stopped the stirring
B: Stopped the stirring at −0.65 V *vs.* SCE

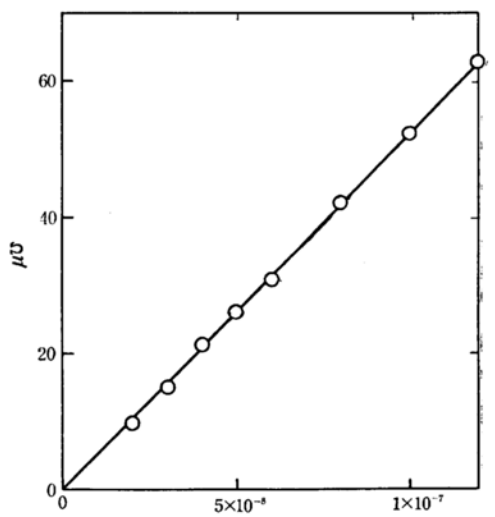

Fig. 2. The relation between thallium(I) concentration and the a.c. peak-height.
Concentration of mercuric ion=1.5×10^{-4}M
0.50M $NaClO_4$, pH=2.0
Scanned anodically from −1.50 V *vs.* SCE and stopped the stirring at −0.65 V *vs.* SCE

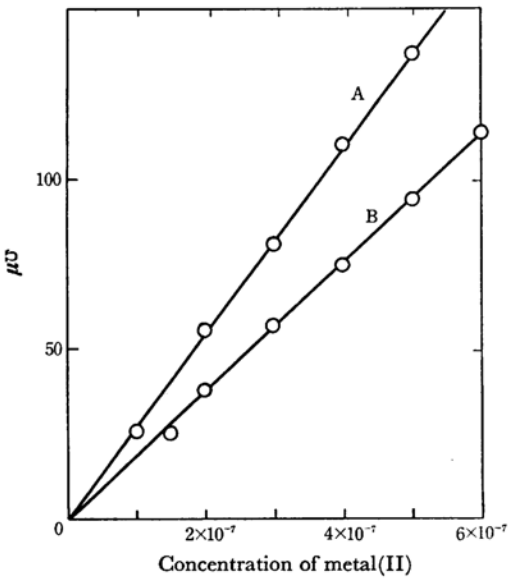

Fig. 3. The relation between metal concentration and the a.c. peak-height.
Concentration of mercuric ion=1.5×10^{-4}M
0.50M $NaClO_4$, pH=2.0
Scanned anodically from −1.50 V *vs.* SCE
A: Lead(II) system, stopped the stirring at −0.50 V *vs.* SCE
B: Cadmium(II) system, stopped the stirring at −0.70 V *vs.* SCE

indicate that the anodic dissolution process of a metal at the mercury-coated platinum electrode is much more reversible than that at the bright platinum electrode.

By employing the above experimental technique, the relation between the concentration of a metal ion and the a.c. peak-height of the anodic dissolution wave was examined. In all cases, at a given initial potential the plot of the a.c. peak-height against the concentration of metal ions gave a straight line passing the point of origin. As is shown in Figs. 2 and 3, thallium(I) ions gave the linear relation in the concentration range from 2×10^{-8} to 1×10^{-6}M, and lead(II) and cadmium(II) ions, in the concentration range from 1×10^{-7} to 3×10^{-6}M. The effect of the presence of copper(II) ions on the a.c. peak-heights of thallium, lead, and cadmium was also studied. The 2×10^{-5}M copper(II) ion had no effect on the a.c. peak-heights of the 5×10^{-8}M thallium(I) or the 2×10^{-7}M lead(II) and cadmium(II) ions.

Although the present a.c. polarographic method has the disadvantage of being restricted to use with solutions not containing anions capable of forming insoluble mercury salts, one can apply this method to the determination of thallium(I), lead(II), and cadmium(II) ions in their micromolar solutions.

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