

CHAPTER 2

EXPERIMENTAL



2.1 Chemicals

All chemicals used were of reagent grade, no further purification was attempted unless otherwise stated. Gallium perchlorate (99% $\text{Ga}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$) was from Venton Corp. U.S.A. Hygroscopic compounds were kept in a desiccator over the anhydrous silica gel. Indium trichloride was dried in the oven at $100 - 105^\circ\text{C}$ for one hour and kept in the desiccator. Thrice deionized water and purified nitrogen used throughout this study were prepared as described in reference 12.

2.2 Apparatus

The cathodic and anodic stripping voltammograms were obtained with a Radiometer Copenhagen Polariter type PO 4g. The cell employed in all analyses was a two compartment cell (H-shaped cell); one compartment served for the reference electrode, saturated calomel electrode (SCE), and another compartment served for the test solution.

The glassy carbon electrode (GCE) with an exposed area approximately 0.071 cm^2 was prepared (11, 13) and employed as a working electrode. In the anodic stripping analyses of Tl (I), In (III), and Ga (III), the glassy carbon rod, $1/8$ " dia., from Beckwith Carbon Corp.

was used for preparing GCE and in the anodic stripping analyses of mixtures of Tl (I), In (III) and Ga (III), the glassy carbon rod, 3 mm dia., from Tokai Electrode Manufacturing Co. was replaced. The electrode surface was freshly polished before each trial with a piece of silicon carbide paper on a polishing wheel, then washed with thrice deionized water and gently rubbed with a piece of filter paper to get rid of dust and moisture.

All potentials were measured against SCE by means of a saturated KCl - agar bridge. The pH value of the solution was measured with a pH meter (Radiometer Copenhagen type PHM 28). All measurements in this work were carried out at room temperature.

2.3 Procedure

2.3.1 Stock solutions

The stock solution of Ga (III), In (III) and Tl (I) were prepared in 250 cm³ volumetric flasks.

2.3.1.1 thallium (I) solution

A 1.00 X 10⁻² M TlNO₃ solution was prepared by dissolving 0.6659 g of TlNO₃ with thrice deionized water and the volume of this solution was made up to 250 cm³.

2.3.1.2 indium (III) solution

Since the dissolution of InCl₃ in acid solution was recommended for preventing hydrolysis of In (III) (14), a 0.5538 g of dried InCl₃ was dissolved and diluted to 250 cm³ with 0.1 M HCl.

This solution has a concentration of $1.002 \times 10^{-2} \text{ M}$.

2.3.1.3 gallium (III) solution

A 1.1945 g of $\text{Ga}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ was dissolved and diluted to 250 cm^3 with 0.1 M HNO_3 , this solution resulted in $1.003 \times 10^{-2} \text{ M Ga (III)}$. Since an aqueous solution of Ga (III) in the presence of perchlorate will slowly be hydrolyzed to form the precipitate of GaOOH , which is readily soluble in acid media of pH less than 3 (15), the stock solution of Ga (III) in this study was prepared in 0.1 M HNO_3 .

2.3.2 Test solution

Test solutions were obtained by the successive dilution of the appropriate concentration of the stock solution desired in the suitable supporting electrolyte and had a pH value adjusted with HNO_3 , HCl or NaOH . A series of mixtures of Ga (III), In (III) and Tl (I) were prepared by varying the concentration of the species desired in the suitable supporting electrolyte.

2.3.3 Salt bridge and reference electrode

Salt bridge and the SCE were prepared as described in reference 16.

2.3.4 Voltammetric and stripping analyses

In order to obtain the deposition potential of any species, a cathodic voltammogram of the species interested was recorded by using potential scan in the negative direction, and the peak potential was measured.

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Before the test solution was placed in the cell for either voltammetric or stripping analysis, the test compartment was washed twice with thrice deionized water and rinsed once with the test solution, then a 15.0 cm³ test solution was transferred to the cell. Oxygen causes a serious effect on suppressing or eliminating peak currents, thus, inert gases such as argon, carbondioxide, or nitrogen have to be used to dearate the test solution (17). In this study, purified nitrogen gas (12) was employed; the test solution was deareated for 5 to 10 minutes and maintained in nitrogen gas atmosphere during the process of analysis. The GCE was then inserted in the test compartment. The desired potential range, current sensitivity and polarity were set on the equipment, and the voltammogram was recorded using the potential scan rate of 0.8 volt min⁻¹.

In stripping analyses, before the test solution was deareated, a small piece of magnetic stirring bar was placed in the test compartment, and after the GCE was inserted about 1 cm above the bottom of the test cell, the deposition potential was set on the instrument and the electrodeposition of the ion was operated in a known limited time. Then the stripping voltammogram was recorded.