

# POLAROGRAPHIC STUDY OF In(III)-PHTHALATE SYSTEM

by S. L. JAIN, JAI KISHAN and R. C. KAPOOR, *Department of Chemistry, University of Jodhpur, Jodhpur*

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In (III) gives three-electron reversible wave at  $pH \approx 2.6 - 2.8$  in perchlorate medium. At  $pH$  1.25 to 4.5 the reduction of  $2 \times 10^{-4}M$  in (III) was found to be reversible in presence of 0.02M phthalate. Three complex species, viz.,  $[In(Phthalate)]^+$ ,  $[In(Phthalate)_2]^-$  and  $[In(Phthalate)_3]^{2-}$  were detected. The logarithmic values of overall stability constants of these species are 5.00, 7.81 and 9.03 respectively at 30°C.

## INTRODUCTION

THE POLAROGRAPHIC reduction of In(III) has created much interest due to differences observed in the nature of its reduction in various supporting electrolytes (Engel *et al.* 1965; Florence *et al.* 1974; Gaur *et al.* 1968; Moorhead & Mac Nevin 1962; Pospisil & Levie 1970; Radhakrishnan & Sundaram 1963; and Visco 1965). Moorhead and Mac Nevin (1962) observed that In(III) in non-complexing media such as perchlorate and nitrate ions did not produce a well defined reduction wave while well formed waves were obtained in halide or thiocyanate medium. Engel *et al.* (1965) observed that in the absence of complexing anions the rate and extent of electroreduction of  $In(H_2O)_6^{3+}$  was remarkably sensitive to the proton concentration. They found that at  $pH$  3 the reduction was polarographically reversible with a half-wave potential of  $-0.52$  Volt vs. S.C.E. At  $pH > 3$ , the limiting current dropped sharply due to precipitation of the hydroxide (Engel *et al.* 1965; and Levitskaya *et al.* 1971). Pospisil and Levie (1970) concluded that in solutions containing only perchlorate, nitrate or sulphate ions, the reduction of aquo-indium ions is extremely slow. At  $pH \approx 2$  it proceeds almost exclusively *via* hydrolysis products. It has been assumed that  $In(H_2O)_4(OH)_3^+$  provides an effective path for the reduction of In(III) (Lawson & Aikens 1967; and Molodov & Losev 1965). The specifically adsorbed halides and thiocyanate and some organic anions at DME also catalyse the reduction (Engel *et al.* 1965; and Loskarev & Kazarov 1967).

Hampson and Piercy (1974) observed that at  $pH$ 's  $\approx 2.7$  the potential of an indium electrode changed markedly for small changes of  $pH$  indicating that the electrode reaction  $In^{3+} + 3e \rightarrow In$  was complicated by the presence of phase hydroxide (or oxide) at the electrode.

In the present paper, we have studied the polarographic reduction of In(III) in pure perchlorate medium and also in the presence of phthalate ion. The stability constants and distribution of In(III)-phthalate species have also been calculated.

## MATERIALS AND METHODS

All the reagents used were of analar grade. Potassium hydrogen phthalate was obtained from BDH (England). Indium nitrate (Schuchardt Munchen, Germany)

solution was prepared in 0.3M perchloric acid medium and was standardized by titrating against EDTA using PAN indicator (Welcher 1958). Sodium perchlorate (Riedel, Germany) was used as the supporting electrolyte. The pH of the solution was maintained at 4.0 by using CO<sub>2</sub>-free sodium hydroxide and dil. perchloric acid solution. The test solutions were degassed with pure nitrogen.

Polarograms were recorded with an automatic polarograph type OH-102 (Radelkis, Hungary) and Manual Toshniwal polarograph in conjunction with PYE (Cambridge, England) galvanometer. Digital pH meter NIG 333 was used to measure the pH of the solutions. All measurements were made at 30±0.1°C, except otherwise stated, using Ultra thermostate (Type E-149, Hungary). The dropping mercury electrode (DME) had the following capillary characteristics at -0.8 V vs. S.C.E. in 0.1 M sodium perchlorate at 40 cm. mercury head

$$m = 8.14 \text{ mg/sec. and } t = 3.21 \text{ seconds.}$$

### RESULTS AND DISCUSSION

In (III) in perchlorate medium did not give well formed wave at pH < 2. Only around pH ≈ 2.6—2.8 reversible wave was obtained with a half-wave potential of -0.515 volt vs. S.C.E. It was also observed that diffusion current decreased at pH > 3 as observed by previous workers (Engel *et al.* 1965; and Zebreva *et al.* 1971). At pH 1.5, to 4.5 the reduction of 2 × 10<sup>-4</sup> M In (III) was reversible in presence of 0.02 M phthalate while at pH 0.5 the wave was not reversible and diffusion current was low.

It was earlier observed in our laboratory (Kapoor & Jai Kishan 1977) that addition of 2.5 × 10<sup>-5</sup> M phthalate to 2 × 10<sup>-4</sup> M In<sup>3+</sup> (μ = 0.2 NaClO<sub>4</sub>) makes the indium wave reversible. In the present study we have observed that the irreversible wave obtained in the pH range 2.5 to 3.0 becomes reversible on the addition of small concentration of phthalate (2.5 × 10<sup>-5</sup> M) to a 2 × 10<sup>-4</sup> M In (III) solution. Thus it appears that electron transfer is facilitated by the presence of In(III)-phthalate complex.

The measurements were made for the solutions containing 2 × 10<sup>-4</sup> M In<sup>3+</sup>, 2 × 10<sup>-2</sup> M phthalate and NaClO<sub>4</sub> (μ = 0.2) at 35°C. On increasing the pH the E<sub>1/2</sub> shifted towards more negative values and the i<sub>d</sub> values also decreased. The half-wave potential, slopes and diffusion currents observed at different pH are given in Table I.

TABLE I  
Effect of pH on Indium-phthalate system

pH	0.50	1.25	2.05	2.46	2.97	3.50	4.00	4.50	4.95
-E <sub>1/2</sub> V vs. S.C.E.	0.5175	0.5200	0.5250	0.5285	0.5395	0.5540	0.5720	0.5920	—
Slope (—mv)	27.5	22.5	21.0	20.5	18.0	19.5	19.0	19.0	—
i <sub>d</sub> (μA)	1.87	2.43	2.22	2.06	2.03	1.98	1.97	1.82	1.09

The values indicate that reduction became reversible at  $pH$  1.25. Slight precipitation was observed at  $pH$  4.5 and the diffusion current became less than half at  $pH$  5.0. The precipitation was nearly complete above  $pH$  5.5 and therefore it was decided to study the reaction at  $pH$  4.0.

In 0.2  $M$  sodium perchlorate, precipitation occurred at higher phthalate concentration at  $pH$  4.0 due to the formation of sparingly soluble potassium perchlorate. The study was therefore made in 0.1  $m$  sodium perchlorate solution; in this medium no precipitation occurred since the amount of potassium perchlorate formed was within its solubility limit.

Polarograms were recorded of solutions containing  $2 \times 10^{-4} M$   $In^{3+}$  in presence of requisite amount of sodium perchlorate (to maintain ionic strength) with varying concentration of phthalate ion at  $pH$  4.0. The half-wave potential shifted towards more negative values on increasing the concentration of ligand from 0.01 to 0.2  $M$ . The phthalate ion concentration was calculated using  $pK_1$  (2.76) and  $pK_2$  (4.92) reported elsewhere (Sillen & Martell 1964).

In each case a single well-defined wave was obtained. The plots of  $-E$  vs.  $\log i/i_d - i$  gave slope values of  $-19.5 \pm 0.5 mV$ , indicating reversible three-electron reduction. The plot of  $i_d$  vs.  $\sqrt{h}$  (corrected) gave a straight line passing through the origin, which indicated that the reduction wave was diffusion controlled.

Smooth curve was obtained when  $-E_{1/2}$  were plotted against  $-\log [X^-]$  indicating the presence of more than one complex species. Hence, the DeFord and Hume (1951) method was used to determine the overall stability constants of the consecutive complexes.

According to DeFord and Hume (1951)

$$F_0(X) = \left[ \text{antilog } 0.4343 \frac{nF}{RT} \left\{ (E_{1/2})_m - E_{1/2} \right\} c \right] + \log \frac{I_m}{I_0}$$

where  $m$  and  $c$  represents simple and complex metal ions respectively. The functions  $F_1(X)$ ,  $F_2(X)$  and  $F_3(X)$  were calculated from the following relations :

$$F_1(X) = \frac{F_0(X) - 1}{[X^-]}$$

$$F_2(X) = \frac{F_1(X) - \beta_1}{[X^-]}$$

$$\text{and } F_3(X) = \frac{F_2(X) - \beta_2}{[X^-]}$$

The functions  $F_j(X)$  vs. phthalate ion were plotted (Fig. 1). The following values of overall stability constants were obtained from the plots :

$$\log \beta_1 = 5.00, \log \beta_2 = 7.81 \text{ and } \log \beta_3 = 9.03$$

Recently Sarine and Munshi (1977) have reported potentiometrically the formation of 1 ; 1 complex with  $\log \beta_1 = 3.96$  at  $35^\circ$  for the same system. The values

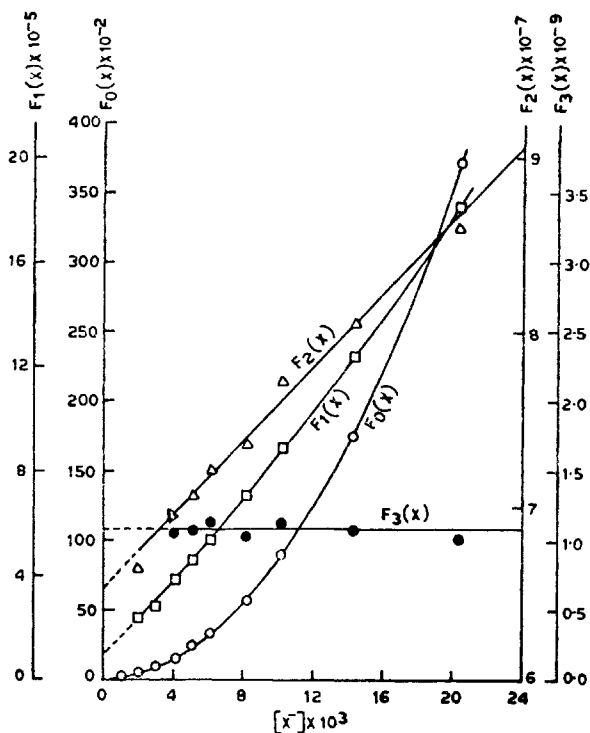


Fig. 1. Plot of  $F_j(X)$  vs. | Phthalate. |

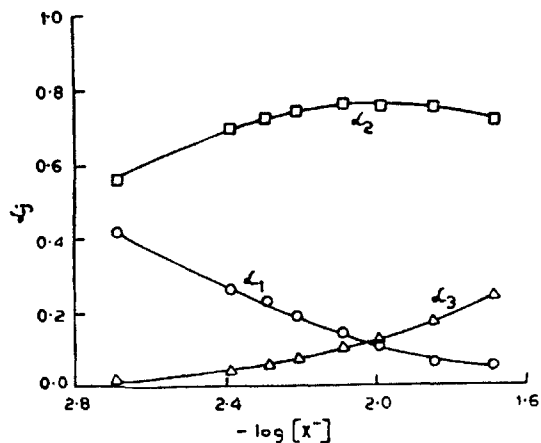


Fig. 2. Distribution of indium in various forms as a function of free phthalate ion concentration.

indicate that the phthalate ion forms stronger complexes with In (III) in comparison to Cd(II) and Pb(II) (Jain *et al.* 1969) and Cu(II) (Sillen & Martell 1964).

## COMPOSITION OF THE COMPLEX SPECIES

The degree of formation  $\alpha_j$  (Fig. 2) for each complex species has been calculated from the following equation (Crow 1969) at 30°C.

$$\alpha_j = \frac{\beta_j(X)^j}{F_0(X)}$$

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