# POLAROGRAPHIC STUDY OF MIXED LIGAND COMPLEXES OF INDIUM(III) WITH THIOGLYCOLATE AND FORMATTE IONS

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Radhakrishnan and Sundaram [1] have reported that polarographic reduction of In (III) metal ion as well as its complex with thiocyanate in aqueous medium is reversible and that In(III) forms six successive complexes with thiocyanate ions ($CNS^-$). On the other hand Sundaresan [2] reports that the reduction of In(III) is irreversible but its complexes with methionine under-go reversible reduction. Gaur et al [3] report the reduction of In(III) as well as its glycollate complexes to be quasireversible.

A survey of literature reveals that mixed ligand complexes of In(III) with thioglycolate and formate ions have not been studied polarographically so far. Hence the title study has been undertaken.

## EXPERIMENTAL

Stock solution (0.025 M) of $In(NO_3)_3$ (Fluka AR) was prepared by dissolving it in the minimum amount of dilute $HNO_3$ and diluting with doubly distilled water. The concentration of In(III) was kept at 1 mM in each case. Sodium salts of thioglycolic acid and formic acids were used as the source of thioglycolate and formate ions. $NaNO_3$ was used as a supporting electrolyte and also to maintain a constant ionic strength ( $\mu$ = 2.0). No maximum suppressor was required. Polarograms of the solutions obtained were by means of a digital polarograph (Toshniwal CL02B). Purified hydrogen was used for removing the dissolved oxyen. All the measurement were made at a constant temperature 25 ± 1°C. The pH was adjusted to 5.0 by adding very dilute solutions of HCl or KOH.

The number of electrons involved in the polarographic reduction of In(III) in the presence of ligands was determined by the millicoulometric method of DeVries and Kroon [4]. This gave the value of 'n' equal to 3 in each case. The current at the end of the drop i.e., the maximum current was noted in each case. The dme had the following characteristics (in 2.0 M $NaNO_3$, open circuit) m = 1.54 mg/sec, t = 3.0 sec, $m^{2/3}t^{1/6}$ = 1.60 $mg^{2/3}$ $sec^{1/2}$ $h_{corr}$ = 32.5 cm.

## RESULTS AND DISCUSSIONS

In(III) yields well-defined reduction waves in the presence of increasing amounts of thioglycolate (TGA) and formate (FA) ions. In each case the wave height is diffusion - controlled as the plots of $i_d$ verses $h_{corr}^{1/2}$ are linear and pass through the origin. The slope of linear plots of log $[i/(i_d - i)]$ vs $E_{d.e.}$ lie in the range 24-30 mv (Table 1) which is appreciably greater than the theoretical value of 20 mv expected at 25°C for a 3- electron reversible reduction process. The values of standard rate constant ($K_{s,h}$) of the electrode reaction of In(III), determined by Gelling's method [5] in the presence of increasing concentrations of the ligands lie in the range 1.0 x $10^{-3}$ to 3.0 x $10^{-3}$ cm/sec. This clearly shows [6] that the polarographic reduction of In(III) in the presence of increasing concentrations of the ligands is quasi-reversible. This is true for both the simple and the mixed ligand systems.

### Composition and Stability Constants of Simple Complexes of In(III) with Thioglycolate and Formate Ions

The composition and stability constants of simple complexes of In(III) with thioglycolate and formate ions were determined separately prior to the study of the mixed systems. Identical conditions were maintained in both the simple and the mixed systems.

With the addition of increasing amount of thioglycolate or formate ion, $E_{1/2}$ of In (III) is shifted to more negative potentials thereby showing the complex formation. In each case, the values of $E_{1/2}^r$ have been obtained by Gellings' method [5]. The plot of $E_{1/2}^r$ vs log $[TGA^-]$ is straight line. This shows the formation of a single complex. However, the plot of $E_{1/2}^r$ vs log $[FA^-]$ is smooth curve thereby showing the formation of successive complexes. The composition and stability constants of the former system have been determined by Lingane's method [7] while that of the latter by DeFord and Hume method [8]. The results have been summarised in Table 2.

### Composition and Stability Constants of In(III) TGA-FA Mixed System

$E_{1/2}$ values were measured keeping the concentration of formate ion constant while varying the concentration of thioglycolate ion. $E_{1/2}$ values were found to be more negative than those obtained in the case of binary system thereby showing the formation of mixed complexes. The polarographic characteristics and



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TABLE 1

POLAROGRAPHIC CHARACTERISTICS AND $F_{ij}$ [X,Y] FUNCTIONS FOR In(III)-TGA-formate system
$[In^{3+}]$ = 1 mM, $\mu$ = 2.0 ($NaNO_3$), pH = 5.0, Temp. = 25 ± 0.1°C, m = 1.54 mg/sec, t = 3.0 sec, $h_{corr}$ = 32.5 cm $(E_{1/2})_5$ = -0.572 V (SCE), $(E^r_{1/2})_5$ = -0.546 V

| [TGA] (M) | $i_d$ ($\mu$A) | $-E_{1/2}$ V (SCE) | $-E^r_{1/2}$ V (SCE) | Slope mV | $F_{oo}$ [X,Y] $\times 10^{-4}$ | $F_{10}$ [X,Y] $\times 10^{-5}$ | $F_{20}$ [X,Y] $\times 10^{-6}$ | $F_{30}$ [X,Y] $\times 10^{-7}$ | $F_{40}$ [X,Y] $\times 10^{-9}$ |
|---|---|---|---|---|---|---|---|---|---|
| Series I : $[FA^-]$ = 0.2 M | | | | | | | | | |
| 0.025 | 7.2 | 0.650 | 0.630 | 25 | 1.84 | 3.36 | 5.43 | - | - |
| 0.050 | 7.0 | 0.660 | 0.640 | 25 | 5.92 | 9.84 | 15.68 | 23.37 | - |
| 0.075 | 7.0 | 0.675 | 0.648 | 26 | 15.08 | 18.78 | 22.37 | 34.50 | 4.5 |
| 0.100 | 6.8 | 0.680 | 0.660 | 29 | 61.35 | 60.35 | 58.35 | 54.35 | 5.3 |
| 0.125 | 6.6 | 0.687 | 0.668 | 26 | 143.54 | 114.03 | 89.62 | 68.50 | 5.4 |
| 0.150 | 6.6 | 0.690 | 0.676 | 27 | 279.66 | 185.75 | 122.50 | 79.00 | 5.2 |
| Series II : $[FA^-]$ = 0.4 M | | | | | | | | | |
| 0.025 | 6.8 | 0.660 | 0.640 | 26 | 6.09 | 4.35 | - | - | - |
| 0.050 | 6.2 | 0.670 | 0.650 | 28 | 21.53 | 33.06 | 58.13 | 16.25 | 2.8 |
| 0.075 | 6.2 | 0.685 | 0.666 | 28 | 123.71 | 158.28 | 205.70 | 20.76 | 2.5 |
| 0.100 | 6.0 | 0.690 | 0.672 | 25 | 290.42 | 285.42 | 281.42 | 23.14 | 2.1 |
| 0.125 | 6.0 | 0.700 | 0.680 | 25 | 635.59 | 504.48 | 400.38 | 28.03 | 2.1 |
| 0.150 | 5.8 | 0.705 | 0.690 | 26 | 1508.75 | 1002.50 | 665.00 | 41.00 | 2.6 |

TABLE 2

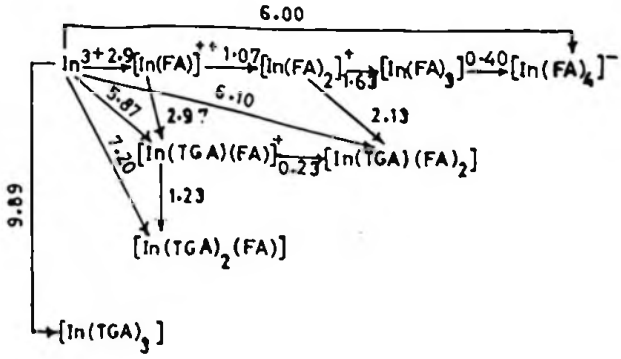
| System | Composition | Stability constant |
|---|---|---|
| In(III)-$TGA^-$ | $[In(TGA)_3]$ | log $\beta_3$ = 6.89 |
| In(III)-FA | $[In(FA)]^{2+}$ | log $\beta_1$ = 2.90 |
| | $[In(FA)_2]^+$ | log $\beta_2$ = 3.97 |
| | $[In(FA)_3]$ | log $\beta_3$ = 5.60 |
| | $[In(FA)_4]^-$ | log $\beta_4$ = 6.00 |
| In(III)-TGA-FA | $[In(TGA)(FA)]^+$ | log $\beta_{11}$ = 5.87 |
| | $[In(TGA)(FA)_2]$ | log $\beta_{12}$ = 6.10 |
| | $[In(TGA)_2(FA)]$ | log $\beta_{21}$ = 7.20 |

$F_{ij}$[X,Y] functions for the mixed-ligand system have been listed in Table 1.

From the analysis of these functions the values of constants [9] A, B, C, D and E have been calculated as detailed below.

**In(III)-TGA-Formate System**

For Series I : $[FA^-]$ = 0.2 M (fixed)
log A = 4.00, log B = 5.30
log C = 6.60, log D = 7.00
log E = 9.69




Scheme 1

For Series II: $[FA^-]$ = 0.4 M (fixed)
log A = 4.69, log B = 5.69,
log C = 6.70, log D = 7.30
log E = 9.45

From the values of these constants, the composition and stability constants of the mixed complex species have been determined. The results have been summarised in Table 2.

The various equilibria involved in this mixed ligand system have been represented in the Scheme 1. The equilibrium constant (log K) for the disproportionation reaction.

$$2\,[In(TGA_2)\,(FA)] \rightleftharpoons In(TGA_3) + In(FA_2^+) + TGA^-$$

works out to be -3.54. The large negative log value of equilibrium constant indicates that mixed complex is strongly favoured over the simple ones.

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