

## Reduction of In(III) at d.m.e. in Presence of Glyoxalate Ions & Determination of Composition & Stability Constants of the Complexes

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The reduction of In (III) at d.m.e. in aqueous medium in the presence of glyoxalate ions has been studied at constant ionic strength ( $\mu=1.0$ ) and  $30^\circ$  and  $40^\circ$ . The reduction is found to be diffusion-controlled but the electrode process is quasi-reversible. The  $E_{1/2}^r$  have been determined by Gellings method. The composition and formation constants of the complexes formed have been calculated using DeFord and Hume's method. Five complex species, viz.  $[\text{In}(\text{CHO.COO})]^{2+}$ ,  $[\text{In}(\text{CHO.COO})_2]^+$ ,  $[\text{In}(\text{CHO.COO})_3]$ ,  $[\text{In}(\text{CHO.COO})_4]^-$  and  $[\text{In}(\text{CHO.COO})_5]^{2-}$  with  $\beta_1=20 \times 10^6$ ,  $\beta_2=5 \times 10^7$ ,  $\beta_3=50 \times 10^7$ ,  $\beta_4=25 \times 10^8$  and  $\beta_5=93 \times 10^{10}$  at  $30^\circ$  and  $\beta_1=1 \times 10^6$ ,  $\beta_2=2 \times 10^7$ ,  $\beta_3=8 \times 10^8$ ,  $\beta_4=45 \times 10^9$  and  $\beta_5=36 \times 10^{10}$  at  $40^\circ$ , are found to be present. The percentage distribution of In (III) at different [glyoxalate] have been calculated. The kinetic parameters have been determined by Gellings method. The  $K_s$  values confirm the quasi-reversible nature of the electrode process.

THE reduction of In(III) at d.m.e. in various complexing and non-complexing media<sup>1,8</sup>, has been found by some workers to be reversible and by others as quasi-reversible. In view of these conflicting results it was thought of interest to study the reduction of In(III) at d.m.e. in the presence of glyoxalate ions to throw light on the nature of reduction. Kinetic parameters, composition and stability constants of the complexes formed by  $\text{In}^{3+}$  with glyoxalate ions have also been determined.

### Materials and Methods

Reagent grade chemicals were used for the preparation of solutions. Stock solution ( $M/40$ ) of  $\text{In}^{3+}$  was prepared by dissolving weighed amount of indium nitrate in doubly distilled water and standardized as usual<sup>9</sup>. Sodium salt of glyoxalic acid was used as the complexing agent. Solutions containing  $0.5 \text{ mM}$  of  $\text{In}^{3+}$  with different concentrations of glyoxalate ions were prepared. The ionic strength of the solutions was maintained at 1.0 by the addition of  $\text{NaClO}_4$ .

The pH of all the solutions were measured using Toshriwal pH-meter and was found to  $6.1 \pm 0.1$ . The other details are same as described earlier<sup>10</sup>.

### Results and Discussion

In each case, a single well-defined reduction wave appeared. The plots of  $i_d$  versus  $\sqrt{h}$  ( $h$  is effective height of mercury column after applying back pressure) and  $i_d$  versus  $C$  ( $C=[\text{In}^{3+}]$ ) were linear and passed through origin, thereby indicating that the reduction was diffusion-controlled. The plots of  $\log i/i_d - i$  versus  $E_{d.e.}$  were also linear with values of slopes found to be of the order of  $25 \pm 2 \text{ mV}$  which were higher than that needed for 3 electron reversible reduction (20 mV). As the reduction was not reversible, the observed half-wave potential could not be used for the calculation of stability con-

stants. For this purpose, the reversible half-wave potential,  $E_{1/2}^r$  values were determined by Gellings method<sup>11</sup>, which involved plotting of  $E + (RT/nF) \log (i/i_d - i)$  versus  $i$ , and extrapolating the curves to zero current value gives  $E_{1/2}^r$  (Fig. 1). The reversible half-wave potential ( $E_{1/2}^r$ ) shifted towards more negative values and the diffusion current decreased with increasing concentration of glyoxalate anion, indicating the formation of complexes between  $\text{In}^{3+}$  and glyoxalate ions.

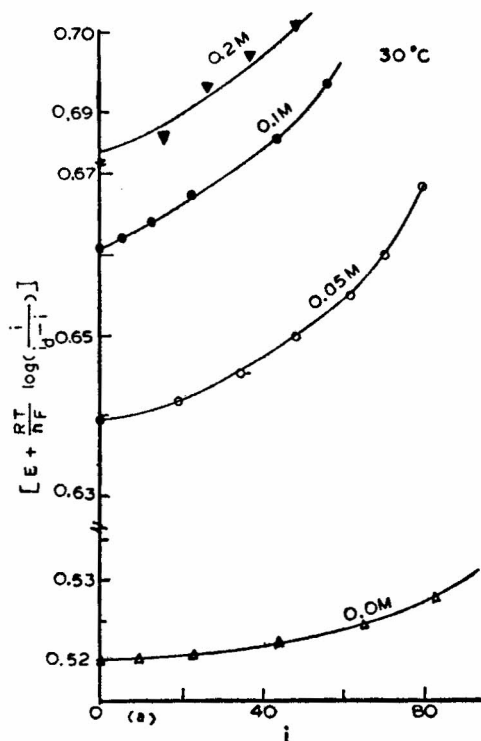


Fig. 1 — Plots of  $i$  versus  $[E + (RT/nF) \log (i/i_d - i)]$  for  $\text{In}^{3+}$ -glyoxalate system

The plot of  $E_{\frac{1}{2}}$  versus  $-\log C_x$  gave a smooth curve indicating the formation of two or more complex species which are in equilibrium. The DeFord and Hume treatment<sup>12</sup> for stepwise complex formation has been used for calculation of composition and stability constants of the complexes formed. The values of  $F_j([X])$  functions together with polarographic characteristics for  $\text{In}^{3+}$ -glyoxalate system at 30° are given in Table 1 and Fig. 2. The results show the existence of five complex species, viz.  $[\text{In}(\text{CHO.COO})]^{2+}$ ,  $[\text{In}(\text{CHO.COO})_2]^+$ ,  $[\text{In}(\text{CHO.COO})_3]$ ,  $[\text{In}(\text{CHO.COO})_4]^-$  and  $[\text{In}(\text{CHO.COO})_5]^{2-}$  ( $\mu = 1.0$ ) having  $\beta_1 = 20 \times 10^6$ ,  $\beta_2 = 5 \times 10^7$ ,  $\beta_3 = 50 \times 10^7$  and  $\beta_4 = 25 \times 10^8$ ,  $\beta_5 = 93 \times 10^{10}$  respectively at 30°.

The percentage distribution of  $\text{In}(\text{III})$  in various species at different ligand concentrations has also been calculated (Fig. 3).

In order to determine the thermodynamic functions, similar calculations were made at 40° under identical conditions. The reduction was again found to be diffusion-controlled but quasi-reversible at 40°. The  $E_{\frac{1}{2}}$  values were also determined at 40° as described earlier. The nature of the plots of  $F_j([X])$  versus  $C_x$  was similar to that obtained at 30° except that the stabilities of complexes decreased with increasing temperature. The polarographic characteristics and  $F_j([X])$  function values are summarized in Table 1 and stability constants at 40° for the different complex species are  $\beta_1 = 1 \times 10^6$ ,  $\beta_2 = 2 \times 10^7$ ,  $\beta_3 = 8 \times 10^8$ ,  $\beta_4 = 45 \times 10^9$  and  $\beta_5 = 36 \times 10^{10}$  respectively.

As the electrode process is quasi-reversible, the kinetic parameters have been calculated by Gellings method. The plots of  $\log(Z-1)$  versus  $E-E_{\frac{1}{2}}$  were linear (Fig. 4) where  $Z$  is defined as

$$\log(Z-1) = \log \frac{1.13}{\Lambda \sqrt{i_d}} - \frac{(1-\alpha)nF}{2.303RT} (E-E_{\frac{1}{2}})$$

$$Z = \text{antilog} \left[ \frac{nF}{2.303RT} (E_{\frac{1}{2}} - E) - \log(i/i_d - i) \right]$$

where  $R$ ,  $T$ ,  $n$  and  $F$  have their usual significance.

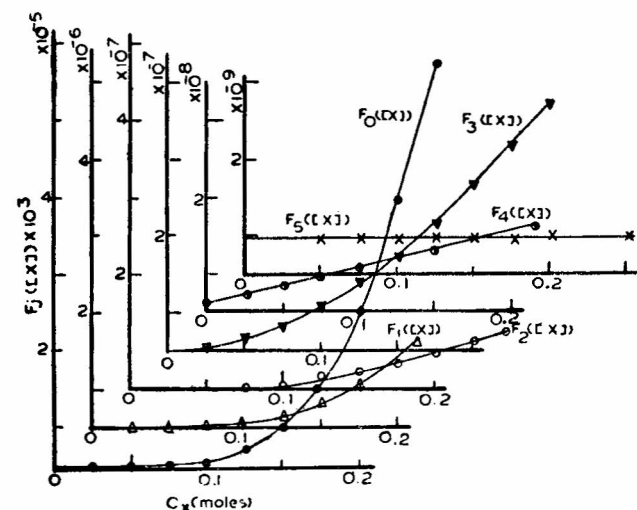


Fig. 2—Plots of  $F_j([X])$  versus  $C_x$  for  $\text{In}^{3+}$ -glyoxalate system at 30°

TABLE 1—POLAROGRAPHIC CHARACTERISTICS OF  $\text{In}^{3+}$ -GLYOXALATE COMPLEXES AT  $\mu=1.0$

$C_x$ (mcles)	$-E_{\frac{1}{2}}$ V (vs SCE)	$-E_{\frac{1}{2}}'$ V (vs SCE)	$i_d$ (div.)
30°			
0.000	0.5625	0.5250	96.0
0.025	0.6500	0.6428	84.5
0.050	0.6550	0.6482	80.0
0.075	0.6660	0.6590	64.0
0.100	0.6750	0.6642	60.0
0.125	0.6780	0.6697	57.5
0.150	0.6865	0.6809	57.5
0.175	0.6915	0.6866	58.5
0.200	0.6985	0.6929	58.5
40°			
0.000	0.5230	0.5205	102.5
0.025	0.6280	0.6190	100.5
0.050	0.6505	0.6395	99.5
0.075	0.6660	0.6535	78.0
0.100	0.6725	0.6619	78.0
0.125	0.6785	0.6695	74.0
0.150	0.6872	0.6752	59.0
0.175	0.6915	0.6824	66.0
0.200	0.6950	0.6865	66.0

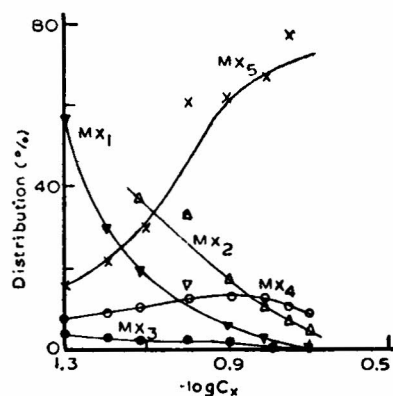


Fig. 3—Composition of various species of  $\text{In}^{3+}$ -glyoxalate system versus  $-\log C_x$

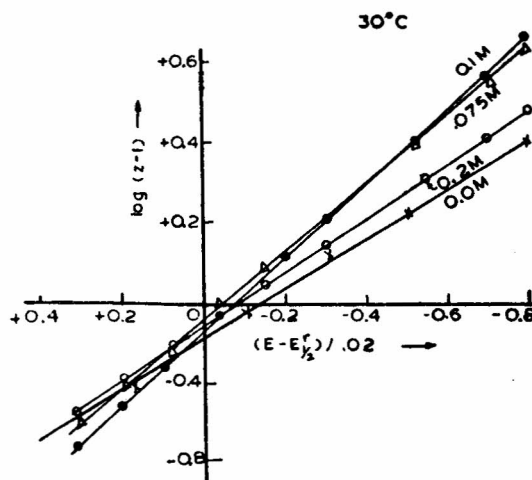


Fig. 4—Plots of  $(E-E_{\frac{1}{2}})/0.02$  versus  $\log(Z-1)$  at 30°

TABLE 2 — KINETIC PARAMETERS FOR REDUCTION OF In<sup>3+</sup> IN SODIUM GLYOXALATE MEDIUM ( $\mu=1.0$ )

[Glyoxalate] (moles) $C_x$	sec <sup>-1</sup>	$D\frac{1}{2} \times 10^3$ cm <sup>2</sup> /sec	$K_s \times 10^3$ cm/sec	
TEMP., 30°				
0.0	2.2047	0.52	1.88	4.15
0.025	0.6214	0.34	1.65	0.103
0.075	0.5799	0.36	1.21	0.705
0.10	0.6813	0.38	1.40	0.776
0.20	0.6507	0.45	1.10	0.723
TEMP., 40°				
0.0	2.167	0.52	2.02	4.38
0.025	0.927	0.24	1.98	0.187
0.10	0.9505	0.25	1.48	0.95
0.125	0.8955	0.26	1.40	0.85
0.20	0.6400	0.25	1.25	0.80

From the slopes and intercept of these plots, the values of  $\alpha$  and  $\Lambda$  were obtained. The standard rate constant  $K_s$  is given by the relation  $K_s = \Lambda \times D^{\frac{1}{2}}$ , where  $D$  is the diffusion coefficient and is determined from diffusion current data by Ilkovic equation. The values of  $K_s$  in the case of

In-glyoxalate system were found to be of the order of  $10^{-4}$  cm/sec for complex species and  $10^{-3}$  cm/sec for the reduction of In<sup>3+</sup> in NaClO<sub>4</sub> ( $\mu = 1.0$ ), indicating that the irreversibility of electrode process for the reduction of In<sup>3+</sup> increased in the presence of glyoxalate ions. The kinetic parameters are given in Table 2.

$\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  values for 1:5 complex species are found to be  $-18.006$  kcal/mole,  $-16.70$  kcal/mole and  $-35.5$  cal/mole/deg respectively.

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