TECHNICAL REPORT

FORMATION CONSTANTS OF COMPLEXES OF INDIUM WITH PROPYLENEDIAMINE

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The polarographic, reduction of indium-propylenediamine complexes in various concentrations of propylenediamine (0 – 0.45M) is diffusion controlled, but not reversible. The kinetic parameters α and K_s have been calculated by Gelling's method. The value of K_s was about 10^{-3} cm/sec., showing that the reduction is a quasi reversible process. The stability constants of the complexes have been evaluated by DeFord and Hume's treatment Since the reduction is diffusion controlled, indium can be estimated polarographically in propylenediamine solution.

Polarography is successful in analysing the various types of reversible waves, but it could not be applied to the waves which involves the determination of kinetic parameters (K_s and α) of an electrochemical reaction, taking into account the slow rates of mass-transfer and charge – transfer phenomena. Various method have been developed to determine the kinetic parameters[1–11]. It has been reported that indium is reduced quasi reversibly in most supporting electrolytes.[12–19]

The complexes of indium are not reduced reversibly at DME. The half wave potential shifts towards more negative values with the concentration of propylenediamine, which shows that complex formation is between indium and propylenediamine. The present paper deals with the determination of kinetic parameters, composition and stability constants of the complexes formed.

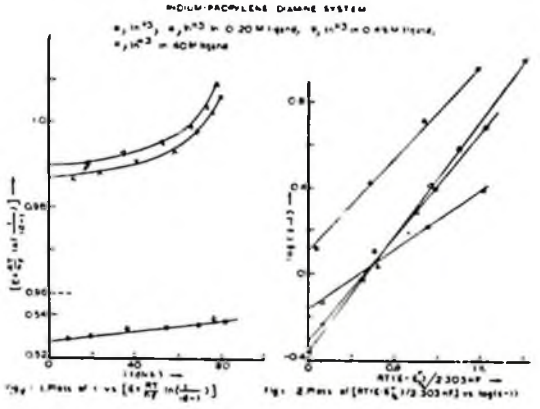
Experimental

Reagent grade chemicals were used. Solution of indium was prepared by dissolving a weighed amount of indium trichloride in double distilled water. The ionic strength was kept constant ($\mu = 0.1$) by Sodium perchlorate. Triton X-100 was used as maxima suppressor All the observations were taken by a manually operated polarograph. The dropping mercury electrode had the following characterstics : $m = 2.12^{mg}/_{sec}$ $t = 6.4$ sec. (in an open circuit). H-type cell saturated with sodium chloride agar-agar bridge was used. The temperature was kept at 30 ± 0.02°C. Purified nitrogen was used for deaeration.

Results and Discussion

In each case, a single well-defined reduction wave appeared, whose half-wave potential shifted towards more negative values and the diffusion current decreased with increasing concentration of propylenediamine, This indicates the occurrence of complex formation between In^{+3} and propylenediamine. Plots of $\log \frac{i}{(i_d - i)}$ against f. d. e. were linear, but the slope was about 24 ± 2 mV. Plots of i_d against $\sqrt{h}$ (h = effective height of mercury column after applying back pressure correction) were straight lines which passed through origin.

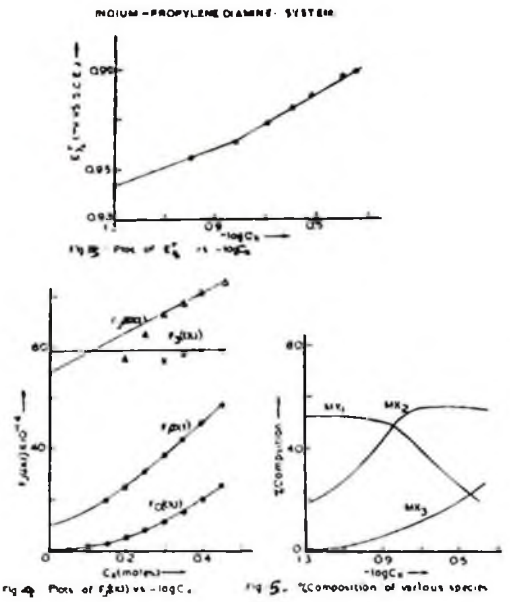
Furthermore, plots of i_d against concentration of In(III) were linear. The above results indicate that,



although the reduction is diffusion-controlled it is not a reversible process. The reversible half-wave potential ($E_{\frac{1}{2}}^{r}$) was obtained from the observed $E_{\frac{1}{2}}$ by a method[20] which involves the plotting of $E + \frac{RT}{nF} \ln \frac{i}{(i_d - i)}$ vs. i and extrapolating it to i = 0. (Fig. 1). The values of K_s and α were determined from the intercept and slope of a plot of log (Z-1) against $(E - E_{\frac{1}{2}}^{r})$ (Fig. 2) and table. 1

TABLE—1 Kinetic parameters for I_n^{+++}– Propylenediamine system.

C x (Moles)	$D_{\frac{1}{2}} \times 10^3$ (Cm^2/Sec)	α	$K_s \times 10^3$ (Cm/Sec)
0 0	1.942	0.647	1.27
0.20	1.895	0.455	0.688
0.40	1.862	0.37	1.84
0.45	1.840	0.345	2.019



The plots of $E_{\frac{1}{2}}^{r}$ against—log Cx is a segmented curve (Fig 3). Therefore, DeFord and Hume's method[21] as extended by Irving[22] was used to calculate the composition and successive stability constants of the complexes. From the graphical extrapolations of F_j ([X]) to zero concentration (Fig. 4), the presence of three species In $(PDA)^{+3}$, In $(PDA)^{+3}_2$ and In $(PDA3^{+3})$, having stability constants $\beta_1 = 1 \times 10^{15}$, $\beta_2 = 7 \times 10^{15}$ and $\beta_3 = 7.8 \times 10^{15}$, respectively were evaluated. Authors have found that indium forms complexes stronger than Zinc, Cadmium, and Lead, and weaker then Copper with propylenediamine.[23,24]

The percentage distribution of indium in various forms as a function of logarithm of propylenediamine concentration are shown in Fig. 5. The results are in table 2.

TABLE-2 Analysis of F_j ([x]) values for In^{+++} propylenediamine system

C_x (Moles)	$-E^r_{1/2}$ (vs SCE)	i_d (div.)	F_o ([x]) (10^{-13})	F_1 ([x]) (10^{-14})	F_2 ([x]) (10^{-14})	F_3 ([x]) (10^{-14})
0.0	0.5275	84.0	—	—	—	—
0.05	0.9435	65.0	9.506	—	—	—
0.10	0.9550	71.0	21.04	—	—	—
0.15	0.9610	77.0	30.75	20.50	—	—
0.20	0.9685	84.0	50.12	25.06	75.30	—
0.25	0.9745	86.0	77.59	31.03	84.12	—
0.30	0.9795	86.5	113.20	37.73	92.43	74.76
0.35	0.9835	86.5	153.90	43.97	97.06	77.31
0.40	0.9870	86.0	202.50	50.62	101.50	78.75
0.45	0.9900	85.0	257.90	57.33	105.18	78.17

As the reduction is diffusion controlled, indium can be estimated polarographically in propylenediamine solution.

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