REDUCTION OF INDIUM(III) AT DROPPING MERCURY ELECTRODE IN THE PRESENCE OF PYRIDINE IN AQUEOUS AND ETHANOL–WATER MEDIA

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The reduction of indium(III) at dropping mercury electrode in aqueous as well as in 25% ethanol–water media in the presence of pyridine has been studied at a constant ionic strength (0.1 M KNO_3) and at 30 and 40 °C. The reduction is diffusion-controlled but the electrode process is quasi-reversible in both media. The reversible half-wave potential values, $E_{1/2}^r$, have been obtained by Gelling's method. The plot of $E_{1/2}^r$ versus pyridine concentration is a straight line and the number of ligands, j, was determined from the slope. This shows the formation of a single complex. The stability constant has been determined by Lingane's method. In(III) forms one complex species with composition 1:1, $[In(py)]^{3+}$. The values of thermodynamic parameters ΔG, ΔH and ΔS of the complexation reaction have also been determined at 30 °C.

Keywords: Electroreduction; Indium; Pyridine; Polarography; Stability constants; Thermodynamics.

Polarography can be advantageously applied to the study of complex metal ions when the reductions of both metal ion and metal ion complex proceed reversibly at the dropping mercury electrode. Theoretical developments[1–10] have not made it possible to study the complexes of these metal ions, which reduce quasi-reversibly or even irreversibly at the dropping mercury electrode (DME). Indium has been reported to reduce quasi-reversibly in most solvents in the presence of many supporting electrolytes.

Potentiometric[11–18] and spectrophotometric[19–27] studies on the complex of indium have been reported. A survey of literature reveals that contradictory results in respect of polarographic reduction of In(III) have been reported in the presence of various complexing and non-complexing media[28–38]. The polarographic reduction of In(III) has created much interest

due to differences observed in the nature of its reduction in various supporting electrolytes[39–45]. Moorhead and MacNevin[42] 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.[39] 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 V vs SCE. At pH > 3, the limiting current dropped sharply due to precipitation of the hydroxide[39,46]. Pospisil and Levie[43] concluded that in solutions containing only perchlorate and nitrate or sulfate ions, the reduction of aquo-indium ions is extremely slow. At pH ≥ 2 it proceeds almost exclusively via hydrolysis products. It has been assumed that $In(H_2O)_4(OH)_2^+$ provides an effective path for the reduction of In(III)[47,48]. The specifically adsorbed halides and thiocyanate and some organic anions at the dropping mercury electrode also catalyses the reduction[39,49]. Hampson and Piercy[50] observed that at pH ≥ 2.7 the potential of an indium electrode changed markedly for small changes of pH indicating that the electrode reaction $In^{3+} + 3 e \rightarrow In$ was complicated by the presence of phase hydroxide (or oxide) at the electrode.

Irreversible reduction of In(III) has been reported in perchlorate and nitrate media[51–57] while in halides, thiocyanate and non-complexing media[58–60] the reduction has been found to be reversible. In certain supporting electrolytes[61–63], however, the reduction has been reported to be quasi-reversible. In view of these conflicting results, it was thought of interest to study the reduction of In(III) at the dropping mercury electrode in the presence of pyridine to throw light on the nature of reduction. The present paper deals with the polarographic study of indium–pyridine complexes in aqueous and ethanol–water media with the aim to study the effect of solvents on complexation and electrode kinetics.

EXPERIMENTAL

Reagents

All the chemicals used were of analytical grade and the stock solutions were prepared in double-distilled water. Potassium nitrate (0.1 mol l^{-1}) was used as the supporting electrolyte and Triton-X-100 (0.002%) as the maximum suppressor. The concentration of metal ion in test solutions was 1.0 mmol l^{-1} and pH of the test solution was adjusted to 4.6 using dilute HCl or NaOH solutions. The concentration of ligand was varied from 0.2 to 1.2 mmol l^{-1}.

Apparatus

An Elico digital polarograph (CL-357) was used for obtaining the current–voltage curves. Polarograph contains counter electrode, standard calomel electrode and the dropping mercury electrode. De-oxygenation of solutions was done by bubbling purified nitrogen for 15 min. The potentials were measured against a saturated calomel electrode (SCE). U7^c type German
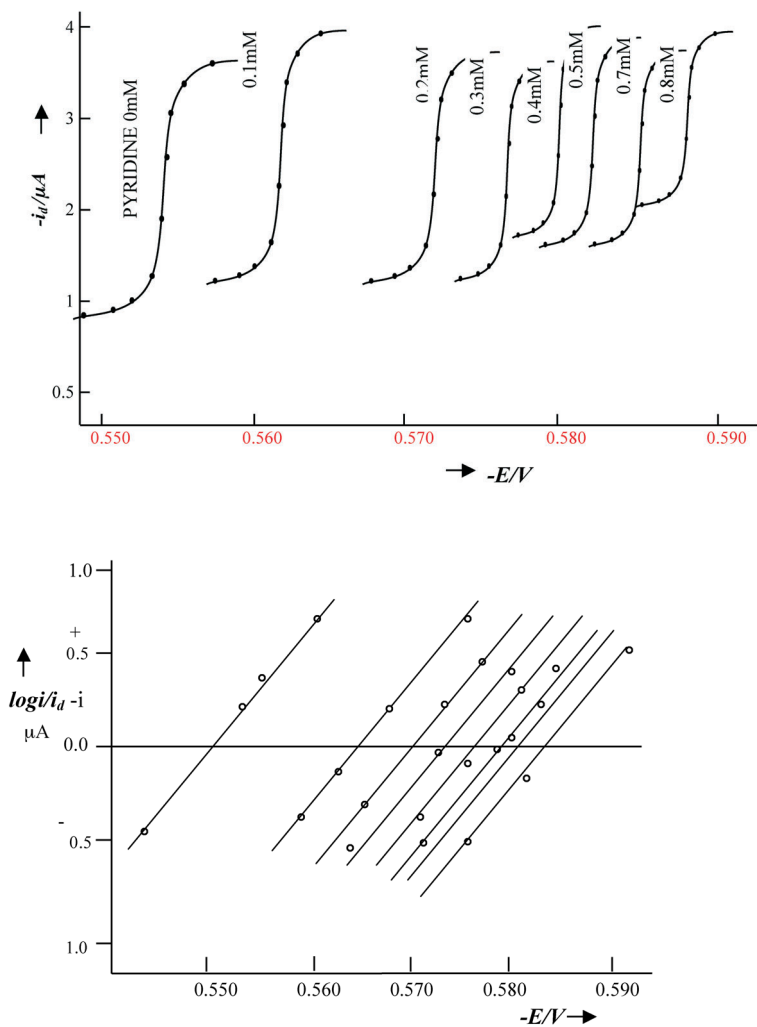

FIG. 1
In(III)–pyridine system in aqueous media at 30 °C: polarograms (a) and corresponding log plots (b)

thermostat having an accuracy ±0.1 °C was employed to maintain the temperature constant in all the experiment work. The pH measurements were carried out by the Toshnial CL 54 pH meter (accuracy ±0.01 pH). The apparatus was calibrated with standard buffers of different pH values before and after each series of measurements. The capillary had following characteristics: the rate of flow of mercury from DME m = 4.66 mg s^{-1}, drop time t = 3.0 s, $m^{2/3}t^{1/6}$ = 3.350 at height of the mercury column h = 100 cm.

TABLE I
Polarographic measurements and $F_j[X]$ values for In(III)–pyridine system in aqueous media at 30 (a) and 40 °C (b)

(a)

Pyridine conc. mmol l^{-1}	$-\log C_x$	i_d, μA	$-E_{1/2}^r$, V	$\Delta E_{1/2}^r$, V
0.00		3.0	0.5500	
0.1	4	2.95	0.5650	0.015
0.2	3.69	2.85	0.5720	0.022
0.3	3.52	2.8	0.5750	0.025
0.4	3.39	2.75	0.5780	0.028
0.5	3.30	2.65	0.5800	0.030
0.7	3.15	2.5	0.5820	0.032
0.8	3.09	2.2	0.5850	0.035

(b)

Pyridine conc. mmol l^{-1}	$-\log C_x$	i_d, μA	$-E_{1/2}^r$, V	$\Delta E_{1/2}^r$, V
0.00		3.3	0.5450	
0.1	4	3.25	0.5635	0.0185
0.2	3.69	3.15	0.5650	0.020
0.3	3.52	3.0	0.5675	0.0225
0.4	3.39	2.95	0.5700	0.025
0.5	3.30	2.85	0.5730	0.028
0.7	3.15	2.7	0.5750	0.030
0.8	3.09	2.6	0.5775	0.0325

RESULTS AND DISCUSSION

In all the cases single well-defined reduction waves appeare. The plots of the diffusion current i_d versus the effective height of mercury column after applying back pressure $h_{eff}^{1/2}$ and i_d versus the concentration of In(III) are linear and passing through origin, thus indicating that the reduction is

TABLE II
Polarographic measurements and $F_j[X]$ values for In(III)–pyridine system in 25% ethanol–water (v/v) media at 30 (a) and 40 °C (b)

(a)

Pyridine conc. mmol l^{-1}	$-\log C_x$	i_d, µA	$-E_{1/2}^r$, V	$\Delta E_{1/2}^r$, V
0.00		3.0	0.5520	
0.1	4	2.85	0.5670	0.015
0.2	3.69	2.75	0.5740	0.022
0.3	3.52	2.45	0.5770	0.025
0.4	3.39	2.4	0.5800	0.028
0.5	3.30	2.25	0.5820	0.030
0.7	3.15	2.25	0.5840	0.032
0.8	3.09	2.2	0.5870	0.035

(b)

Pyridine conc. mmol l^{-1}	$-\log C_x$	i_d, µA	$-E_{1/2}^r$, V	$\Delta E_{1/2}^r$, V
0.00		3.0	0.5490	
0.1	4	2.95	0.5640	0.015
0.2	3.69	2.9	0.5710	0.022
0.3	3.52	2.75	0.5740	0.025
0.4	3.39	2.7	0.5760	0.027
0.5	3.30	2.65	0.5780	0.029
0.7	3.15	2.65	0.5810	0.032
0.8	3.09	2.5	0.5830	0.034

diffusion-controlled. The plots of log $i/i_d - i$ vs E_{DME} are also linear (Figs 1 and 2) with slopes of the order of 25 ± 2 mV, which are higher than that needed for three-electron reversible reduction (20 mV). As the reduction is not reversible, the observed half-wave potential can not be used for the calculation of stability constants. For this purpose, the reversible half-wave
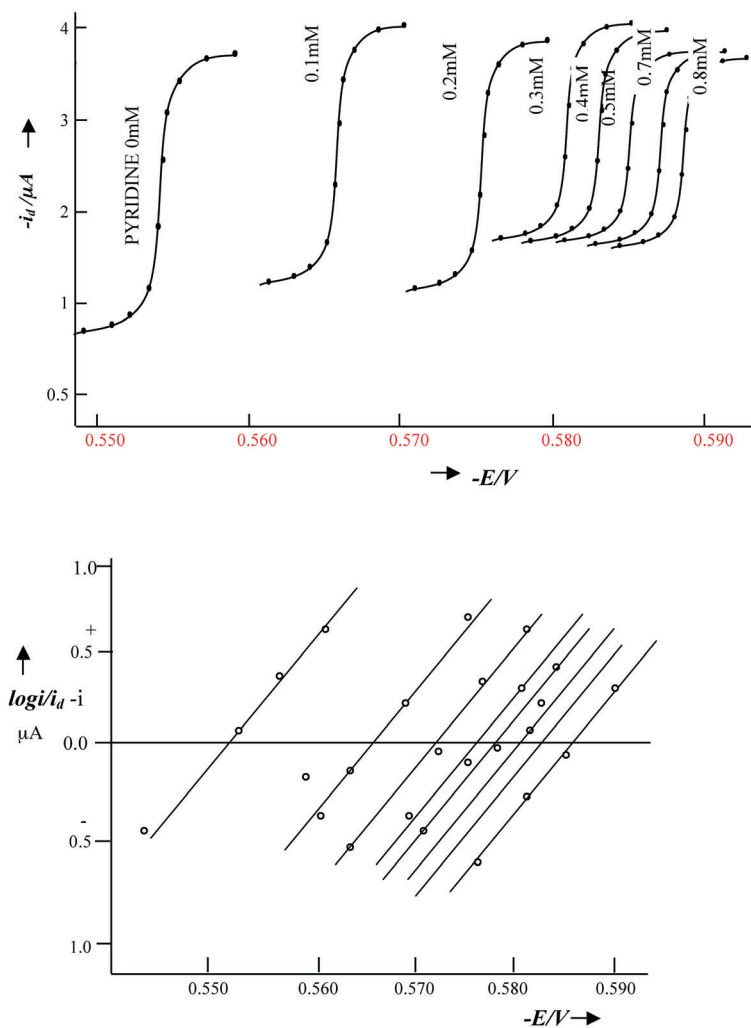

Fig. 2
In(III)–pyridine system in 25% ethanol–water media at 30 °C: polarograms (a) and corresponding log plots (b)

potential values, $E_{1/2}{}^r$, are determined by Gelling's method[64] which involved plotting of $[E + (RT/nF) \log i/i_d{-}i]$ vs i. Extrapolating the curves to zero current values give $E_{1/2}{}^r$ (Tables I and II, Fig. 3). The reversible half-wave potential, $E_{1/2}{}^r$, shifts towards more negative values and the diffusion current decreases with an increasing concentration of pyridine, C_X (in mol l^{-1}), in both the media, indicating the formation of complexes of In^{3+} and pyridine. The plot of $E_{1/2}{}^r$ vs $-\log C_X$ gives a straight line (Fig. 4) indicating the formation of a single complex. The stability constant has been determined from $F_j[X]$ function by Lingane's method[65]. The number of ligands, j, is 1.015 at 30 °C and 1.01 at 40 °C in aqueous media, and 1.142
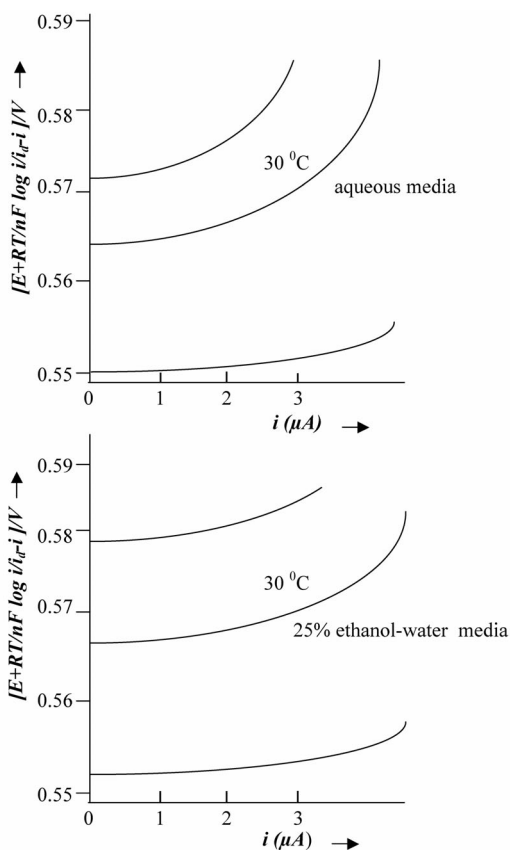

FIG. 3
Plots of $[E + (RT/nF) \log i/i_d - i]$ vs i for In(III)–pyridine system at 30 °C in aqueous (a) and 25% ethanol–water media (b)

at 30 °C and 1.05 at 40 °C in 25% ethanol–water media. Thus they show the formation of one complex.

In order to determine the thermodynamic functions, similar calculations are made at 40 °C under the same conditions. The reduction is again diffusion-controlled but quasi-reversible at 40 °C. The $E_{1/2}{}^r$ values are also determined at 40 °C as described earlier (Tables Ib and IIb). The nature of the plot of $\Delta E_{1/2}{}^r$ vs $-\log C_X$ is similar to that obtained at 30 °C except that
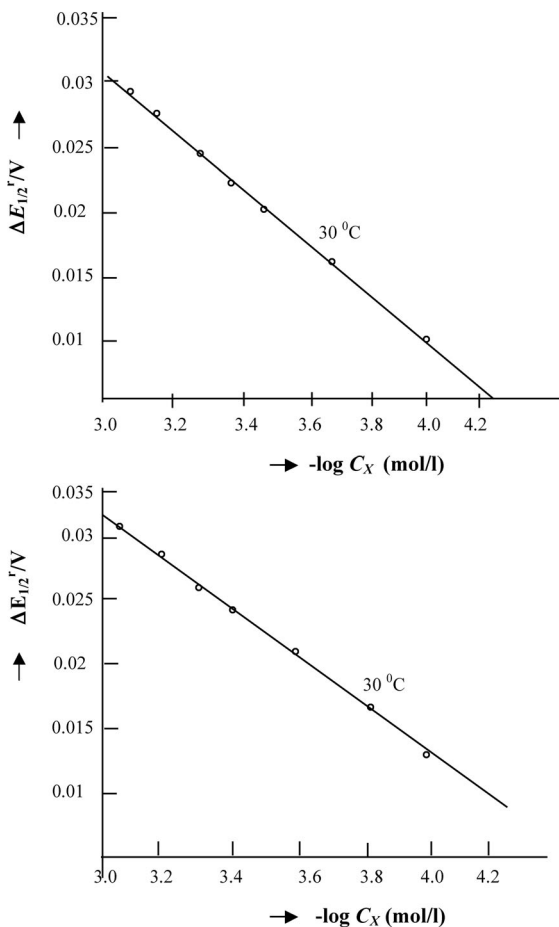

Fig. 4
Plots of $\Delta E_{1/2}{}^r$ vs $-\log C_X$ for In(III)–pyridine system at 30 °C in aqueous (a) and 25% ethanol–water media (b)

the stabilities of the complex decreased with increasing temperature (Table III). The values of change of enthalpy (ΔH), Gibbs energy (ΔG) and entropy (ΔS) accompanying the complexation determined at different temperatures (30 and 40 °C) are reported in Table III. The negative values of ΔG show that the reaction tends to proceed spontaneously. The negative enthalpy changes indicate the exothermic nature of the reaction. It was observed that the $-E_{1/2}$ is shifted to more positive values with the increasing temperature, showing easier reduction and a high degree of reversibility of the electrode process[66]. The stabilities of complexes decrease with the increasing percentage of ethanol. This may be due to the decrease in the dielectric constant of the medium.

TABLE III

Stability constants and thermodynamic functions of In(III)–pyridine complexes at different temperatures and at constant ionic strength (0.1 M KNO_3)

In(III) complexes	Temp. °C	Stability constants log β	Thermodynamic functions		
			ΔH, kcal mol^{-1}	ΔG, kcal mol^{-1}	ΔS, cal mol^{-1} K^{-1}
Aqueous media	30	4.67	–8.22	–6.47	–5.77
	40	4.48			
25% Ethanol–water media	30	5.31			
	40	4.98	–15.66	–7.36	–27.39

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