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A polarographic study of indium complexes with sulphoxine

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Abstract. Indium complexes with sulphoxine were studied by polarography. The reduction was quasireversible. The kinetic parameters for the reduction and the stability constants of the complexes were determined.

Keywords. Polarography ; indium ; sulphoxine ; stability constants.

1. Introduction

Studies of indium complexes by polarography are relatively few probably because the complexes are reduced irreversibly at the dropping mercury electrode. Sarin and Munshi (1977) employed potentiometry for the study of indium complexes with 8-hydroxyquinoline-5-sulphonic acid (sulphoxine or HQS). The results obtained by a polarographic study are reported here.

2. Experimental

A stock solution of indium perchlorate was prepared by dissolving the meta (Albert Victor, Bombay, 99·999% pure) in concentrated nitric acid, fumed with perchloric acid and was estimated by titration with EDTA (Welcher 1958). Potassium nitrate and potassium chloride, used as supporting electrolytes, were of either BDH, Analar or E Merck, GR grade. HQS (E Merck, AG) was used without purification and a 0·05 M standard solution was prepared in 0·05 N sodium hydroxide. The pH of the solutions was measured with a Philips pH-meter (PP 9040). A potentiostat based on the circuit of Greenough *et al* (1951) was used to prepare indium amalgam by constant potential electrolysis.

Polarograms were obtained on a manual set-up using a H-cell and a saturated calomel electrode (SCE) as the reference electrode. Currents are reported after correcting for the residual currents.

3. Results and discussion

Polarograms of indium were obtained in 1·0 M potassium nitrate as well as potassium chloride in the presence of varying concentrations of HQS. The waves were well defined in potassium chloride medium and the half-wave potentials (figure 1) were the same indicating the absence of complexation by the chloride ions in the presence of HQS. Hydroxy complexes were also precluded since the half-wave potential was constant at a constant concentration of the ligand in the region of pH 9 to 10.

The reduction of indium is generally irreversible in noncomplexing media but becomes reversible in the presence of complexing agents (Moorhead and MacNevin 1962). In the case of indium–HQS system, the reduction of the complex was not reversible. The log plots were either curved or had slopes that were slightly higher than the theoretical values indicating quasireversible reduction.

Koryta (1962) has developed a method by which the reversible half-wave potential $E^r_{1/2}$ as well as the standard rate constant k_s and the transfer coefficient α could be determined from the curved log plots using the expression

$$k_s = \frac{i'}{i_d - 2i'} \frac{1}{0 \cdot 886} (D/\tau)^{1/2}, \qquad (1)$$

where i' is the current at $E^r_{1/2}$ and τ is the drop-time. The transfer coefficient was obtained from the slope of the log plot at the top of the wave. Determination of $E^r_{1/2}$ from the log plot is depicted in figure 2. The value of k_s, α and $E^r_{1/2}$ determined at different concentrations of the ligand are reported in table 1.

The data on the indium–HQS system were also analysed by the method of Hale and Parsons (1962). They assume that the upper part of the wave may be considered totally irreversible and the equation for a purely cathodic wave is given by

$$i/i_d = F(\chi), \qquad (2)$$

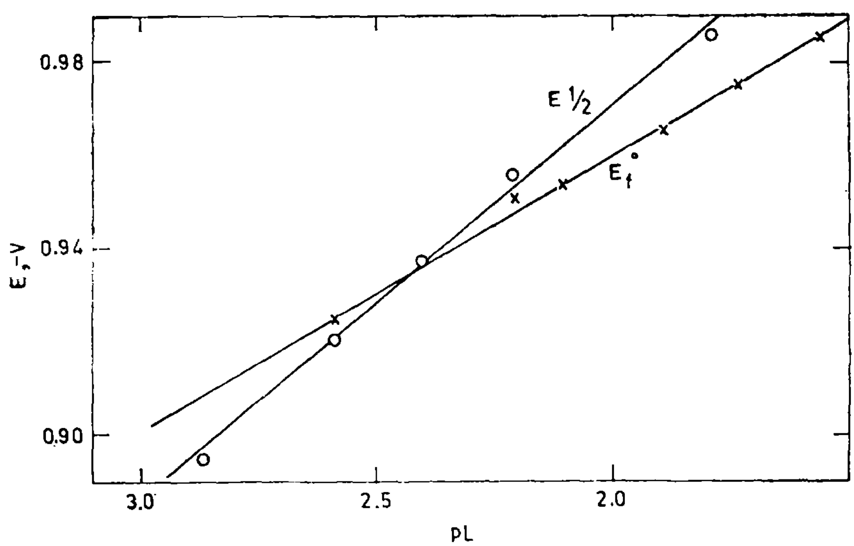

Figure 1. Indium–HQS system : $E_{1/2}$ and E^0_f vs pL.

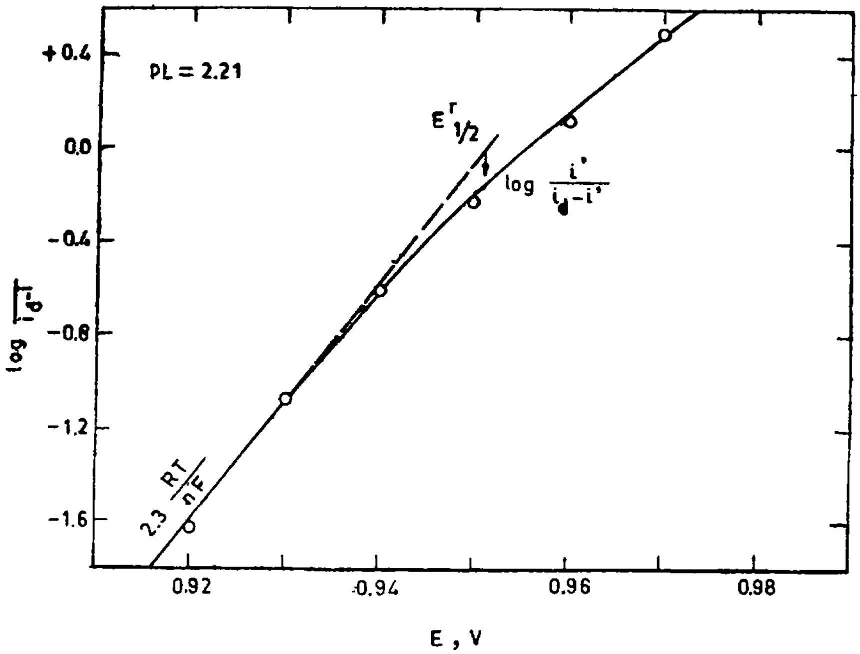

Figure 2. Evaluation of $E^r_{1/2}$, k_s and α by Koryta's (1962) method.

Table 1. Indium-HQS system. Values of α, k_s, $E_{1/2}$ and E^0_f and stability constants.

	Koryta's (1962) method			Hale and Parsons (1962) method			Amalgam polarography	
pL	$E^r_{1/2}$ $-V$	$k_s \times 10^3$ cm.sec^{-1}	α	$E^r_{1/2}$ $-V$	$k_s \times 10^3$ cm.sec^{-1}	α	E^0_f $-V$	log β_3
2·87	0·863	2·1	0·44	0·865	3·4	0·57	..	..
2·59	0·915	2·1	0·68	0·917	3·5	0·59	0·925	28·5
2·41	0·933	2·3	0·73	0·936	3·5	0·58	..	..
2·21	0·951	2·0	0·53	0·953	3·6	0·59	0·951	28·7
2·11							0·954	28·5
1·89							0·965	28·4
1·74							0·976	28·5
1·79	0·986		0·61				..	..
1·56							0·986	28·5
1·40							0·994	28·4

In = 0·5 mM; μ = 1·0 (KCl); $E^r_{1/2(s)}$ = − 0·510 V; $D = 5{\cdot}23 \times 10^{-6}$ cm^2 sec^{-1}; $m^{2/3} \tau^{1/6}$ = 1·89 mg$^{2/3}$ sec$^{-1/2}$

where $F(\chi)$ is a function (Koutecky 1953) of χ given by

$$\chi = (12\tau/7D)^{1/2}\, k_f^0 \exp(-\alpha nFE/RT), \tag{3}$$

where k_f^0 is the forward rate constant at zero applied potential. Another function χ_s is defined as

$$i_s/i_d = F(\chi_s)/2, \tag{4}$$

with $$\chi_s = 2\,(12\tau/7D)^{1/2}\, k_f^0 \exp(-\alpha nFE/RT). \tag{5}$$

χ becomes equal to χ_s when E is equal to $E_{1/2}^r$. i_s and i become identical under these conditions and the potential at which i/id and i_s/i_d are the same gives the reversible half-wave potential (figure 3). The standard rate constant was calculated from k_f^0, $E_{1/2}^r$ and α using the expression

$$k_s = k_f^0 \exp(-\alpha nFE_{1/2}^r/RT). \tag{6}$$

The values reported in table 1 showed good agreement with those obtained by Koryta's method.

The reduction of the indium–HQS complexes was quasireversible with a small overvoltage. It was decided to check the values by determining the formal potentials E_f^0 by amalgam polarography. Composite polarograms of indium were obtained in 0·1 M potassium chloride at different concentrations of HQS at pH 9·5. S-shaped curves were obtained indicating a reversible or quasireversible reduction. The potential E_r corresponding to zero current in the composite polarograms was used to calculate the formal potential from

$$E_r = E_f^0 + RT/nF \ln [i_{d(s)}/i_{d(a)}] \tag{7}$$

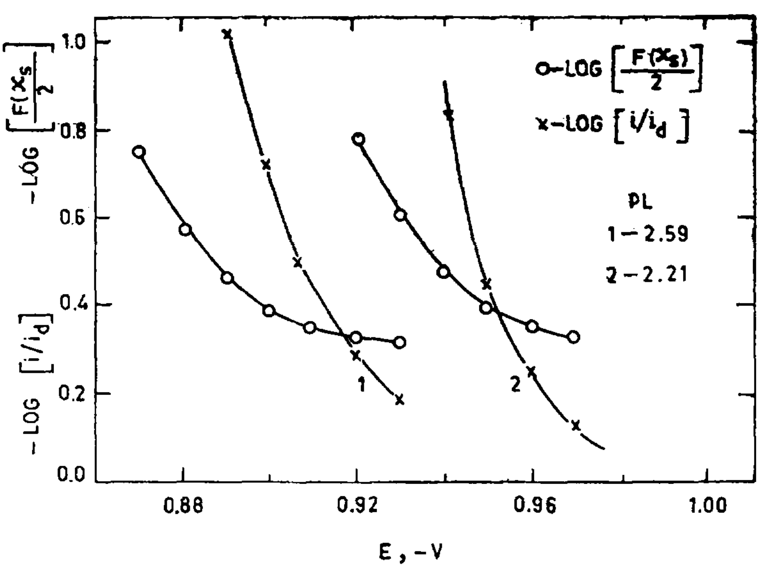

Figure 3. Indium–HQS system: Method of Hale and Parsons (1962).

where $i_{d(c)}$ and $i_{d(a)}$ are the cathodic and anodic diffusion currents. The formal potentials determined by amalgam polarography (table 1) agreed with those obtained by the two methods reported earlier.

The formal potentials were also used for the calculation of the stability constants of the indium–HQS complexes. A plot of E_f^0 vs log [HQS] resulted in a straight line (figure 1) with a slope of 58 mV indicating the predominance of In $(HQS)_3$. The stability constant was calculated by the method of Lingane (1941) as $10^{28.5}$, substituting E_f^0 or $E_{1/2}^r$ in place of $E_{1/2}$ and using a value of $-0 \cdot 510$ V for the reversible half-wave potential for uncomplexed indium (Sundaresan 1979). This compared well with the value of $10^{27.8}$ reported earlier (Sarin and Munshi 1977).

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