INDIRECT POLAROGRAPHIC DETERMINATION OF STABILITY CONSTANTS

IV. Thiosulphate Complexes

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ABSTRACT

The stability constants of cadmium thiosulphate complexes have been determined in 25% methanol medium. The stability constants of thiosulphate complexes of zinc and lanthanum have been determined by the indirect method using cadmium as the indicator ion.

INTRODUCTION

IN continuation of our earlier work[1-3] on the determination of the stability constants of complexes which are either irreversibly reduced or even not reducible at the dropping mercury electrode, the thiosulphate complexes of zinc and lanthanum have been studied by the indirect method.

EXPERIMENTAL

The apparatus was the same as that used in our earlier studies. Stock solutions of cadmium sulphate (E. Merck, G.R.), zinc sulphate (E. Merck, G.R.), lanthanum nitrate (E. Merck, G.R.) and sodium thiosulphate (B.D.H., AnalaR) were standardised by conventional methods.[4]

RESULTS AND DISCUSSION

Cadmium was chosen as the indicator ion for the determination of the stability constants of zinc and lanthanum thiosulphate complexes. The half-wave potentials of cadmium were measured at different concentrations of sodium thiosulphate. The plot of $E_{\frac{1}{2}}$ *vs.* pA indicated the presence of the third complex and the logarithm of the stability constant was calculated as 6·3 which was in good agreement with the reported value of 6·33.[5]

Polarograms of cadmium were also taken in 25% methanol in the presence of thiosulphate. The stability constants of the complexes were calculated as $\log \beta_2 = 5 \cdot 6$ and $\log \beta_3 = 7 \cdot 6$.

Zinc.—Polarograms of solutions containing 0·4 mM cadmium and 0·1 M zinc were taken at different concentrations of thiosulphate. The half-wave potentials are represented in Fig. 1. The nature of the electrode reaction for cadmium was not affected in the presence of zinc. The free ligand concentration (A) was calculated from the shift in the half-wave potential of cadmium (read from the smooth curve) in the presence of zinc.

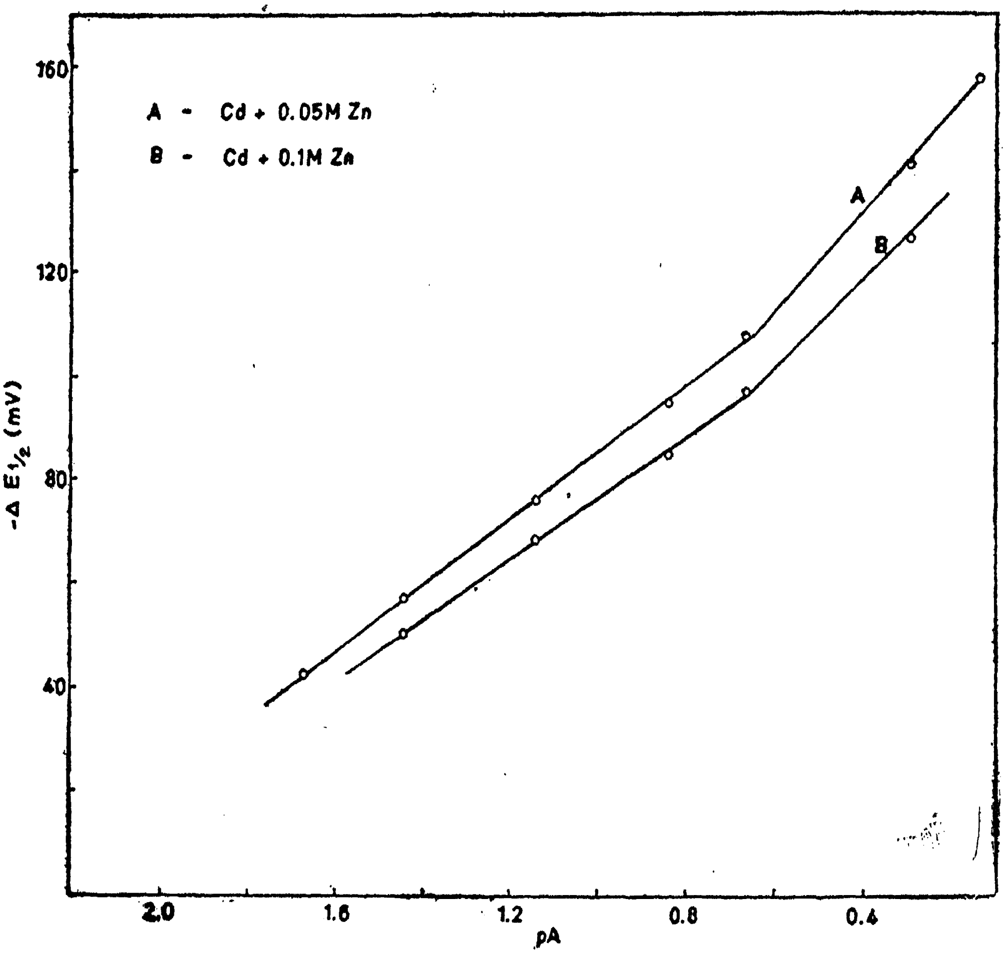

FIG. 1. Plots of $\Delta E_{\frac{1}{2}}$ *vs.* pA.

The results were also confirmed with 0·05 M zinc. Bjerrum's function, $\bar{n}$, calculated from the equation

$$\bar{n} = \frac{C_A - A}{C_{zn}} \tag{1}$$

is given in Fig. 2 B. These values were solved for the stability constants by the method of Rossotti and Rossotti.[6] The values of β_2, β_3 and β_4 are 110, 50 and 2150 respectively, β_1 being absent as indicated by the negative intercept. $\bar{n}$ values calculated from these values agreed well with the experimental values (Table I).

TABLE I

Experimental and calculated $\bar{n}$ values

$\beta_2 = 110$, $\beta_3 = 50$, $\beta_4 = 2150$.

pA	$\bar{n}$ Experimental	$\bar{n}$ Calculated
1·6	0·14	0·14
1·5	0·215	0·21
1·4	0·33	0·32
1·3	0·49	0·48
1·2	0·71	0·71
1·1	1·00	1·00
1·0	1·40	1·36
0·9	1·82	1·76
0·8	2·21	2·17
0·7	2·57	2·57
0·6	2·92	2·92
0·5	3·24	3·22
0·4	3·53	3·45

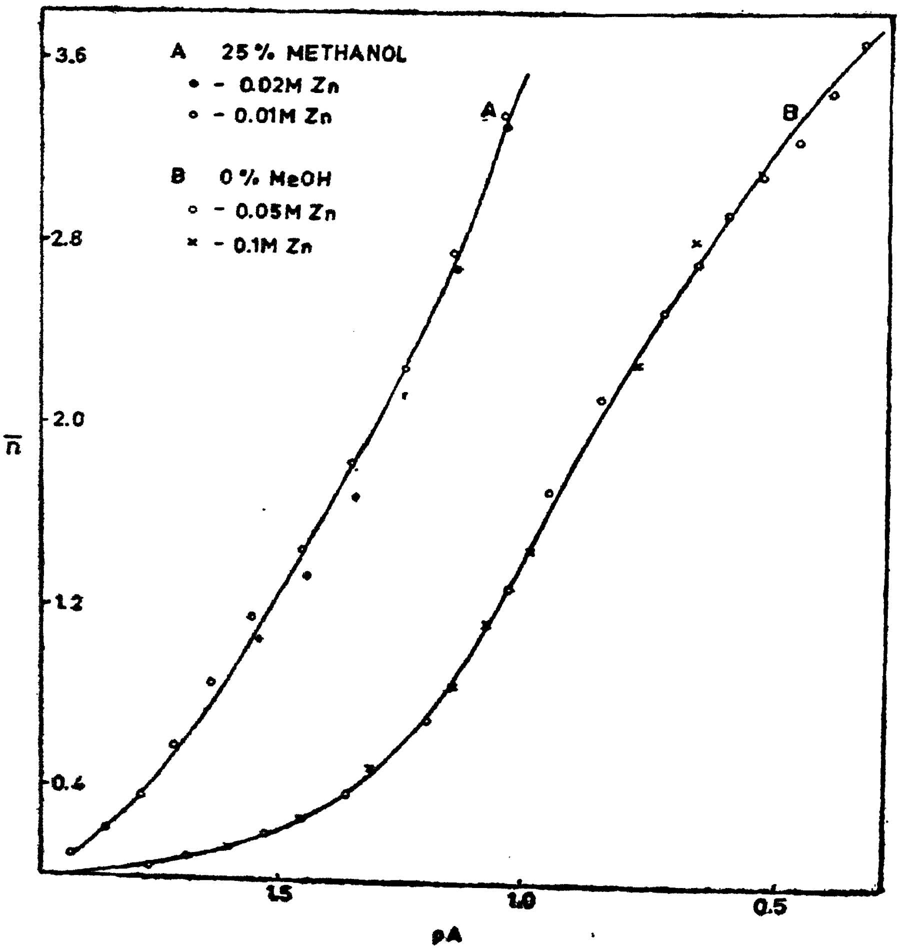

FIG. 2. $\bar{n}$ *vs.* pA.

Similar experiments were carried out in 25% methanol for the determination of the stability constants of zinc thiosulphate complexes. The results are given in Figs. 3 and 2 A. The stability constants were calculated as log $\beta_2 = 2{\cdot}79$, log $\beta_3 = 4{\cdot}0$ and log $\beta_4 \simeq 4{\cdot}78$ (from slope).

TABLE II

Free ligand and n̄ values for La-S_2O_3 system

$-\log C_A$	$-\log A$	$C_A - A$	$\bar{n}$
	La = 0·096 M		
1·8	2·065	0·0073	0·076
1·6	1·870	0·0115	0·12
1·4	1·670	0·0184	0·19
1·2	1·480	0·0300	0·31
1·0	1·275	0·0469	0·49
0·8	1·080	0·0760	0·79
0·6	0·890	0·1220	1·27
	La = 0·048 M		
1·6	1·75	0·007	0·14
1·4	1·55	0·012	0·25
1·2	1·35	0·018	0·38
1·0	1·15	0·029	0·60
0·9	1·06	0·039	0·81
0·8	0·96	0·049	1·02
0·7	0·86	0·062	1·50
0·6	0·76	0·077	1·60

Lanthanum.—The stability constants of lanthanum thiosulphate complexes were also determined by this method. The half-wave potentials of cadmium were measured in the presence and absence of lanthanum at different concentrations of thiosulphate (Fig. 4). The concentration of the free ligand and $\bar{n}$ values (Table II) were calculated by the method explained earlier. The stability constants calculated by the method of Rossotti and Rossotti are log $\beta_1 = 0{\cdot}82$, log $\beta_2 = 0{\cdot}6$ and log $\beta_3 = 2{\cdot}58$. The reported value for log β_1 from spectrophotometric and distribution studies is 0·81[7] and the existence of the third species has also been indicated.[8]

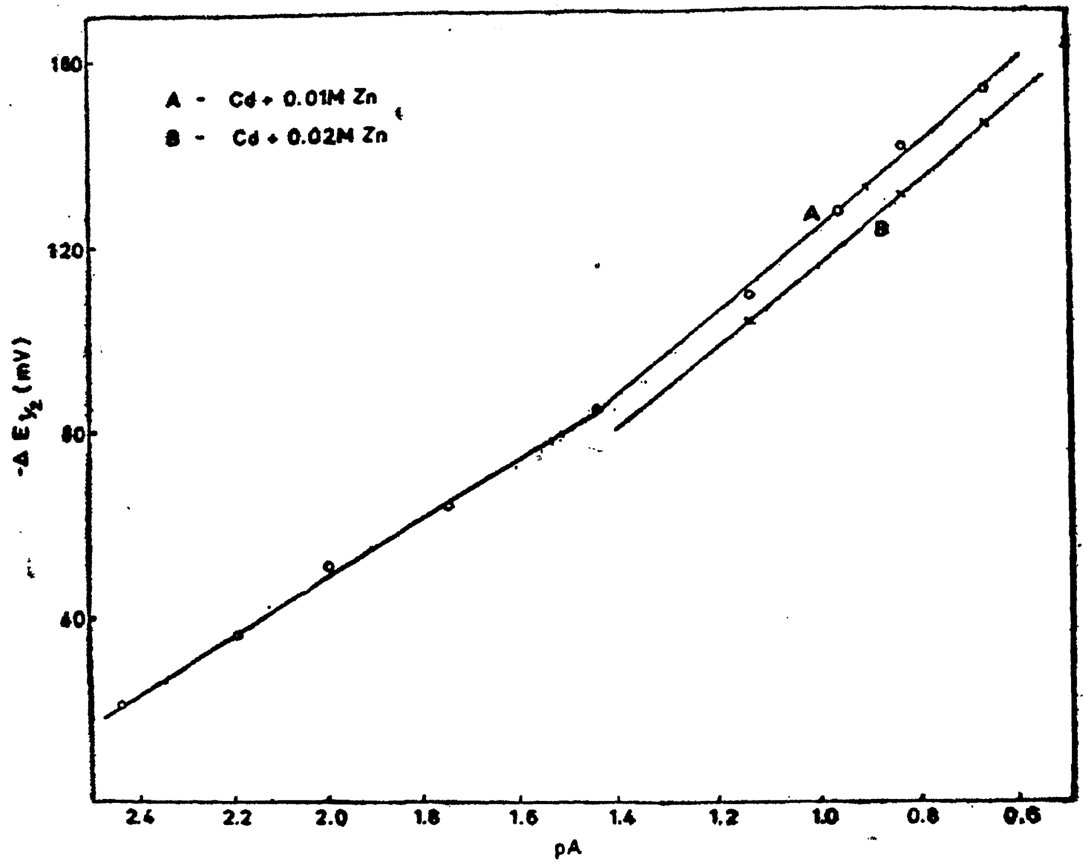

FIG. 3. Plot of $\triangle E_{\frac{1}{2}}$ *vs.* pA (25% methanol).

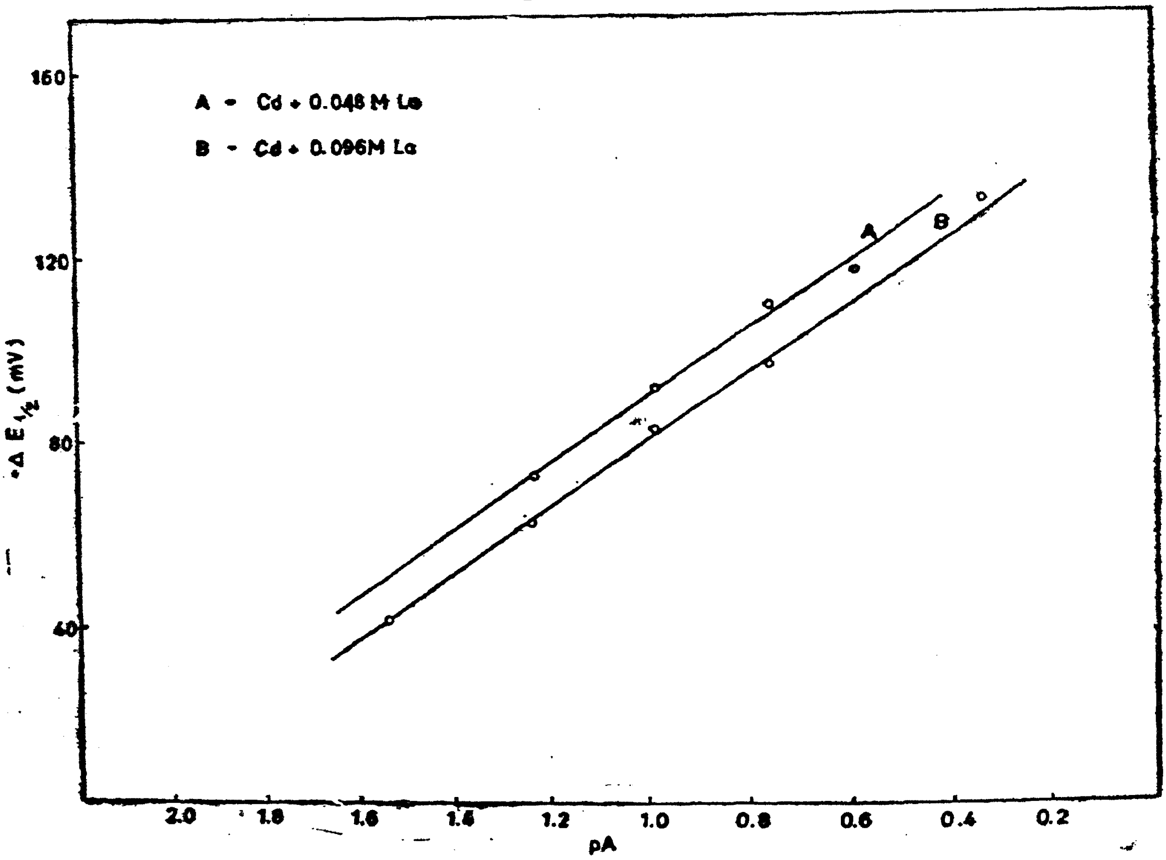

FIG. 4. Plots of $\triangle E_{\frac{1}{2}}$ *vs.* pA.

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