

**ACETYLACETONE COMPLEXES OF  
CADMIUM AND LEAD:  
A POLAROGRAPHIC STUDY**

THIS note reports a study of the polarography of acetylacetonate complexes of cadmium and lead. A manual set-up was used for measuring the current-voltage curves using an H-cell with a saturated calomel electrode (S.C.E.) as a reference electrode. All experiments were carried out at  $30 \pm 0.5^\circ \text{C}$ . with deaerated solutions. The diffusion currents were corrected for the residual currents.

The capillary had the following characteristics:  $m^{2/3} t^{1/6} = 1.89 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$ . A Cambridge Bench Type pH Meter was used for the pH measurements. All chemicals were of Analar grade. Acetylacetonate was dried and distilled before use. The purity of the reagent was checked by the density measurement. The concentration of acetylacetonate corresponded to  $9.7 \times 10^{-2} \text{ M}$  when 0.1 ml. was diluted to 10 ml. The stock solutions of cadmium and lead were standardised by the gravimetric methods.

The experimental conditions and the results are shown in Tables I and II. In the case of

TABLE I  
Half-wave potentials of cadmium acetylacetonate complex at different pH

Cadmium =  $1.0 \times 10^{-3} \text{ M}$   
Acetylacetonate =  $2.91 \times 10^{-1} \text{ M}$   
Ionic strength = 0.7

pH	$E_{1/2}$ vs. S.C.E. -V	$\Delta E$ -V	$-\log(A^-)$
7.97	0.660	0.078	1.56
8.12	0.667	0.085	1.43
8.36	0.681	0.109	1.23
8.75	0.690	0.115	0.96
8.85	0.704	0.122	0.89
9.1	0.718	0.136	0.70

TABLE II  
Half-wave potentials of lead acetylacetonate complex at different pH

Lead =  $1.0 \times 10^{-3} \text{ M}$   
Acetylacetonate =  $2.91 \times 10^{-1} \text{ M}$   
Ionic strength = 0.7

pH	$E_{1/2}$ vs. S.C.E. -V	$\Delta E$ -V	$-\log(A^-)$
8.37	0.490	0.114	1.22
8.60	0.500	0.124	1.05
8.78	0.506	0.120	0.93
9.22	0.517	0.141	0.73
9.56	0.526	0.150	0.63

cadmium the ionic strength was maintained at 0.7 by the addition of requisite amounts of

potassium nitrate. No maximum suppressor was found necessary. In the case of lead the ionic strength was kept constant at 0.7 by the addition of suitable amounts of sodium perchlorate.  $1.0 \times 10^{-3}\%$  thymol in the final solution was used as a maximum suppressor. The pH in these cases was altered by the addition of alkali.

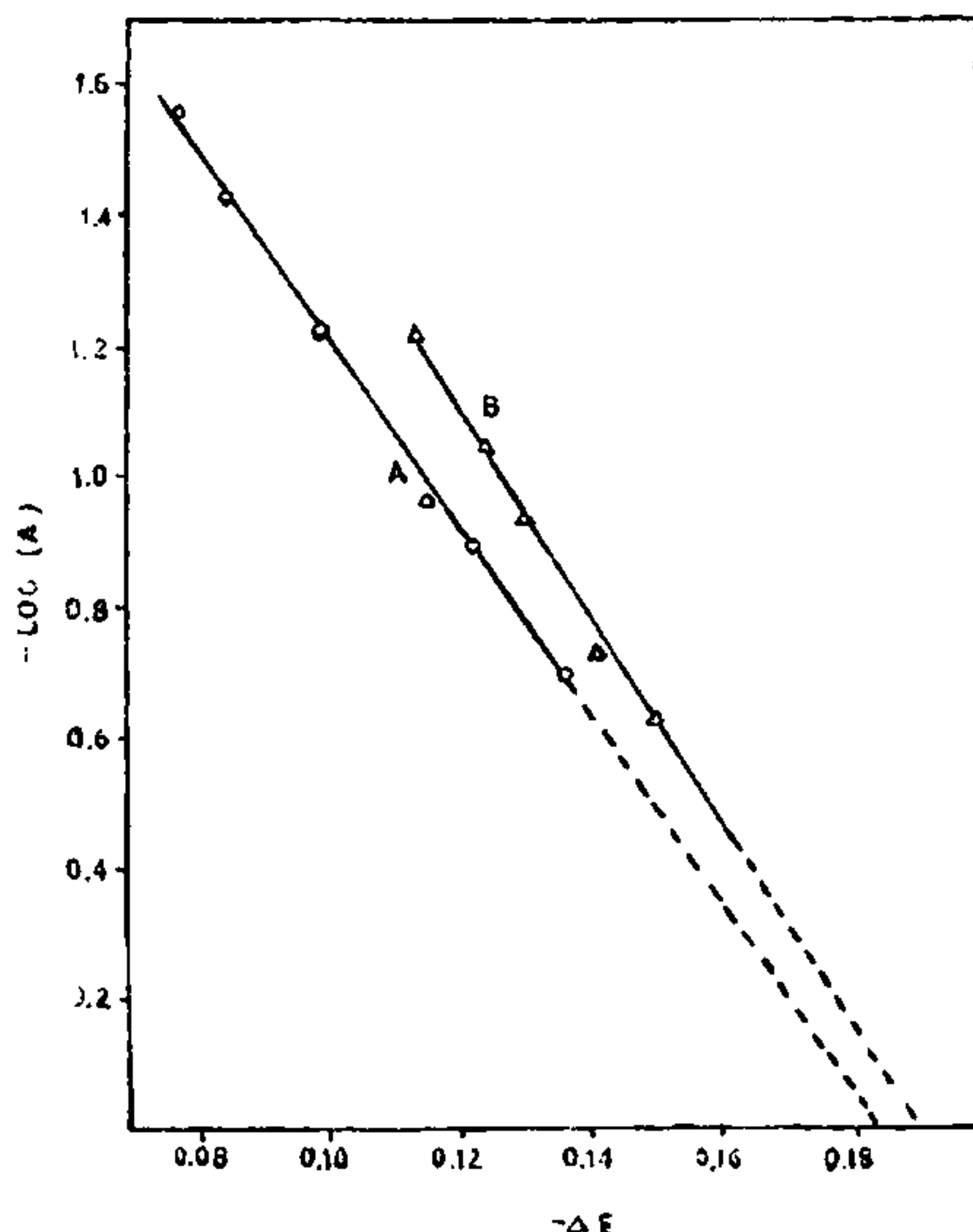
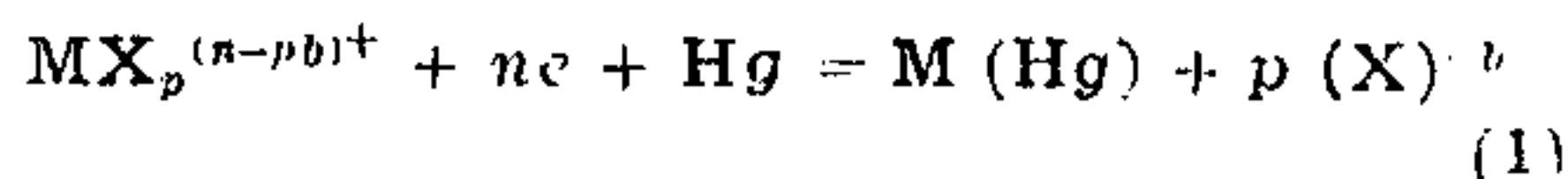


FIG. 1. Plot of  $\Delta E$  vs.  $\log(A^-)$  for cadmium and lead ion in acetylacetonate solutions.  
A—Cadmium. B—Lead.

The reduction of the complex metal ion to a metallic state (amalgam) may be represented by



where  $\text{X}^{-b}$  is the complex-forming substance. Lingane<sup>1</sup> has derived a relationship for the above reaction taking place rapidly and reversibly at the dropping mercury electrode, as given by

$$\frac{\Delta E}{\Delta \log(\text{X}^{-b})} = 0.06 \frac{p}{n} \quad (2)$$

where  $\Delta E$  is the change in the half-wave potential. The co-ordination number,  $p$ , can be determined from the slope of the plot of the half-wave potential vs. log activity of the complex-forming substance. The dissociation constant

$$K = \frac{(\text{M}^{+2})(\text{X}^{-b})^p}{[\text{MX}_p^{(n-pb)^+}] \quad (3)$$

can be obtained from

$$\Delta E = (E_1)_c - (E_1)_s = \frac{0.06 \log K f_c k_s}{n f_s k_c} - \left(\frac{p}{n}\right) 0.06 \log (X^{-b}) \quad (4)$$

where the subscripts *s* and *c* refer to the simple and complex ions respectively.

The concentration of uncombined acetylacetonone is obtained by subtracting the concentration of acetylacetonone combined with the metal ions (assumed as  $MX_2$ ) from the total amount taken. The concentration of free acetylacetonate ion is calculated from the concentration of the free ketone, pH and the dissociation constant for acetylacetonone.<sup>2</sup>

#### CADMIUM

The reversibility of the electrode reaction has been tested for each analysis by plotting  $\log [i/i_{\frac{1}{2}} - i]$  vs. *E*. A slope of  $31 \pm 2$  mV. indicates a two-electron reversible reduction. The half-wave potentials are obtained in the usual manner and are reproducible to  $\pm 2$  mV.

The half-wave potential for the simple ion is determined as  $-0.582$  V. vs. S.C.E. Table I gives the relative shift in the half-wave potential,  $\Delta E$ , and  $-\log (A^-)$ . A plot of  $\Delta E$  vs.  $-\log (A^-)$  for equation (2) (Fig. 1A) is a straight line with the slope equal to 68 mV. and the co-ordination number *p* is therefore two. The concentration values are substituted in equation (4) since the activity coefficients are not known. An intercept of  $-0.1835$  V. is obtained and therefore

$$\frac{0.06 \log k_s}{2 k_c} + \frac{0.06}{2} \cdot \log K = -0.1835. \quad (5)$$

The ratio  $k_s/k_c$  determined from the experimental diffusion currents is 1.16. The pK value for the cadmium-acetylacetonone complex has been calculated to be 6.12. The pK value for this complex has been reported by Izatt and others<sup>3</sup> at an ionic strength of zero from the glass electrode studies.

#### LEAD

A slope of  $30 \pm 1$  mV. for the log plot indicates a two-electron reversible reduction. The half-wave potential of the simple ion in this medium is measured as  $-0.376$  V. vs. S.C.E. A straight line plot (Fig. 1B) for  $\Delta E$  vs.  $-\log (A^-)$  (Table II) with a slope of 62 mV. gives a co-ordination number of two. From the value of the intercept ( $-0.1895$  V.) and as has been shown for cadmium, the pK value for the lead complex has been calculated to be 6.32.

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1. Lingane, J. J., *Chem. Revs.*, 1941, 29, 1.
2. Bjerrum, J., *Stability Constants*, The Chemical Society, 1957, Part I, p. 29.
3. Izatt, R. M., Fernelius, W. C. and Block, B. P. *J. Phys. Chem.* 1955, 59, 80.