ACETYLACETONE COMPLEXES OF
CADMIUM AND LEAD:
A POLAROGRAPHIC STUDY

This note reports a study of the polarography of acetylacetone 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 ± 0.5°C with deaerated solutions. The diffusion currents were corrected for the residual currents.

The capillary had the following characteristics: m²/s¹² = 1.89 mg/s² cm⁻¹/². A Cambridge Bench Type pH Meter was used for the pH measurements. All chemicals were of Analar grade. Acetylacetone was dried and distilled before use. The purity of the reagent was checked by the density measurement. The concentration of acetylacetone corresponded to 0.77 x 10⁻¹ M when 0.1 M was diluted to 10 ml. The stock solutions of cadmium and lead were standardized by the gravimetric methods.

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

<table>
<thead>
<tr>
<th>pH</th>
<th>E₁ vs. S.C.E.</th>
<th>e</th>
<th>-log (A⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.97</td>
<td>0.660</td>
<td>0.078</td>
<td>0.59</td>
</tr>
<tr>
<td>8.12</td>
<td>0.667</td>
<td>0.085</td>
<td>1.43</td>
</tr>
<tr>
<td>8.36</td>
<td>0.681</td>
<td>0.099</td>
<td>0.23</td>
</tr>
<tr>
<td>8.59</td>
<td>0.690</td>
<td>0.115</td>
<td>0.96</td>
</tr>
<tr>
<td>8.85</td>
<td>0.704</td>
<td>0.122</td>
<td>0.69</td>
</tr>
<tr>
<td>9.11</td>
<td>0.718</td>
<td>0.136</td>
<td>0.70</td>
</tr>
</tbody>
</table>

FIG. 1. Plot of ΔE vs. log (A⁻) for cadmium and lead ion in acetylacetone solutions.


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

MXₐⁿ⁺ + uc + Hg → M (Hg) + p (X)ᵇ

(1)

where X⁻ᵇ is the complex-forming substance. Lingane¹ has derived a relationship for the above reaction taking place rapidly and reversibly at the dropping mercury electrode, as given by

Δ log (X⁻ᵇ) = 0.06

(2)

where ΔE 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 = (M⁺²⁻)(X⁻ᵇ)ᵖ

[MXₐⁿ⁺·(X⁻ᵇ)]ência

(3)

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 x 10⁻⁹% thymol in the final solution was used as a maximum suppressor. The pH in these cases was altered by the addition of alkali.
can be obtained from
\[ \triangle E = (E_1) - (E_2) = \frac{0.06 \log K_f k_s}{n} - \left( \frac{P}{n} \right) 0.06 \log (X - b) \] (4)

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

The concentration of uncombined acetylacetone is obtained by subtracting the concentration of acetylacetone combined with the metal ions (assumed as MX₂) 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 acetylacetone².

**Cadmium**

The reversibility of the electrode reaction has been tested for each analysis by plotting log \([i/i_o - i]\) vs. E. A slope of 31 ± 2 mV. indicates a two-electron reversible reduction. The half-wave potentials are obtained in the usual manner and are reproducible to ± 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. 1 A) 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
\[ \frac{0.06 \log k_s}{2} + \frac{0.06}{2} \cdot \log K = -0.1835. \] (5)

The ratio \(k_s/k_c\) determined from the experimental diffusion currents is 1.16. The pK value for the cadmium-acetylacetone complex has been calculated to be 6.12. The pK value for this complex has been reported by Izatt and others⁸ at an ionic strength of zero from the glass electrode studies.

**Lead**

A slope of 30 ± 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. 1 B) 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.

The authors wish to thank Dr. V. T. Athavale, Head, Analytical Division, for his kind interest and encouragement.

Analytical Division, S. C. SABAIYA.
Atomic Energy Estab., V. S. SRINIVASAN.
Trombay, Bombay, India, A. K. SUNDARAM.
March 30, 1962.