

Short Communication

Polarographic studies of zinc with succinic, glutaric and adipic acids

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Abstract

The succinate, glutarate and adipate complexes of zinc have been examined polarographically and their overall stability constants evaluated. Since zinc is reduced quasi-reversibly at the dropping mercury electrode, the Gelling's method was used to obtain the reversible half-wave potential ($E_{1/2}^r$) from the observed ($E_{1/2}$). The standard rate constant, k_s , was of the order of 10^{-3} cm/s, showing a quasi-reversible reduction.

Key words: Polarography, metal complexes, diabasic acid.

Various methods¹ developed to determine the kinetic parameters (k_s and α) are due to Neiman, Koutecky, Delahay, Kivalo and Oldham, Tamamushi and Tanaka, Tachi, Matsuda and Ayabe, Randles, Stromberg and Sathyanarayana.

Tartarate, citrate, acetate complexes of zinc have been studied by Matsuda and co-workers²⁻³. However, very little attention has been paid to the complexes of zinc which are not reversibly reduced at the dropping mercury electrode.

The present paper deals with the determination of kinetic parameters, composition and stability constants of the zinc complexes with succinic, glutaric and adipic acids.

Reagent grade chemicals were used. The 0.001 M solution of zinc was prepared from zinc nitrate. Sodium perchlorate was used to keep the ionic strength constant at 2.0. Solution of the sodium salts of succinic, glutaric and adipic acids were prepared by adding sodium hydroxide to the respective acids and adjusting the pH to approximately 6.8.

The apparatus used and the working procedure is similar to Gaur *et al*¹ with minor modifications (Table I).

Solutions containing 1 mM Zn^{+2} and 0.00, 0.05, 0.1, 0.15 up to 0.5 M sodium succinate, glutarate and adipate were prepared. Requisite amount of sodium perchlorate was added to

Table I

Overall formation constants of zinc complexes with various dibasic acids *

Complexing agent	β_1	β_2	β_3
Succinate	15	100	625
Glutarate	10	75	385
Adipate	9	70	350

* Operating conditions:

Reference electrode: Calomel

Temp: $30 \pm 0.02^\circ\text{C}$

Characteristics of dropping mercury electrode:

m = 1.33 mg/s, t = 4.9 sec at

1.0 V vs SCE in 2 M sodium perchlorate.

keep constant ionic strength ($\mu = 2.0$). In each case, a single well-defined reduction wave appeared whose half-wave potential was found to shift towards more negative side and the diffusion current was found to decrease with the increasing concentration of succinate, glutarate and adipate ion. The plots of $\log [i / (i_d - i)]$ vs E_{de} , were found to be linear but the slope comes to be of the order of $40 \pm \text{mV}$. The plots of i_d vs \sqrt{h} (h is effective height of mercury column after applying back pressure correction) were linear passing through the origin.

Furthermore, the plots of i_d vs concentration of Zn^{+2} were found to be linear. The above results clearly indicate that the reduction process, though diffusion-controlled, is not reversible. The reversible half-wave potential ($E'_{1/2}$) was obtained from plots of $[E - RT/nF \ln (i_d - i) / i]$ vs i (fig 1). The plots of $\log (z-1)$ vs $(E - E'_{1/2})$ for zinc adipate system are given in fig. 2. The method for calculating ($E'_{1/2}$) has been described elsewhere¹.

The plots of $(E'_{1/2})$ vs $-\log C_x$ were found to be smooth curves (fig. 3), showing the formation of two or more complex species which are in equilibrium. The composition and stability constants were calculated by DeFord and Hume's method⁵. The values of overall

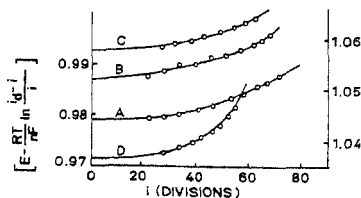


FIG. 1. (a): Determination of $E'_{1/2}$ A, Zinc; B, Zinc containing 0.05 M Succinate; C, Zinc containing 0.1 M Glutarate (Left hand ordinate); D, Zinc containing 0.5; M, Succinate (Right hand ordinate) in NaClO_4 ($\mu = 2.0$).

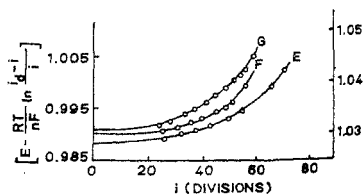


FIG. 1 (b): Determination of $E'_{1/2}$, E, Zinc containing 0.05 M Adipate (Left hand ordinate); F, Zinc containing 0.5 M Adipate, G, Zinc containing 0.5 M Glutarate (Right hand ordinate) in NaClO_4 ($\mu = 2.0$).

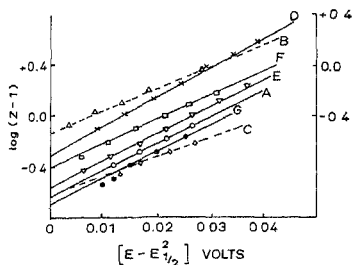


FIG. 2. Plots of $\log(Z-1)$ vs $(E-E_{1/2})$ volts. A, C, E, F & G (Left hand ordinate) B & D (Right hand ordinate).

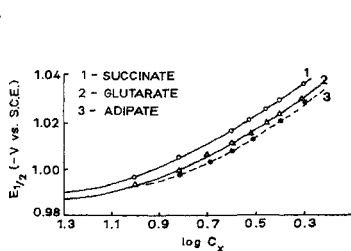


FIG. 3. Plot of half-wave potentials ($E_{1/2}$) vs $\log C_x$, C_x - Molar concentration of succinate, glutarate and adipate.

formation constants β_j were calculated by the graphical extrapolation method. In each case zinc forms complex species $Zn(A)$, where A stands for succinate, glutarate or adipate as the case may be. The formation constants *i.e.* β_1 , β_2 and β_3 (Table I) for zinc are lesser than the corresponding values of lead and cadmium. The distribution of zinc present in various forms was calculated as a function of the logarithm of the ligand concentration.

The values of k_s ($4 \pm 1 \times 10^{-3}$ cm/sec), calculated by Gelling's⁴ method, were determined in sodium perchlorate and complexing media indicating that the reduction process is quasi-reversible.

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