

method for the quantitative determination of the metal ion.

The effect of height of mercury column on i_d has been studied and the plot between i_d vs \sqrt{h} is linear indicating diffusion-controlled limiting current of all these reductions. However, the log plots obtained gave values for slope different from those required for reversible reduction except in the case of cadmium. Hence these metals, except cadmium, are reduced irreversibly.

The $E_{1/2}$ values were well separated and in view of the analytical applications of different metal ions in mixtures, different synthetic mixtures were prepared. The analysis of the following mixtures were carried out in $pH \sim 10.5$ using $0.5M$ tris and $0.1M$ KNO_3 : (i) Cu^{2+} , Zn^{2+} and Mn^{2+} (Table 2); (ii) Cu^{2+} , Cd^{2+} and Zn^{2+} (Table 3); and (iii) Cu^{2+} , Ni^{2+} , and Zn^{2+} (Table 4). The results obtained are satisfactory.

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Reduction of Cd(II)-Itaconate & Cd(II)-Oxalate-Itaconate Complexes at d.m.e.

PRATAP D. JADHAV & RAMESH A. BHOBE*

Department of Chemistry, Marathawada University
Aurangabad

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Electrode reactions of Cd(II) with itaconate and with oxalate-itaconate as mixed ligand ions have been studied polarographically. Cadmium(II) forms three complexes with itaconate ions (ITA) with their respective stability constants, in two different electrolytes (KNO_3 and $NaNO_3$) at ionic strength $2.5M$, as follows: $\log \beta_1 = 1.73, 1.78$; $\log \beta_2 = 2.36 \pm 0.09, 2.30 \pm 0.04$; and $\log \beta_3 = 3.20 \pm 0.05, 3.39 \pm 0.07$. Schaap and McMasters treatment points to the existence of three mixed ligand chelates having 1:1:1, 1:1:2 and 1:2:1 ratio of Cd(II)-Ox-ITA. The observed enhancement of the complexation constant of the mixed ligand chelates has been explained on statistical considerations and on the possibility of simultaneous n -bonding of Cd(II) with both the ligands.

THE formation of mixed ligand chelates of Nd^{3+} and VO^{2+} with itaconate and phenolic acids were investigated potentiometrically in this laboratory^{1,2}. In continuation of our earlier studies³⁻⁷, we report here the polarographic determination of the formation constants of Cd(II) with itaconate and mixed ligand complex with oxalate.

*To whom all correspondence should be addressed.

Reagents used were of AR grade. Potassium oxalate and potassium itaconate, at $pH 7.0$, were used as complexing agents. KNO_3 and $NaNO_3$ were used as supporting electrolytes and to maintain the ionic strength at $2.5M$. The experimental technique was the same as described earlier^{3,4}.

DeFord and Hume's⁸ method was applied to evaluate stability constants for the two-electron, reversible and diffusion-controlled reduction of Cd(II)-oxalate system at $pH 7.0$ and at ionic strength of $2.5M$ (KNO_3). The values came out to be $\log \beta_{10} = 2.70 \pm 0.04$, $\log \beta_{20} = 4.07 \pm 0.15$ and $\log \beta_{30} = 5.14 \pm 0.06$ and agreed well with those obtained by earlier workers^{3,9-11}.

In each solution of the system Cd(II)-itaconate, Cd^{2+} was $1 mM$. The [ligand] was varied from 0.05 to $0.70M$, and the ionic strength was adjusted to $2.5M$ by adding appropriate quantity of KNO_3 . In a second set instead of KNO_3 , the supporting electrolyte used was $NaNO_3$. A single well-defined reduction wave appeared in both the sets and the plots of i_d vs \sqrt{h} (h = effective height of mercury column) were linear, passing through the origin. Again, as expected, the plot of i_d vs [metal ion] was linear. The results obtained showed that the reduction was diffusion-controlled. The plots of $\log i/i_d - i$ vs $E_{d.e.}$ were linear with slopes = 32 ± 1 mV, corresponding to reversible reduction with $n = 2$. The half-wave potential shifted continuously towards more negative values and the diffusion current decreased with increasing [ligand], indicating positively a complex formation of metal ion with the ligand.

Plots of $-E_{1/2}$ vs $-\log C_L$ (C_L = ligand concentration) were smooth curves pointing to the formation of two or more complex ions, in equilibrium. The DeFord and Hume⁸ method, as modified by Irving¹², was used for calculating successive stability constants of various species. The values of overall log stability constants, as obtained from $F_{i0}[X]$ vs C_L curves for the complex species $[Cd(ITA)]$, $[Cd(ITA)_2]^{2-}$ and $[Cd(ITA)_3]^{-4}$ are: $1.78, 2.30 \pm 0.04, 3.39 \pm 0.07$ and $1.73, 2.36 \pm 0.09, 3.20 \pm 0.05$ respectively at $\mu = 2.5M$ ($NaNO_3$ and KNO_3). The stability constants of Cd(II)-itaconate at $\mu = 2.5M$ (KNO_3) were used in the calculation of stabilities of mixed ligand systems, since the experimental conditions were identical in the both.

For the mixed ligand study the two concentrations of itaconate chosen were 0.08 and $0.24M$ at which 1:1 and 1:2 species predominated. Each solution contained $1 mM$ Cd^{2+} , $0.08M$ itaconate and only the oxalate concentration was varied from 0.02 to $0.50M$. The ionic strength was adjusted to $2.5M$ by adding appropriate amount of KNO_3 at $pH 7.0$. The exact procedure was repeated for [itaconate] = $0.24M$.

The plots of $-E_{d.e.}$ vs $\log i/(i_d - i)$ in the two sets studied were linear with the slope values lying in the range $30-32$ mV, which clearly showed that the reduction of Cd(II) ion in the absence and presence of the ligands is reversible involving two electrons. That the reduction was diffusion-controlled was evidenced by the direct proportionality of diffusion current to the square root of the effective height of the mercury head.

The shifts in $-E_{1/2}$ values observed in the presence of itaconate and oxalate ions is greater than that in oxalate ions alone. This proves the formation of Cd(II)-oxalate-itaconate mixed complexes. The relationships between $-(E_{1/2})_c$ and $\log C_L$, at two concentrations of itaconate, were represented by three distinct segments.

With the help of Schaap and McMasters method⁹, the values of coefficients A , B , C and D in both the sets were obtained. These are given below:

At 0.08M [itaconate]: $\log A = 1.18$, $\log B = 3.04 \pm 0.02$, $\log C = 4.14 \pm 0.06$ and $\log D = 5.10 \pm 0.06$.

At 0.24M [itaconate]: $\log A = 1.78$, $\log B = 3.51 \pm 0.02$, $\log C = 4.23 \pm 0.05$ and $\log D = 5.23 \pm 0.08$.

Complete replacement of itaconate by oxalate is further confirmed from the mean value of coefficient D coinciding exactly with the stability constant β_{30} for $[\text{Cd}(\text{OX})_3]^{4-}$ complex ($\log \beta_{30} = 5.14$ and mean $\log D = 5.17$).

From the coefficients A , B , C and D , the stability constants for mixed complex species existing in solutions, $[\text{Cd}(\text{Ox})(\text{itaconate})]^{2-}$, $[\text{Cd}(\text{Ox})(\text{itaconate})_2]^{4-}$ and $[\text{Cd}(\text{Ox})(\text{itaconate})]^{4-}$ were calculated by applying the method of Schaap and McMasters. These are: $\log \beta_{11} = 3.75$ (3.52), $\log \beta_{12} = 4.37$ (3.75) and $\log \beta_{21} = 4.36$ (4.23), values in parentheses were calculated according to the procedure of Watters *et al.*¹³, which is elaborated in our previous papers^{3,4}.

In all the three mixed complex species, the experimentally observed stability constants are greater than those predicted on statistical considerations. The observed trend in the enhancement values is $\beta_{12} > \beta_{11} > \beta_{21}$. Mixed complex is formed when both the ligands are attached to the central metal ion simultaneously. It is possible that simultaneous π -bonding between the metal ion and ligands accounts for the higher values. The simultaneous displacement of four water molecules, during the mixed ligand complexation, will also lead to a favourable entropy factor.

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TLC Separation of Closely Related Amino Acids

S. P. SRIVASTAVA & V. K. DUA

Chemistry Department, University of Roorkee, Roorkee

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A method for TLC separation of sixteen closely related amino acids on silica gel-calcium oxalate mixed adsorbent system has been developed and the probable mechanism of separation has been indicated. The Martin relationship for R_m is found to be obeyed by similarly constituted amino acids.

MIXED adsorbents for TLC separation of closely related phenols¹, aromatic amines² and aliphatic amines³ were developed in this laboratory. It offers promise for a successful TLC separation of other class of compounds. The present paper deals with the TLC separation of closely related amino acids on silica gel-calcium oxalate plates.

TLC plates (0.5 mm thick) were prepared from silica gel (40 g) and calcium oxalate (20 g, mesh size 200). The plates were activated at 60° for 24 hr. Solutions of amino acids (1%, w/v) in distilled water were used for spotting.

The chromoplates after development (180 min) were sprayed with 1% ninhydrin in 50% aq. methanol. Violet spots appeared after heating at 60° for 15 min. Various adsorbents and developers were tried and it was found that a mixture of silica gel-calcium oxalate (40:20) was most suitable for the separation of all the amino acids studied in the presence of a mixed developer (a) butanol-acetic acid-ethyl acetate-water (50:20:30:20) or (b) butanol-acetic acid-chloroform-water (50:20:30:40). The results are presented in Table 1.

It is seen that the R_M values of the similarly constituted amino acids, viz. glycine, alanine, valine and leucine, in the solvent systems (a) and (b)

TABLE 1 — R_F VALUES OF THE VARIOUS AMINO ACIDS ON SILICA GEL-CALCIUM OXALATE CHROMOPLATES

Amino acid	$R_F \times 100$	
	a	b
Glycine	22	42
Aspartic acid	28	46
Glutamic acid	34	53
Serine	24	40
Leucine	53	67
Methionine	48	60
Asparagine	20	37
Alanine	29	45
Valine	42	56
Threonine	26	35
Cysteine	39	50
Lysine	14	30
Phenylalanine	57	70
Histidine	17	26
Tyrosine	62	73
Tryptophane	67	76

(a) Butanol-acetic acid-ethyl acetate-water (50:20:30:20).
 (b) Butanol-acetic acid-chloroform-water (50:20:30:40) (chloroform layer).