

Polarographic Study on Mixed Ligand Complexes of Pb(II) with Nitrogen Donor Ligands & Carboxylate Ions

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The mixed ligand complexes of Pb(II) with α -, β -, γ -picolines and pyridine and tartrate (Tart^{2-}), succinate (Succ^{2-}), malonate (Mal^{2-}), citrate (Cit^{3-}) and maleate (Male^{2-}) have been studied polarographically at $25 \pm 0.1^\circ\text{C}$, $\mu = 2.0$ (NaNO_3) and $\text{pH} = 6.0$. The polarographic reduction of the complexes in each case is reversible and diffusion-controlled. The composition and stability constants of mixed complexes have been determined by Schaap and McMasters method.

In earlier publications¹⁻³ we have reported polarographic studies on the compositions and stability constants of mixed ligand complexes of Cd(II) with imidazole, and tartrate and malonate, and of Eu(III) with succinate and imidazole. Polarographic studies on mixed ligand complexes of Pb(II) with nitrogen donor ligands such as α -, β - and γ -picolines and various carboxylate ions do not appear to have been carried out so far. This paper reports results of our efforts on such mixed ligand complexes of Pb(II).

Materials and Methods

All the chemicals used were of AR grade and their stock solutions were prepared in conductivity water. Potassium salts of tartaric acid (Tart), succinic acid (Succ), malonic acid (Mal), citric acid (Cit) and maleic acid (Male) were used. The concentration of Pb(II) was maintained constant at $1 \times 10^{-3} M$. Polarograms of the deaerated solutions were obtained using a digital polarograph (Toshniwal CLO2 B) at a constant ionic strength, $\mu = 2.0$ (NaNO_3) and $\text{pH} = 6$ in the presence of Triton X-100 at $25 \pm 0.1^\circ\text{C}$. The d.m.e. had the following characteristics (in 2.0 NaNO_3 , open circuit):

(i) For Pb(II)-male-picolines systems:

$$m = 2.18 \text{ mg s}^{-1}; t = 4.6 \text{ s}; m^{2/3} t^{1/6} = 2.17 \text{ mg}^{2/3} \text{ s}^{-1/2}; h_{\text{corr}} = 84 \text{ cm}.$$

(ii) For Pb(II)-pyridine- Tart^{2-} / Succ^{2-} / Mal^{2-} / Cit^{3-} systems: $m = 1.52 \text{ mg s}^{-1}$; $t = 3.04 \text{ s}$; $m^{2/3} t^{1/6} = 1.58 \text{ mg}^{2/3} \text{ s}^{-1/2}$; $h_{\text{corr}} = 51 \text{ cm}$.

Results and Discussion

The polarographic reduction of Pb(II) in the presence of Tart^{2-} , Succ^{2-} , Mal^{2-} , Cit^{3-} and Male^{2-} , pyridine (Py) and α -, β - and γ -picolines (abbreviated as α -pico, β -pico, and γ -pico respectively) was found to be reversible and diffusion-controlled as the slopes of log plots were of the order of

$31 \pm 1 \text{ mV}$ and the plots of i_d versus $h_{\text{corr}}^{1/2}$ were linear passing through the origin. The same was true in the case of mixed ligand systems.

Free ligand concentrations were calculated from the pK_a values and pH of the solution. The stability constants of simple complexes of Pb(II) with carboxylate ions and pyridine and α -, β - and γ -picolines were determined separately prior to the study of mixed ligand systems. Identical conditions were maintained in both the simple and the mixed systems.

Plots of $E_{1/2}$ versus $\log [\text{ligand}]$, except those with Cit^{3-} , Py, α -pico and γ -pico were smooth curves thereby indicating the formation of successive complexes, which were studied by DeFord and Hume⁴ method. The plots of $E_{1/2}$ versus $\log [\text{Cit}^{3-}]$, $\log [\text{Py}]$, $\log [\alpha\text{-pico}]$ and $\log [\gamma\text{-pico}]$ were linear and hence the composition and stability constants of the complex species were determined by Lingane's⁵ method. The values are presented in Table 1.

Mixed complexes

The concentration of each carboxylate ion was varied from 0 to $0.6 M$ while keeping the concentration of nitrogen donor ligand constant. It was seen that $E_{1/2}$ values shifted to more negative values than those obtained in the absence of nitrogen donor ligands, indicating the formation of mixed complexes. The composition and stability constants of mixed complexes were determined by Schaap and McMasters method⁶. The polarographic characteristics and $F_{ij}[\text{X}, \text{Y}]$ functions ($\text{X} = \text{Tart}^{2-}$, Succ^{2-} , Mal^{2-} , Cit^{3-} , Male^{2-} , $\text{Y} = \text{Py}$, α -pico, β -pico and γ -pico) of the systems were determined. From the intercept of the plots of $F_{ij}[\text{X}, \text{Y}]$ versus $[\text{carboxylate ion}]$ on $F_{ij}[\text{X}, \text{Y}]$ axis, the values of the constants⁷, A , B , C and D etc. in each case, were determined. From the analysis of the values of these constants, the composition and stability constants were determined. The salient

Table 1—Composition and Stability Constants of Simple and Mixed Complexes of Pb(II) with Tart²⁻, Succ²⁻, Mal²⁻, Citr³⁻ and Male²⁻ and Py, α -pico, β -pico and γ -pico at 25 $\pm$ 0.1°C

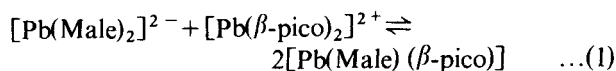
System	Composition	Stability constant
(i) Pb(II)-Tart ²⁻	[Pb(Tart)]	log β_1 = 1.30
	[Pb(Tart) ₂] ²⁻	log β_2 = 2.90
(ii) Pb(II)-Succ ²⁻	[Pb(Succ)]	log β_1 = 2.7
	[Pb(Succ) ₂] ²⁻	log β_2 = 3.4
	[Pb(Succ) ₃] ⁴⁻	log β_3 = 3.9
(iii) Pb(II)-Mal ²⁻	[Pb(Mal)]	log β_1 = 2.6
	[Pb(Mal) ₂] ²⁻	log β_2 = 3.3
	[Pb(Mal) ₃] ⁴⁻	log β_3 = 4.5
(iv) Pb(II)-Citr ³⁻	[Pb(Citr)] ⁻	log β_1 = 3.4
(v) Pb(II)-Male ²⁻	[Pb(Male)]	log β_1 = 1.70
	[Pb(Male) ₂] ²⁻	log β_2 = 2.60
	[Pb(Male) ₃] ⁴⁻	log β_3 = 3.56
(vi) Pb(II)-Py	[Pb(Py)] ²⁺	log β_1 = 1.50
(vii) Pb(II)- α -pico	[Pb(α -pico)] ²⁺	log β_1 = 1.83
(viii) Pb(II)- β -pico	[Pb(β -pico)] ²⁺	log β_1 = 0.90
	[Pb(β -pico) ₂] ²⁺	log β_2 = 1.85
(ix) Pb(II)- γ -pico	[Pb(γ -pico)] ²⁺	log β_1 = 1.56
(x) Pb(II)-Tart ²⁻ -Py	[Pb(Tart)(Py)]	log β_{11} = 2.40
(xi) Pb(II)-Succ ²⁻ -Py	[Pb(Succ)(Py)]	log β_{11} = 2.8
	[Pb(Succ) ₂ (Py)] ²⁻	log β_{21} = 3.1
(xii) Pb(II)-Mal ²⁻ -Py	[Pb(Mal)(Py)]	log β_{11} = 3.2
	[Pb(Mal) ₂ (Py)] ²⁻	log β_{21} = 3.7
(xiii) Pb(II)-Citr ³⁻ -Py	[Pb(Citr)(Py)] ⁻	log β_{11} = 3.9
(xiv) Pb(II)-Male ²⁻ -Py	[Pb(Male)(Py)]	log β_{11} = 3.63
	[Pb(Male) ₂ (Py)] ²⁻	log β_{21} = 3.18
(xv) Pb(II)-Male ²⁻ - α -pico	[Pb(Male)(α -pico)]	log β_{11} = 3.24
	[Pb(Male) ₂ (α -pico)] ²⁻	log β_{21} = 3.30
(xvi) Pb(II)-Male ²⁻ - β -pico	[Pb(Male)(β -pico)]	log β_{11} = 3.40
	[Pb(Male)(β -pico) ₂]	log β_{12} = 3.70
	[Pb(Male) ₂ (β -pico)] ²⁻	log β_{21} = 3.42
(xvii) Pb(II)-Male ²⁻ - γ -pico	[Pb(Male)(γ -pico)]	log β_{11} = 3.00
	[Pb(Male) ₂ (γ -pico)] ²⁻	log β_{21} = 3.30

features of various mixed systems are summarised below:

Pb(II)-carboxylate ion-Py and Pb(II)-Male²⁻-pico mixed systems

The relative tendencies of carboxylate ions and the base to add on to simple complexes can be compared. It is seen that carboxylate ions have a stronger tendency to add on to simple complexes to form mixed complexes as compared to that of the base. This can be attributed to the electrostatic factor whereby the negative charge on the carboxylate ion facilitates its entry into the coordination sphere of the positively charged metal ion.

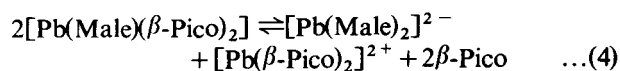
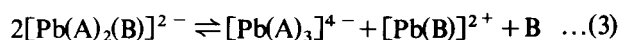
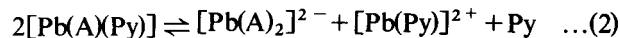
The mixing constant K_M (log value) for the reaction (1)



works out to be +1.175. The positive log K_M value shows that the mixed complex [Pb(Male)(β -pico)] is

more stable than the simple binary complex of Pb(II) with either maleate or β -picoline.

The log value of equilibrium constants for the disproportionation reactions (2-4) work out to be negative, indicating that the formation of mixed complexes is favoured over the simple ones.



(where A = Tart²⁻ or Succ²⁻ or Mal²⁻ or Male²⁻, B = Py or α -, β - and γ -pico).

The compositions and stability constants of simple and mixed complexes are summarised in Table 1.

It is seen that 1:2:1 or 1:1:2 complexes are more stable than the 1:1:1 species, except in the case of Male²⁻ and Py system where 1:1:1 species is stronger than the 1:2:1. This may be attributed to the steric hindrance caused

by the incoming of the second maleate ion owing to its existence in *cis* and *trans* forms. The increased stability of 1:2:1 and 1:1:2 complexes over the 1:1:1 species may be attributed to the steric effect exerted by the second molecule of the incoming ligand on the coordination sphere of Pb^{2+} .

Variation of degree of formation (% distribution) with the concentration of carboxylate ion

Since pyridine and picolines are weaker ligands than the carboxylate ions, in all mixed systems the concentration of nitrogen donor ligand was kept constant while that of carboxylate ions was varied. The variation in percentage distribution of various complex species with the concentration of carboxylate ion shows that: (i) 1:1:1 species predominate in all the systems; (ii) as the concentration of carboxylate ion increases the degree of formation of 1:1:1 species decreases while that of 1:2:1 increases; and (iii) at a certain concentration of carboxylate ion, the proportions of 1:1:1 and 1:2:1 species tend to be similar and these appear to exist in equilibrium with each other.

The predominance of 1:1:1 complex species over the others may be attributed to the preponderance of the electrostatic factor. However, with the increasing concentration of carboxylate ion the degree of formation of 1:1:1 species decreases while that of 1:2:1 increases. The reason for this behaviour is not far to seek. With the formation of 1:1:1 species the coordination sphere of the metal ion is not still saturated i.e. its secondary valencies are yet to be satisfied by the ligand which is possible only when more carboxylate ion (whose concentration is being varied in the present systems) is added. Hence the percentage of 1:1:1 species decreases while that of 1:2:1 increases.

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