

Polarographic Study of Europium(III)-Succinate-Ethylenediamine, Europium(III)-Succinate-Pyridine, Europium(III)-Malonate-Ethylenediamine and Europium(III)-Malonate-Pyridine Mixed Systems

(Miss) MADHU SHIVHARE & MUKHTAR SINGH*

Department of Chemistry, Agra College, Agra 282 002

Received 28 October 1983; accepted 27 January 1984

The mixed complexes of Eu(III) with dicarboxylate ions, viz., succinate (Succ^{2-}) and malonate (Mal^{2-}), and with nitrogen containing ligands, viz., ethylenediamine (en) and pyridine (Py) have been studied polarographically at 25°C and at constant ionic strength, $\mu = 0.1$ (NaNO_3) and pH 6. The reduction of the complexes in each case is quasi-reversible and diffusion-controlled. Eu(III) forms three mixed complexes each with Succ^{2-} and en; Succ^{2-} and Py; and mal^{2-} and en, having the compositions $[\text{Eu}(\text{Succ})(\text{en})]^+$, $[\text{Eu}(\text{Succ})(\text{en})_2]^+$ and $[\text{Eu}(\text{Succ})_2(\text{en})]^-$ with stability constants $\log \beta_{11} = 9.2$, $\log \beta_{12} = 17.5$ and $\log \beta_{21} = 11.7$; $[\text{Eu}(\text{Succ})(\text{Py})]^+$, $[\text{Eu}(\text{Succ})(\text{Py})_2]^+$ and $[\text{Eu}(\text{Succ})_2(\text{Py})]^-$ with stability constants $\log \beta_{11} = 5.6$, $\log \beta_{12} = 7.0$ and $\log \beta_{21} = 6.1$; $[\text{Eu}(\text{Mal})(\text{en})]^+$, $[\text{Eu}(\text{Mal})_2(\text{en})_2]^-$ and $[\text{Eu}(\text{Mal})_3(\text{en})]^{3-}$ with stability constants $\log \beta_{11} = 11.4$, $\log \beta_{22} = 19.08$ and $\log \beta_{31} = 13.5$. With Mal^{2-} and Py, five mixed complexes, viz., $[\text{Eu}(\text{mal})(\text{Py})]^+$, $[\text{Eu}(\text{Mal})(\text{Py})_2]^+$, $[\text{Eu}(\text{mal})_2(\text{Py})]^-$, $[\text{Eu}(\text{Mal})_2(\text{Py})_2]$ and $[\text{Eu}(\text{Mal})_3(\text{Py})]^{3-}$ with stability constants $\log \beta_{11} = 5.3$, $\log \beta_{12} = 7.8$, $\log \beta_{21} = 7.4$, $\log \beta_{22} = 9.4$ and $\log \beta_{31} = 8.8$ are formed.

Polarographic behaviour of Eu(III) has been studied in various supporting electrolytes and in complexing media by several workers¹⁻⁵. Lal^{6,7} has reported that the reduction of Eu(III) complexes with L-proline and DL-tryptophan is quasi-reversible and diffusion-controlled. The present paper reports the results of our studies on the mixed ligand complexes of Eu(III) with succinate (Succ^{2-}) and malonate (Mal^{2-}); and ethylenediamine (en) and pyridine (Py) which have not been studied polarographically so far.

Materials and Methods

All the chemicals used were of AR grade. Stock solution (0.025 M) of Eu_2O_3 (Sigma, U.S.A.) was prepared by dissolving the oxide in the minimum amount of perchloric acid and diluting it with doubly distilled water. The concentration of Eu_2O_3 was kept constant at 0.5×10^{-3} M in each case. Ethylenediamine, pyridine, potassium succinate and malonate were used as ligands. The ionic strength was maintained constant at $\mu = 0.1$ (NaNO_3). Polarograms were obtained by means of a manual polarograph (Toshniwal CLO2) in conjunction with a Toshniwal polyflex galvanometer (PL 50). Purified nitrogen was used for removing the dissolved oxygen. All the measurements were made at $25 \pm 0.1^\circ\text{C}$. Saturated calomel electrode (S.C.E.) was used as the reference electrode. The d.m.e. had the following characteristics (0.1 M NaNO_3 , open circuit): $m = 3.98$ mg/sec $t = 2.2$ sec, $m^{2/3} t^{1/6} = 2.90$ $\text{mg}^{2/3} \text{sec}^{-1/6}$, $h_{\text{corr}} = 55$ cm.

The pK values of ethylenediamine and pyridine at $25 \pm 0.1^\circ\text{C}$ and at $\mu = 0.1$ (NaNO_3) were determined by

the titration method⁸. These worked out to be: $pK_1 = 7.18$ and $pK_2 = 9.96$ (for en) and $pK = 5.3$ (for Py). The free ligand concentrations, [en] or [Py], were calculated from the pH of the solution and pK values of the ligands.

Results and Discussion

Eu(III) gives a well-defined wave in the presence of increasing concentrations of succinate, malonate ethylenediamine and pyridine and also in mixed ligand systems. The wave heights are diffusion-controlled as the plots of i_d versus $h_{\text{corr}}^{1/2}$ are linear and pass through the origin. The stability constants of simple complexes of Eu(III) with succinate (Succ^{2-}), malonate (Mal^{2-}) ethylenediamine (en) and pyridine (py) were determined separately prior to the study of the mixed ligand systems. Identical conditions were maintained in both the simple and the mixed ligand systems. Millicoulometric⁹ studies indicate that one electron is involved in the reduction process in each case. The slope values of linear plots of $\log i/i_d - i$ versus $E_{\text{d.e.}}$ are of the order of 90 mV. These are appreciably greater than the theoretical value of 59 mV expected for a one-electron reversible reduction process. The fact that the transfer coefficient, α is greater than 0.5 at different concentrations of the ligands shows that the reduction of Eu(III) is not totally¹⁰ irreversible. The standard rate constant ($k_{s,h}$) of the electrode reaction of Eu(III) in the presence of increasing concentrations of the ligands is of the order of 1×10^{-3} cm/sec. This clearly shows¹¹ that the reduction of Eu(III) is quasi-reversible in the presence of increasing concentrations

of the ligands. The reversible half-wave potential ($E_{1/2}^r$) has been determined by Gellings' method¹².

(i) *Eu(III)-Succ²⁻ and Eu(III)-Mal²⁻ systems*

Plots of $E_{1/2}^r$ versus $\log [\text{Succ}^{2-}]$ and versus $[\text{Mal}^{2-}]$ are smooth curves thereby showing the formation of successive complexes. DeFord and Hume's¹³ method has been applied to determine the stability constants of successive complexes. With Succ^{2-} , Eu(III) forms three successive complexes, viz., $[\text{Eu}(\text{Succ})]^+$, $[\text{Eu}(\text{Succ})_2]^-$ and $[\text{Eu}(\text{Succ})_3]^{3-}$ with stability constants, $\log \beta_1 = 2.9$, $\log \beta_2 = 4.5$ and $\log \beta_3 = 5.9$ while with Mal^{2-} , four successive complexes viz. $[\text{Eu}(\text{Mal})]^+$, $[\text{Eu}(\text{Mal})_2]^-$, $[\text{Eu}(\text{Mal})_3]^{3-}$ and $[\text{Eu}(\text{Mal})_4]^{5-}$ with stability constants $\log \beta_1 = 4.1$, $\log \beta_2 = 5.6$, $\log \beta_3 = 6.6$ and $\log \beta_4 = 8.5$ are formed.

(ii) *Eu(III)-en and Eu(III)-Py systems*

Plot of $E_{1/2}^r$ versus $\log [\text{en}]$ is linear thereby showing the formation of a single complex. Employing Lingane's method¹⁴ the composition of the complex works out to be $[\text{Eu}(\text{en})_2]^{3+}$ with stability constant $\log \beta_2 = 14.4$. The plot of $E_{1/2}^r$ versus $[\text{Py}]$ is, however, a smooth curve thereby showing the formation of successive complexes. The composition and stability constants of the complexes have been determined by the method of DeFord and Hume. An analysis of $E_j[X]$ functions reveals the formation of three successive complexes, viz., $[\text{Eu}(\text{Py})]^{3+}$, $[\text{Eu}(\text{py})_2]^{3+}$ and $[\text{Eu}(\text{Py})_3]^{3+}$ with stability constants, $\log \beta_1 = 1.69$, $\log \beta_2 = 3.14$ and $\log \beta_3 = 4.23$ respectively.

(iii) *Eu(III)-Succ²⁻-en and Eu(III)-Succ²⁻-Py Mixed systems*

The concentration of succinate was varied from 0 to 0.1 M keeping $[\text{en}]$ constant at 0.72×10^{-7} M and $[\text{Py}]$ at 0.01 M. The $E_{1/2}$ values were more negative than those obtained in the absence of en and Py thereby showing the formation of mixed complexes. The systems were repeated at another concentration of en (1.47×10^{-7} M) and Py (0.02 M). These constant concentrations have been termed as series 1 and 2. The method of Schaap and McMasters¹⁵ was used to determine the compositions and stability constants of the mixed complexes. The polarographic characteristics and $F_{ij}[X,Y]$ functions ($X = \text{Succ}^{2-}$, $Y = \text{en}$ or Py) of these systems were determined. From the plots of $F_{ij}[X,Y]$ data versus $[\text{Succ}^{2-}]$ the following intercept values for constants¹⁶ A, B, C and D were obtained:

(a) *Eu(III)-Succ²⁻-en system*

For series 1: $\log A = 0.30$, $\log B = 3.20$, $\log C = 4.84$ and $\log D = 6.11$.

For series 2: $\log A = 0.90$, $\log B = 3.57$, $\log C = 5.0$ and $\log D = 6.21$.

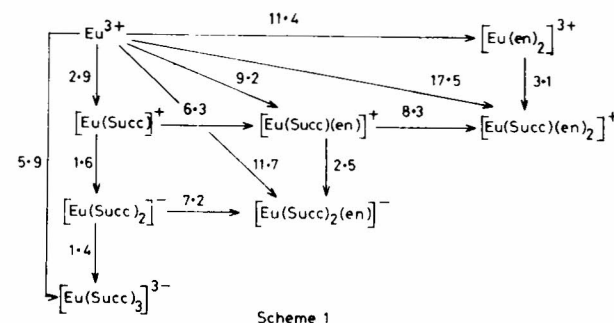
The stability constants have been calculated from these constants. Three mixed complexes, as noted below are formed:

$[\text{Eu}(\text{Succ}(\text{en}))]^+$; $\log \beta_{11} = 9.2$

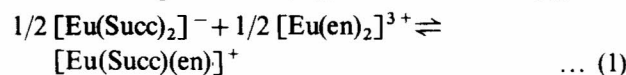
$[\text{Eu}(\text{Succ}(\text{en})_2)]^+$; $\log \beta_{12} = 17.5$

$[\text{Eu}(\text{Succ})_2(\text{en})]^-$; $\log \beta_{21} = 11.7$

The results of this system are summarised in Scheme 1 where the numerical values shown are the equilibrium constants for the reactions indicated.



The mixing constant (K_m) for the reaction (1),

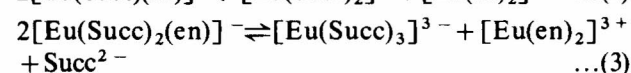


is given by the relation

$$\log K_m = \log \beta_{11} - \frac{1}{2} (\log \beta_{20} + \log \beta_{02})$$

This works out to be +0.3. The positive value of $\log K_m$ indicates that the mixed complex $[\text{Eu}(\text{Succ}(\text{en}))]^+$ is more stable than the parent binary complexes, $[\text{Eu}(\text{Succ})_2]^-$ and $[\text{Eu}(\text{en})_2]^{3+}$.

The equilibrium constants for the disproportionation reactions (2) and (3),



work out to be -0.5 and +3.1 respectively. The negative value of $\log$ equilibrium constant for the reaction (2) shows that the formation of mixed species, $[\text{Eu}(\text{Succ}(\text{en}))]^+$ is favoured over that of the binary complexes. This is in agreement with the conclusion arrived at on the basis of $\log K_m$ value. The positive $\log$ value for the reaction (3), however, shows that the formation of mixed complex $[\text{Eu}(\text{Succ})_2(\text{en})]^-$ is not favoured over that of the binary complexes.

The stabilities of the three mixed complexes follow the order: $[\text{Eu}(\text{Succ}(\text{en})_2)]^+ > [\text{Eu}(\text{Succ})_2(\text{en})]^- > [\text{Eu}(\text{Succ}(\text{en}))]^+$.

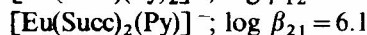
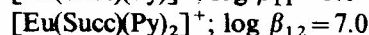
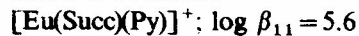
(b) *Eu(III)-Succ²⁻-Py system*

For series 1: $\log A = 0.4$, $\log B = 3.7$, $\log C = 4.6$ and $\log D = 6.1$.

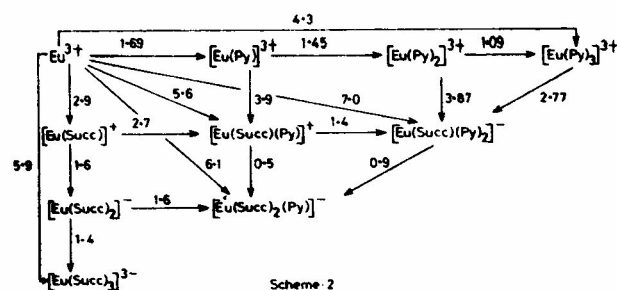
For series 2: $\log A = 0.7$, $\log B = 4.1$, $\log C = 4.8$ and $\log D = 6.2$.

The stability constants have been calculated from

these constants. Three mixed complexes as noted below are formed:

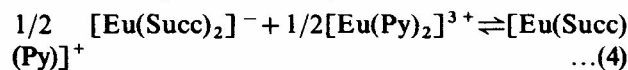


The results of this system are summarised in Scheme 2 where the numerical values shown are the logarithms of the equilibrium constants for the reactions indicated.



Scheme 2

The mixing constant (K_m) for the reaction (4),

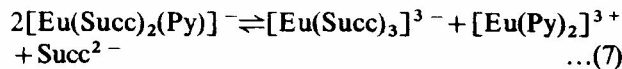
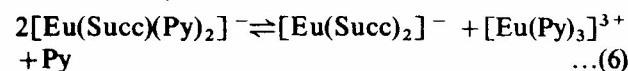


is given by the relation

$$\log K_m = \log (\beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02}))$$

This works out to be +1.65. The positive log value shows that the mixed complex $[\text{Eu}(\text{Succ})(\text{Py})]^+$ is more stable than the simple complexes, $[\text{Eu}(\text{Succ})_2]^-$ and $[\text{Eu}(\text{Py})_2]^{3+}$.

The equilibrium constants for the disproportionation reactions (5)-(7),



work out to be -3.3, -5.0 and -3.2 respectively. The large negative log values of equilibrium constants show that formation of mixed complexes, $[\text{Eu}(\text{Succ})(\text{Py})]^+$, $[\text{Eu}(\text{Succ})(\text{Py})_2]^+$ and $[\text{Eu}(\text{Succ})_2(\text{Py})]^-$ is strongly favoured as compared with that of the simple complexes.

The stabilities of three mixed complexes follow the order: $[\text{Eu}(\text{Succ})_2(\text{Py})]^- > [\text{Eu}(\text{Succ})(\text{Py})_2]^+ > [\text{Eu}(\text{Succ})(\text{Py})]^+$.

(iv) Eu(III)-Mal^{2-} -en and Eu(III)-Mal^{2-} -Py mixed systems

The concentration of Mal^{2-} was varied from 0 to 0.1 M keeping [en] and [Py] constant at 0.72×10^{-7} and 0.01 M respectively. The $E_{1/2}$ values were more negative than those obtained in the absence of en and Py thereby showing the formation of mixed complexes. The study of systems was repeated at another concentration of en (1.47×10^{-7} M) and Py (0.02 M). The method of Schaap and McMasters was used to determine the composition and stability constants of the mixed complexes. The polarographic characteristics and $F_{ij}[X,Y]$ functions ($X = \text{Mal}^{2-}$, $Y = \text{en}$ or Py) of this system have been presented in Tables 1 and 2. From the plots of $F_{ij}[X,Y]$ data versus $[\text{Mal}^{2-}]$ the following intercept values for constants A, B, C, D and E are obtained:

(c) Eu(III)-Mal^{2-} -en system

For series 1: $\log A = 0.30$, $\log B = 4.44$, $\log C = 5.77$, $\log D = 6.77$ and $\log E = 8.60$.

For series 2: $\log A = 0.90$, $\log B = 4.60$, $\log C = 6.14$, $\log D = 7.0$ and $\log E = 8.90$.

Table 1—Polarographic Characteristics and $F_{ij}[X,Y]$ Functions of Eu(III)-Mal^{2-} -en System

$\{[\text{Eu}^{3+}] = 0.5 \times 10^{-3} \text{ M}; \mu = 0.1 (\text{NaNO}_3); \text{pH } 6; \text{Temp.} = 25 \pm 0.1^\circ \text{C. } (E_{1/2})_0 = -0.70 \text{ V (S.C.E.)}, (E_{1/2})_h = -0.69 \text{ V (S.C.E.)}\}$

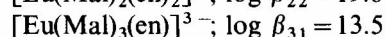
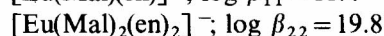
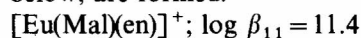
$[\text{Mal}^{2-}]$ (M)	i_d (μA)	$-E_{1/2}$ (V) (S.C.E.)	$-E'_{1/2}$ (V) (S.C.E.)	Slope (mV)	$F_{00}[X,Y]$	$F_{10}[X,Y]$ $\times 10^{-3}$	$F_{20}[X,Y]$ $\times 10^{-5}$	$F_{30}[X,Y]$ $\times 10^{-6}$	$F_{40}[X,Y]$ $\times 10^{-8}$
Series 1: $[\text{en}] = 0.7 \times 10^{-7} \text{ M}$									
0.01	2.58	0.840	0.830	75	252.69	25.06	—	—	—
0.02	2.51	0.869	0.859	78	891.12	44.45	8.22	—	—
0.04	2.48	0.907	0.898	80	3673.32	91.78	15.94	24.85	4.71
0.06	2.44	0.934	0.926	85	11089.70	184.79	26.13	33.55	4.59
0.08	2.41	0.958	0.950	85	28648.37	358.07	41.25	44.06	4.75
0.10	2.33	0.975	0.969	85	60936.85	609.34	58.13	52.13	4.61
Series 2: $[\text{en}] = 1.47 \times 10^{-7} \text{ M}$									
0.01	2.58	0.855	0.845	75	447.30	43.93	—	—	—
0.02	2.51	0.885	0.877	78	1598.60	79.53	19.76	28.80	—
0.04	2.48	0.920	0.913	80	6589.61	164.54	31.13	42.82	8.20
0.06	2.44	0.949	0.941	82	19893.90	331.43	48.57	57.61	7.93
0.08	2.41	0.970	0.965	85	51392.53	642.30	75.28	76.60	8.32
0.10	2.33	0.990	0.984	85	109315.06	1093.07	105.30	91.30	8.13

Table 2—Polarographic Characteristics and $F_{ij}[X,Y]$ Functions of Eu(III)-Mal²⁻-Py System

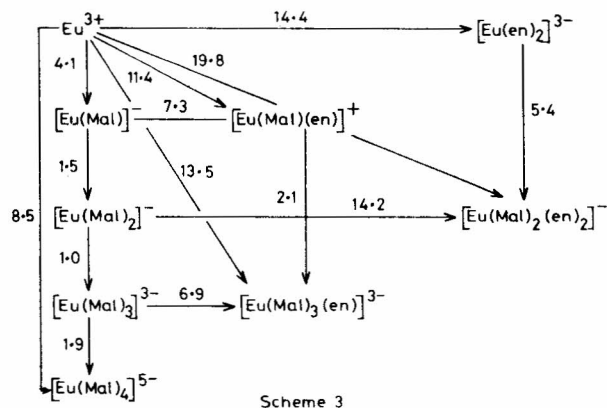
$\{[Eu^{3+}] = 0.5 \times 10^{-3} M; \mu = 0.1 (NaNO_3); pH\ 6; Temp. = 25 \pm 0.1^\circ C. (E_{1/2})_s = -0.70\ V\ (S.C.E.) (E'_{1/2})_s = -0.69\ V\ (S.C.E.)\}$

$[Mal^{2-}]$ (M)	i_d (μA)	$-E_{1/2}$ (V) (S.C.E.)	$-E'_{1/2}$ (V) (S.C.E.)	Slope (mV)	$F_{00}[X,Y]$	$F_{10}[X,Y]$ $\times 10^{-3}$	$F_{20}[X,Y]$ $\times 10^{-5}$	$F_{30}[X,Y]$ $\times 10^{-6}$	$F_{40}[X,Y]$ $\times 10^{-8}$
Series 1: [Py] = 0.1 M									
0.005	2.53	0.827	0.815	78	138.00	27.39	—	—	—
0.01	2.48	0.855	0.845	80	465.90	46.39	—	—	—
0.02	2.38	0.870	0.862	84	942.84	47.04	13.02	20.00	—
0.04	2.31	0.903	0.897	88	3796.99	94.87	18.46	23.65	4.16
0.06	1.93	0.925	0.920	90	11331.82	188.83	27.97	31.61	4.10
0.08	1.65	0.947	0.940	90	28900.14	316.22	42.52	41.90	4.36
0.10	1.65	0.863	0.958	90	59547.00	595.45	57.44	48.44	4.14
Series 2: [Py] = 0.02 M									
0.005	2.53	0.832	0.820	78	168.88	32.77	—	—	—
0.01	2.41	0.874	0.865	80	582.23	57.72	—	—	—
0.02	2.34	0.885	0.878	85	1784.26	88.96	22.48	17.40	—
0.04	2.24	0.920	0.911	85	6751.80	168.67	31.16	30.40	4.60
0.06	1.79	0.935	0.930	88	17692.94	294.79	41.79	37.96	4.33
0.08	1.65	0.955	0.949	90	40186.48	502.26	57.28	47.85	4.48
0.10	1.55	0.970	0.965	90	79946.60	7799.41	75.54	56.54	4.45

The stability constants have been calculated from these constants. Three mixed complexes, as noted below, are formed:

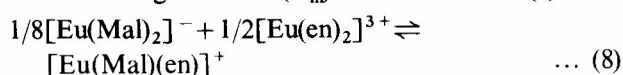


The results of this system are summarised in Scheme 3 where the numerical values shown are the logarithms of the equilibrium constants for the reactions indicated.



Scheme 3

The mixing constant (K_m) for the reaction (8),

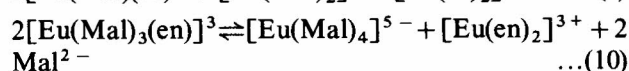
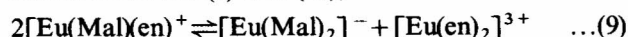


is given by the relation

$$\log K_m = \log \beta_{11} - 1/2(\log \beta_{20} + \log \beta_{02})$$

This works out to be -1.4 . A negative value of $\log K_m$ indicates that the mixed complex, $[Eu(Mal)(en)]^+$ is less stable than the parent binary complexes, $[Eu(Mal)_2]^-$ and $[Eu(en)_2]^{3+}$.

The equilibrium constants for the disproportionation reactions (9) and (10),



work out to be $+2.8$ and $+6.0$ respectively. The large positive values of equilibrium constant for the reactions 1 and 2 show that the formation of the mixed species $[Eu(Mal)(en)]^+$ and $[Eu(Mal)_3(en)]^{3-}$ is not favoured compared with that of the binary complexes.

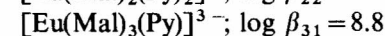
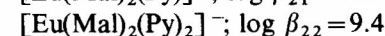
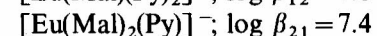
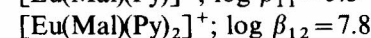
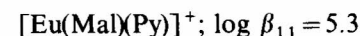
The stabilities of the mixed complexes follow the order: $[Eu(Mal)_2(en)_2]^- > [Eu(Mal)_3(en)]^{3-} > [Eu(Mal)(en)]^+$.

(d) Eu(III)-Mal²⁻-Py system

For series 1: $\log A = 0.3$, $\log B = 4.3$, $\log C = 5.9$, $\log D = 6.8$ and $\log E = 8.6$.

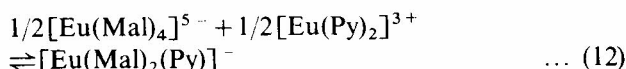
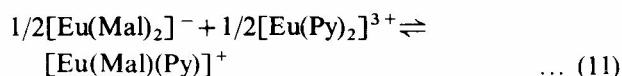
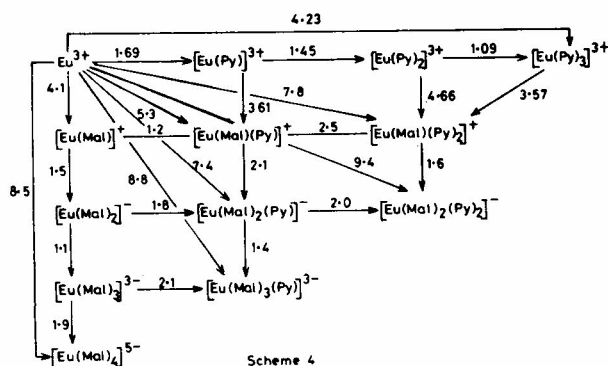
For series 2: $\log A = 0.7$, $\log B = 3.6$, $\log C = 6.3$, $\log D = 7.1$ and $\log E = 8.6$.

The stability constants have been calculated from these constants. Five mixed complexes as noted below are formed:



The results of this system are summarised in Scheme 4 where the numerical values shown are logarithms of the equilibrium constants for the reactions indicated.

The mixing constants (K_m) for the reactions (11) and (12),



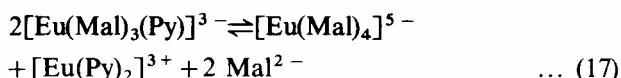
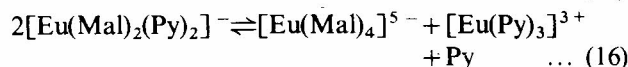
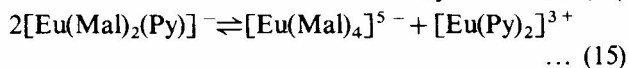
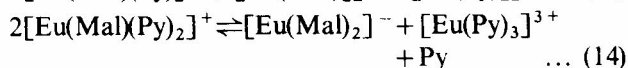
are given by the relations,

$$\log K_{m(1)} = \log \beta_{11} - 1/2 (\log \beta_{20} + \log \beta_{02})$$

$$\log K_{m(2)} = \log \beta_{21} - 1/2 (\log \beta_{40} + \log \beta_{02})$$

These values work out to be +0.05 and +1.6 respectively. The positive value of $\log K_m$ shows that the mixed complexes, $[\text{Eu}(\text{Mal})(\text{Py})]^+$ and $[\text{Eu}(\text{Mal})_2(\text{Py})]^-$ are more stable than the simple complexes, $[\text{Eu}(\text{Mal})_2]^-$, $[\text{Eu}(\text{Mal})_4]^{5-}$ and $[\text{Eu}(\text{py})]^{3+}$.

The equilibrium constants for the disproportionation reactions (13)-(17),



work out to be -1.9, -5.8, -3.2, -6.1 and -6.0 respectively. The large negative log values of equilibrium constants show that the formation of mixed complexes, $[\text{Eu}(\text{Mal})(\text{Py})]^+$, $[\text{Eu}(\text{Mal})(\text{Py})_2]^+$, $[\text{Eu}(\text{Mal})_2(\text{Py})]^-$, $[\text{Eu}(\text{Mal})_2(\text{Py})_2]^-$ and $[\text{Eu}(\text{Mal})_3(\text{Py})]^{3-}$ is strongly favoured over the simple complexes.

The stabilities of five mixed complexes follow the order: $[\text{Eu}(\text{Mal})_2(\text{Py})_2]^- > [\text{Eu}(\text{Mal})_3(\text{Py})]^{3-} > [\text{Eu}(\text{Mal})(\text{Py})_2]^+ > [\text{Eu}(\text{Mal})_2(\text{Py})]^- > [\text{Eu}(\text{Mal})(\text{Py})]^+$.

Acknowledgement

One of the authors (M. Shivhare) is grateful to the CSIR, New Delhi for the award of a Senior Research Fellowship.

References

- 1 Kinard W F & Philip Jr H R, *J electroanal Chem*, **25** (1970) 373.
- 2 Caude M, Delievre D & Rosset R *Bull chim Fr*, **12** (1970) 4554.
- 3 Gutmann V & Psychal-Heiling G, *Mh Chem*, **100** (1969) 1423.
- 4 Salikhshanova R M F & Zhdanov S I, *Electrokhimiya*, **3** (1967) 993.
- 5 Zutshi K, *Rev Polarg Japan*, **46** (1973) 2332.
- 6 Lal S, *Aust J Chem*, **25** (1972) 1571.
- 7 Lal S, *Bull chem Soc Japan*, **46** (1973) 2332.
- 8 Chaberek S & Martell A E, *J Am chem Soc*, **75** (1953) 1430.
- 9 DeVries T & Kroon L, *J Am chem Soc*, **75** (1953) 2489.
- 10 Goto R & Tachi I, *Proc intern polarogr congr*, **1** (1951) 69.
- 11 Delahay P, *J Am chem Soc*, **85** (1953) 1430.
- 12 Gellings P J, *Z Electrochem*, **66** (1962) 477, 481, 799; **67** (1963) 167.
- 13 DeFord D D & Hume D N, *J Am chem Soc*, **73** (1951) 5321.
- 14 Lingane J J, *Chem Rev*, **29** (1941) 1.
- 15 Schaap W B & McMasters D L, *J Am chem Soc*, **83** (1961) 4699.
- 16 Crow D R, *Polarography of metal complexes* (Academic Press, London & New York), 1969, 70.