POLAROGRAPHIC STUDY OF MIXED LIGAND COMPLEXES OF UO_2 (II) WITH PYRIDINE – SUCCINATE AND PYRIDINE–THIOCYANATE

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Uranyl complexation is of importance from both biological as well as analytical view points <1-11>. In the present communication the polarographic behaviour of UO_2 (II) in pyridine, succinate, thiocyanate, pyridine-succinate and pyridine-thiocyanate has been studied systemetically. The composition and stability constants of the binary and ternary complexes have been evaluated.

EXPERIMENTAL

Regent grade chemicals were used throughout and their solutions were prepared in conductivity water. The ionic strength was maintained at μ = 0.6M using KCl as the supporting electrolyte. Pyridine (py), poassium succinate (succ) and potassium thiocyanate (SCN) were used as liganda. Polarograms were recorded using a manual Toshniwal ÇLO2 polarograph in conjuction with a Toshniwal polyflex gavanometer PL 50. Purified nitrogen was used to flushout the dissolved oxygen. All measurements were made at 30 ± 0.2° C. Saturated calomel electrode was used as a reference electrode. The dme had the following characteristics:

$m^{2/3}$ $t^{1/6}$ = 2.01 $mg^{2/3}$ $s^{-1/2}$ in 0.1 M KCl at h=30 cms with open circuit.

RESULTS AND DISCUSSION

The reduction of UO_2 (II) in pyridine, succinate and thiocyanate was found to be reversible and diffusion controlled at pH 5.72 (acetate buffer) and ionic strength, μ = 0.6 M KCl. The slopes of linear plots of log $[i/(id-i)]$ vs E_{dme} were of the order of 59 ± 2 mV indicating one electron change. Same value of n was obtained by the millicoulometric studies <12>. Stability constants of simple complexes of UO^2 (II) with (py) (succ) and (SCN) were determined separately prior to the study of mixed ligand system. Identical conditions were maintained in both the simple and mixed systems.

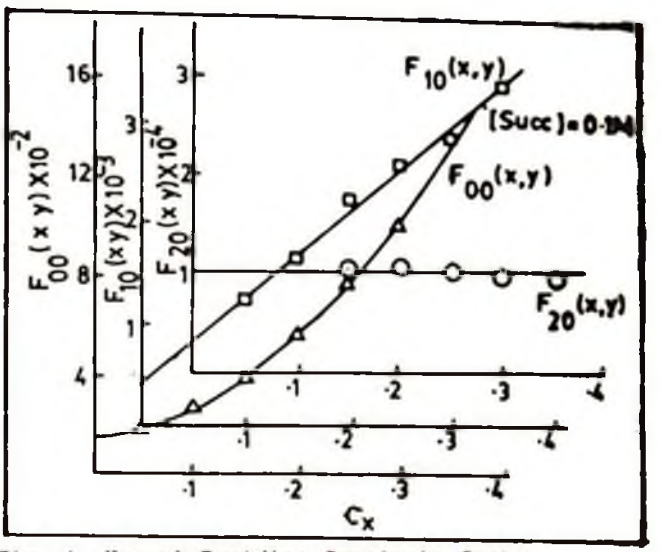


Fig. 1 Uranul-Pyridine-Succinate System Plot of F(X,Y) verses C_x Succinate = 0.1 M UO_2 = 0.5mM. Ionic Strength, μ=0.6M (KCl) Temperature = 30 + 0.1°C, $M^{2/3}$ $t^{1/6}$ = 2.01 $mg^{2/3}$ $sec^{-1/2}$ H_{corr}=30.0 cm

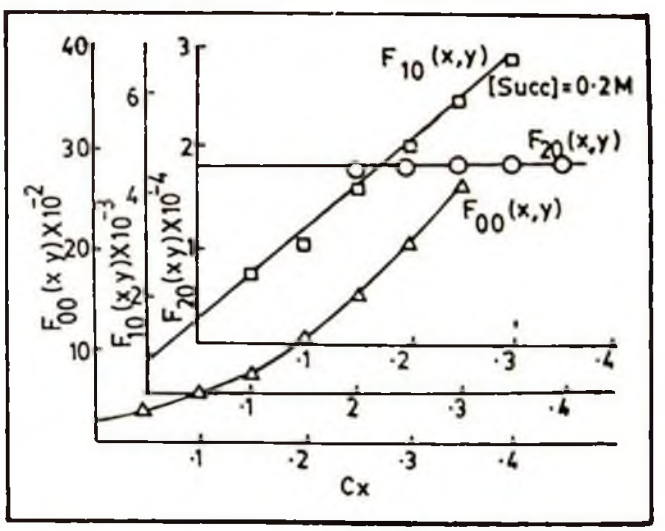


Fig. 2 Uranyl-Pyridine-Succinate System Plot of F (X,Y) verses C_x Thiocyanate = 0.2 M, rest of the condition same as Fig. 1

Binary Systems

A series of polarograms were obtained for the binary systems uranyl (II) -Pyridine, uranyl(II) - succinate and uranyl(II) - thiocyanate. In each set, the concentration of uranyl nitrate solution was kept

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TABLE 1

Characteristics of $[UO_2(py)(succ)]$ system
UO (II) =0.5 mM; μ = 0.6 M KCl;
Temperature = 30 ± 0.2° C
All potentials are measured w.r to SCE.

[py] M	$\Delta E_{1/2}$ mV	log I_s/I_o	$\Delta E_{1/2}$ mV	log I_a/I_c
[SUCC] = 0.1 M (fixed)			[SUCC] =0.4 M	
0.05	130	0.1280	142	0.1932
0.10	138	0.1278	150	0.2037
0.15	148	0.1204	160	0.1934
0.20	158	0.1370	170	0.1942
0.25	166	0.1260	178	0.2052
0.30	172	0.1258	186	0.2038
0.35	180	0.1207	194	0.2128
	Log A= 2.146		Log A= 2.414	
	Log B= 2.60		Log B= 2.698	
	Log C= 4.00		Log C= 4.241	

TABLE 2

Characteristics of $[UO_2(py)(SCN)]$ System
UO_2 (II) = 0.5 mM; μ = 0.6 M KCl;
Temperature = 30 ± 0.2° C.
All potentials are w.r to SCE.

[PY] M	$\Delta E_{1/2}$ mV	log I_s/I_o	$E_{1/2}$ mV	log I_a/I_c
[SCN] = 0.2 M (fixed)			[SCN] = 0.4 M (fixed)	
0.05	85	0.1156	98	0.1540
0.10	92	0.1230	105	0.1460
0.15	105	0.1083	116	0.1383
0.20	115	0.0940	126	0.1622
0.25	125	0.0803	136	0.1156
0.30	132	0.0862	142	0.1462
0.35	138	0.0891	150	0.1432
	Log A= 1.301		Log A= 1.602	
	Log B= 2.079		Log B= 2.380	
	Log C= 3.164		Log C= 3.403	

constant at 0.5 mM while that of the ligand was varied from 0.05 M to 0.35 M. The ionic strength and pH were maintained at 0.6 M with KCl and pH 5.72 (acetate buffer) respectively. A plot of $E_{1/2}$ vs log X (where X is the ligand) was a smooth curve indicating the formation of more than one complex species in each system. The method of Deford and Hume <13> was applied for the determination of composition and stability constants of the complexes. The stability constants of the systems are calculated to be:

Uranyl-pyridine system:
log β_1= 1.54 and log β_2 = 2.71

Uranyl-succinate system:
Log β_1= 2.20 and log β_2= 3.47

Uranyl-thiocyanate system:
Log β_1= 1.176 and log β_2= 1.886

Ternary Systems

In the study of the ternary systems, uranyl(II) -pyridine-succinate and Uranyl(II) -pyridine-thiocyanate, the concentrations of uranyl(II) and succinate (or thiocyanate) were kept constant at a specified value while that of pyridine was varied from 0.05 M to 0.35 M (Table 1 and 2). The ionic strength and pH were maintained as in the case of binary systems. In each case the waves were diffusion-controlled and reversible. The $E_{1/2}$ values were more negative than those obtained in the absence of succinate (or thiocyanate) there by showing the formation of mixed complexes. The measurements were repeated at a second fixed concentration of succinate or thiocyanate (Table 1 and 2). The Schaap and McMasters method <14 > was used for the determination of composition and stability constants of the mixed complexes. It is found that UO_2 (II) forms 1:1:1 mixed complexes, $[UO_2$ (py) (succ)] and $[UO_2$ (py) (SCN)] with the ligands.

The results of the present study have been conveniently summarized in the following diagrams where the numerical values show the log of equilibrium constants of the reactions indicated.

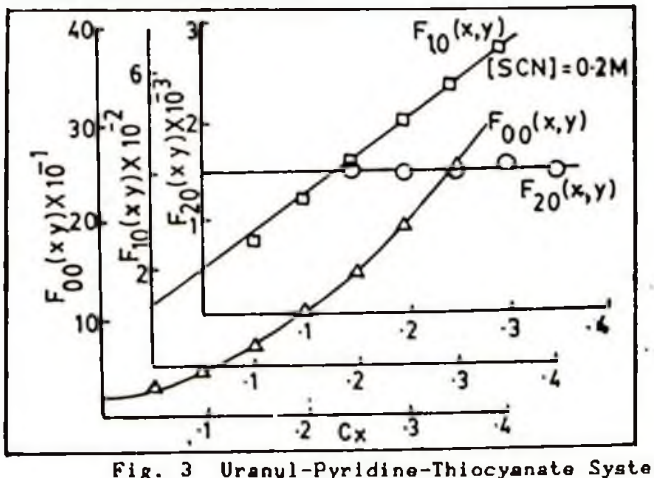


Fig. 3 Uranyl-Pyridine-Thiocyanate System Plot of F(X,Y) verses C_x Thiocyanate = 0.4 M, rest of the conditions same as Fig.1

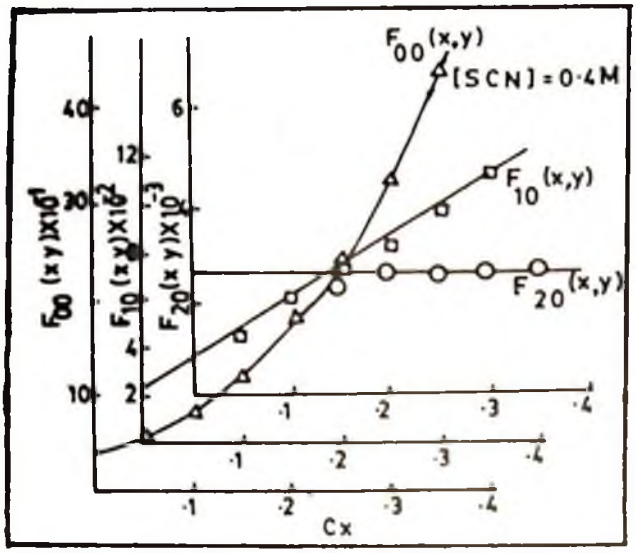
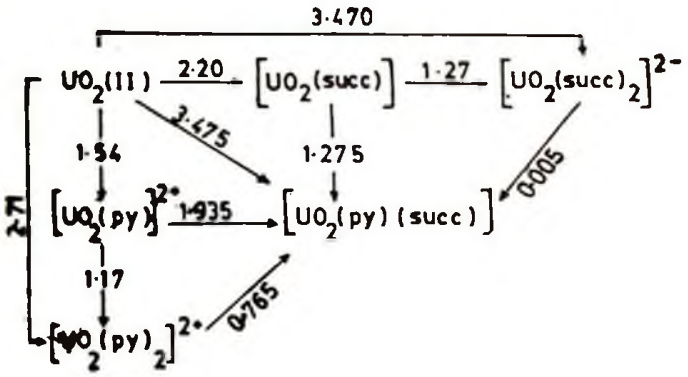
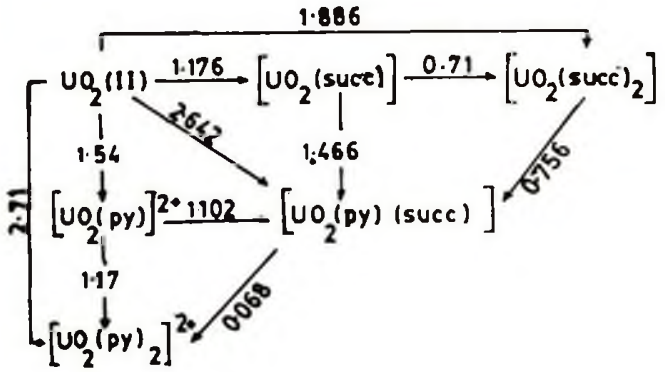


Fig. 4 Uranyl-Pyridine-Thiocyanate System lt of F(X,Y) verses C_x Thiocyanate = 0.4 M, rest of the conditions same as Fig.1





The values of log K_m is found to be 0.385 and 0.772 for $[UO_2(py)(succ)]$ and $UO_2(py)[(SCN)]$ respectively. The positive values indicate that the mixed complexes yare more stable than the simple binar complexes of uranyl (II) with pyridine, succinate and thiocyanate.

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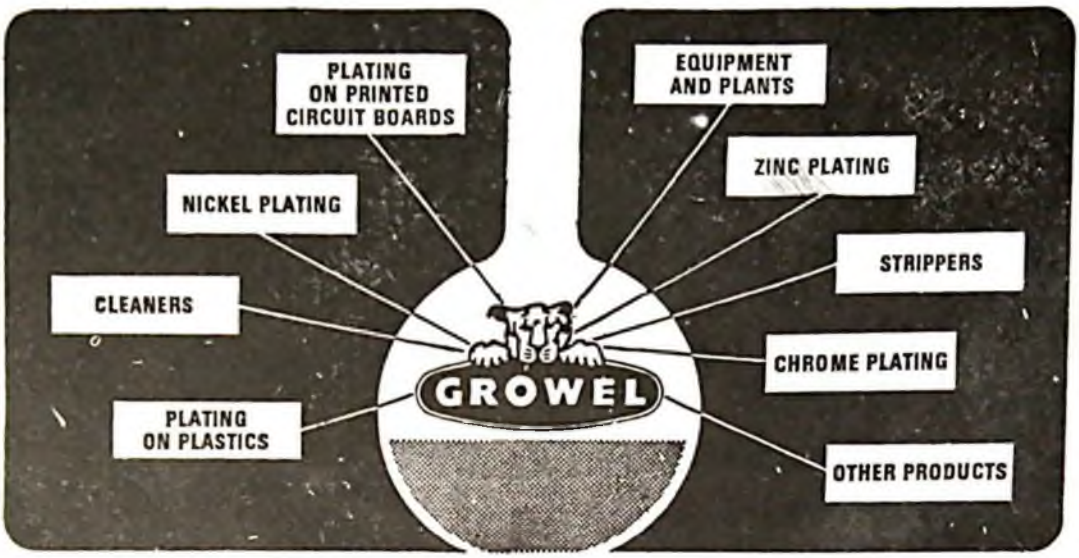
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