MIXED LIGAND COMPLEXES OF THORIUM (VI) WITH SUDAN VIOLET AND SELECTED LIGANDS

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Abstract : There is no report in the literature about the analytical aspects of solution equilibria of 1,4 – diamino anthraquinone, (sudan violet, hereinafter sv). In this paper we describe the P^H – titrimetric behaviour of SV in acetone. Water medium and the complexation equilabria of the binary and mixed lIgand complexes of uranyle ion with this reagent

Index Terms :- 1,4 – Di amino anthraquinone

1.INTRODUCTION

Analytical grade reagents were used. A stock solution of $5x10^{-3}dm^{-3}$ of Th^{VI} was prepared using uranyle nitrate (A nala R). The thorium content was determined as recommended[I] . solution of 1,4 – diamino anthraquinone ($1x10^{-3}$ mole dm^{-3}) was prepared in pure acetone. Stoke solutions (10^{-3} mole dm^{-3} each) of O – AP , pic , 8- HQ and BiPy were prepared by dissolving the ligands in acetone. Potassium hydroxide standard solution (0.1 mol dm^{-3}), sodium perchlorate and perchloric acid standard solutions were prepared using deionised water.

All measurement were performed in the presence of 50% (v/v) acetone at 20 ± 0.1˚.The measured P^H value in acetone – water mixtures were corrected as described else where[2]. The ionic strength was kept constant at 100 m mol dm^{-3} ($NaClO_4$). All titrations were carried out using 35 m mol dm^{-3} KOH as titrant so that any possibility of the precipitation of $KClO_4$ (K_{SP} = 1.1 $X10^{-2}$) under the experimental conditions can be precluded.

II.THEORY

O- Amino phenol (O-AP). Picolinic acid (pic). 8 – hydroxy quinoline (8- HQ) or 2,2- bipyridyl (Bi Py) were used as a secondary ligand. The study was under taken to explore the potentialities of sudan violet (SV) internary complex formation and the effect of the varying complex formation and the secondary ligands on the stability of the ternary complexes of thorium (vi).

III.RESULTS AND DISCUSSIONS

The proton association constants for the free ligands and the stability constants for the binary and ternary complexes were calculated from the titration data using a corrected version of the computer programme SCOGS[3].

Table 1 – ACIDITY CONSTANTS * OF LIGANDS AND STABILITY CONSTANTS OF BINARY * AND MIXED LIGAND COMPLEXES ** OF Th^{VI} AND SOME RELATED DATA

I= 0.1 mol dm^{-3} ($NaClO_4$), Temp . = 20 ± 0.1 , solvent :

50% (v/v) acetone

Ligand	**Pk**	$logk^{Th}_{ThL}$	$logk^{ThL}_{ThL2}$	$log\beta^{Th}_{ThL2}$	$log\beta^{Th}_{Th(SV)L}$	$logk^{Th(SV)}_{Th(SV)L}$	$logk^{ThL}_{ThL(SV)}$	$\Delta logk^{4}_{Th)}$
SV	9.30(H/H_4A)	8.01	4.50	12.51	------	-----	------	------
Pic	5.75(HL/L)	3.87	4.25	8.12	13.82	5.22	9.95	+1.95
S-HQ	5.15(H_2L^+/HL) 10.05(HL/L)	4.10	4.35	8.45	12.95	4.95	8.85	+0.85
BiPy	4.45(LH^+/H)	3.70	4.00	7.70	12.52	4.52	8.82	+0.82
O-PA	3.99(H_2L^+/HL) 9.45(HL/L)	3.95	4.10	8.05	12.01	4.02	8.05	+0.05

*constants accurate to ± 0.02 ** constants accurate to ± 0.05

The formation constants of the ThO_2 – SV binary complexes were calculated taking into account the species H, H_4A, H_3A, ThO_2, ThO_2 (H_3A),, ThO_2 ($H_3A)_2$, where H_4A is the neutral form of SV. For the evaluation of formation constant of the ternary complexes, the species H,H_4 A, H_3A,H_2L^+, HL,L,ThO_2,ThO_2L, ThO_2L_2, ThO_2(H_3A),$ThO_2(H_3A)_2$,$UO_2(H_3A)$ HL.

And ThO_2 (H_3A) L where considered, where H_2L^+= O-AP or 8-HQ. results are presented in

Table 1.

The stability of the ternary complexes were found to increase within the following series of ligands. O-AP< Bi Py <8-HQ<Pic. Ternary complexes containing ligands with hetro aromatic nitrogen are generally more stable than that of containing O-AP as sec ligand [4] , hence Δ log K has more positive value as compare to that of the O-AP complex. The formation of the ThO_2^{2+} ternary complexes containing hetro aromatic nitrogen ligands appears to be dependent on ring size of the chelate which seem to offset in the increasing basicities of the secondary ligands. Picolinic acid acts as a bidentate ligand in which the ligating atoms are the oxygen of the carboxyl OH and the nitrogen of the hetrocyclic ring[5] and gives the most stable ternary chelate. This is part by due to an increasing better neutralization of charge in the ThO_2 (SV) (Pic) ternary complex compared with the [ThO_2 (H_3A)] + binary complex.

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