



STUDIES IN FORMATION CONSTANT OF UO_2 (II) AND Th (IV) METAL ION COMPLEXES WITH SOME SUBSTITUTED BENZOTHAZOLES AT 0.1 M IONIC STRENGTH

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(Received : 20.02.2012; Revised : 17.03.2012; Accepted : 22.03.2012)

ABSTRACT

Substituted 1,3-benzothiazole derivatives are an important class of heterocyclic compounds. In recent years heterocyclic compounds analogues and derivatives have attracted strong interest due to their biological and pharmacological properties. The present study deals with the evaluation of proton-ligand and metal-ligand stability constants of UO_2 (II) and Th (IV) metal ions with 3-(2-hydroxyphenyl)-5-bromo-7-methyl-1,2,4-triazolo (3,4,b) benzothiazole (L_1) and 3-(2-hydroxy-3-methylphenyl)-5-bromo-7-methyl-1,2,4-triazol (1,4,b) benzothiazole (L_2) at 0.1 M ionic strength pH-metrically. The values of \bar{n}_A , \bar{n} , pK and log K are evaluated in 70% dioxane-water mixture.

Key words: Substituted benzothiazoles, UO_2 (II) and Th (IV) metal ions, 70 % Dioxane-water (solvent).

INTRODUCTION

Benzothiazole is a privileged bicyclic ring system. Due to its potent and significant biological activities, it has great pharmaceutical importance. Faham and Chebbo¹ have synthesized amino derivatives of benzothiazoles and determined their biological activities. Evinder et al.² have synthesized aminovenzim imidazole using copper and palladium catalysts. Fenglian et al.³ have prepared 2-difluoromethyl substituted benzo-1,3-diazoles and studied its characters. Francisco and Dolories⁴ synthesized some derivatives of benzothiazoles and studied their optical and redox properties. Andrew and Dora⁵ have done structural modification of some substituted benzothiazole and determined their antimicrobial activity.

No work has been done on metal-ligand stability constants and other physical properties of substituted benzothiazoles. Present work is undertaken to study the stability constants of UO_2 (II) and Th (IV) metal ion complexes with 3-(2-hydroxyphenyl)-5-bromo-7-methyl-1,2,4-triazolo(3,4,b) benzothiazole (L_1) and 3-(2-hydroxy-3-methylphenyl)-5-bromo-methyl-1,2,4-triazol (1,4,b) benzothiazole (L_2) at 0.1 M ionic strength.

EXPERIMENTAL

Experimental procedure involves Calvin-Bjerrum titration method, having three types of titrations (i)

Acid titration, (ii) Acid + Ligand titration and (iii) Acid + Ligand + Metal ion titration. Ionic strength is maintained constant by adding an appropriate amount of 1M KNO₃ solution. Representative graph is shown in Fig. 1.

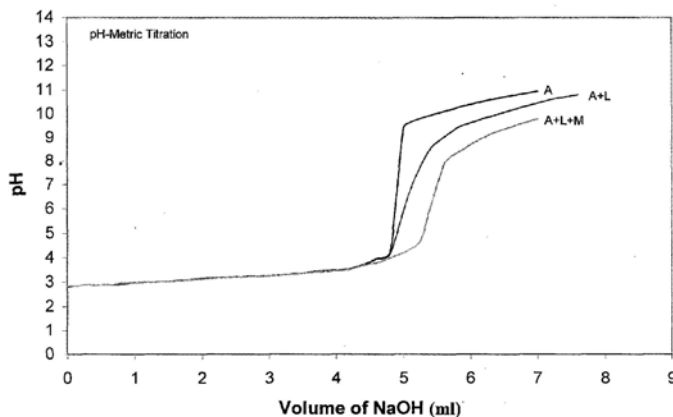


Fig. 1: System –UO₂ (II) – Ligand (L₁)

RESULTS AND DISCUSSION

Deviation between acid curve and ligand curve shows the dissociation of -OH group of ligand and deviation between ligand and metal curve shows the association of ligand species to metal cation for commencement of complex formation. The change in colour from yellow to red wine also shows the formation of complex. The values of \bar{n}_A , \bar{n} , and log K are presented in Table 1 to 7.

Table 1: Determination of \bar{n}_A value system : Ligand (L₁)

$T_L^0 = 20.00 \times 10^{-4} \text{ M}$
 $N = 0.1330 \text{ M}$

$V^0 = 50 \text{ mL}$
 Temp. = 26.5°C

pH	V ₁	V ₂	(V ₂ -V ₁)	\bar{n}_A
6.00	4.95	4.95	0.05	1.9347
6.20	4.90	4.97	0.07	1.9086
6.40	4.90	5.00	0.10	1.8694
6.60	4.90	5.05	0.15	1.8004
6.80	4.90	5.10	0.20	1.7389
7.00	4.90	5.15	0.25	1.6737
7.20	4.90	5.20	0.30	1.6084
7.40	4.90	5.25	0.35	1.5432
7.60	4.90	5.30	0.40	1.4779
7.80	4.90	5.32	0.42	1.4518
8.00	4.90	5.35	0.45	1.4127
8.20	4.90	5.40	0.50	1.3474
8.40	4.90	5.45	0.55	1.2821

Cont...

pH	V ₁	V ₂	(V ₂ -V ₁)	\bar{n}_A
8.60	4.90	5.50	0.60	1.2169
8.80	4.90	5.55	0.65	1.1516
9.00	4.90	5.60	0.70	1.0864
9.20	4.90	5.70	0.80	0.9559
9.40	5.00	5.85	0.85	0.8906
9.60	5.10	6.00	0.90	0.8254
9.80	5.20	6.20	1.00	0.6948
10.00	5.40	6.55	1.05	0.6296
10.20	5.70	6.80	1.10	0.5850
10.40	6.00	7.20	1.20	0.4648

Table 2: Determination of \bar{n}_A values system: Ligand (L₂)T_L⁰ = 20.00 x 10⁻⁴ MV⁰ = 50 mL

N = 0.1330 M

Temp. = 26.5⁰C

pH	V ₁	V ₂	(V ₂ -V ₁)	\bar{n}_A
5.60	4.80	4.85	0.05	1.9346
5.80	4.80	4.90	0.10	1.8692
6.00	4.80	4.95	0.15	1.8038
6.20	4.80	5.00	0.20	1.7385
6.40	4.80	5.05	0.25	1.6731
6.60	4.80	5.10	0.30	1.6077
6.80	4.80	5.14	0.34	1.5554
7.00	4.80	5.15	0.35	1.5423
7.20	4.80	5.16	0.36	1.5293
7.40	4.80	5.16	0.36	1.5293
7.60	4.80	5.16	0.36	1.5293
7.80	4.80	5.17	0.37	1.5262
8.00	4.80	5.30	0.50	1.3464
8.20	4.80	5.45	0.65	1.1501
8.40	4.80	5.50	0.70	1.0842
8.60	4.80	5.60	0.80	0.9540
8.80	4.80	5.80	1.00	0.6925
9.00	4.90	6.00	1.10	0.5643
9.20	5.20	6.35	1.15	0.3555
9.40	5.50	6.70	1.20	0.2872
9.60	5.60	7.05	1.45	0.1974

Table 3: Determination of \bar{n} values system: $\text{UO}_2(\text{II}) - \text{L}_1$

$E^0 = 1.00 \times 10^{-2} \text{ M}$

$T_L^0 = 20.00 \times 10^{-4} \text{ M}$

$T_m^0 = 4.00 \times 10^{-4} \text{ M}$

$V^0 = 50 \text{ mL}$

$N = 0.1330 \text{ M}$

Temp. = 26.5°C

pH	V_2	V_3	$(V_3 - V_2)$	\bar{n}
3.20	2.70	2.72	0.02	0.1352
3.40	3.60	3.64	0.04	0.2660
3.60	4.30	4.37	0.07	0.4565
3.80	4.60	4.77	0.11	0.7174
4.00	4.70	4.85	0.15	1.0229
4.20	4.70	4.90	0.20	1.3034
4.40	4.85	5.10	0.25	1.5598
4.60	4.85	5.13	0.28	1.8198
4.80	4.85	5.15	0.30	1.9498
5.00	4.85	5.20	0.35	2.2784

Table 4: Determination of \bar{n} values system : $\text{Th}(\text{IV}) - \text{L}_1$

$E^0 = 1.00 \times 10^{-2} \text{ M}$

$T_L^0 = 20.00 \times 10^{-4} \text{ M}$

$T_m^0 = 4.00 \times 10^{-4} \text{ M}$

$V^0 = 50 \text{ mL}$

$N = 0.1330 \text{ M}$

Temp. = 26.5°C

pH	V_2	V_3	$(V_3 - V_2)$	\bar{n}
3.20	2.70	2.71	0.01	0.0677
3.40	2.60	3.64	0.04	0.2660
3.60	4.25	4.30	0.05	0.3285
3.80	4.60	4.66	0.06	0.3917
4.00	4.70	4.76	0.06	0.3909
4.20	4.70	4.77	0.07	0.4562
4.40	4.85	4.95	0.10	0.6517
4.60	4.85	5.00	0.15	0.9749
4.80	4.85	5.02	0.17	1.1049
5.00	4.85	5.05	0.20	1.2999
5.20	4.85	5.08	0.23	1.4948
5.40	4.90	5.15	0.25	1.6248
5.60	4.95	5.20	0.25	1.6235
5.80	4.95	5.25	0.30	1.9463

Table 5: Determination of \bar{n} values system: $\text{UO}_2(\text{II}) - \text{L}_2$

$$E^0 = 1.00 \times 10^{-2} \text{ M}$$

$$T_L^0 = 20.00 \times 10^{-4} \text{ M}$$

$$T_m^0 = 4.00 \times 10^{-4} \text{ M}$$

$$V^0 = 50 \text{ mL}$$

$$N = 0.1330 \text{ M}$$

$$\text{Temp.} = 26.5^\circ\text{C}$$

pH	V_2	V_3	$(V_3 - V_2)$	\bar{n}
3.40	3.60	3.61	0.01	0.0665
3.60	4.25	4.26	0.01	0.0625
3.80	4.60	4.62	0.02	0.1305
4.00	4.70	4.73	0.03	0.1955
4.20	4.70	4.75	0.05	0.3258
4.40	4.85	4.95	0.10	0.6541
4.60	4.85	5.00	0.15	0.9749
4.80	4.85	5.03	0.18	1.1699
5.00	4.85	5.05	0.20	1.2999
5.20	4.85	5.05	0.20	1.2999
5.40	4.85	5.07	0.22	1.4248
5.60	4.90	5.15	0.25	1.6234
5.80	4.95	5.23	0.28	1.8165
6.00	4.95	5.25	0.30	1.9463
6.20	4.95	5.28	0.33	2.1409

Table 6: Determination of \bar{n} values system: $\text{Th}(\text{IV}) - \text{L}_2$

$$E^0 = 1.00 \times 10^{-2} \text{ M}$$

$$T_L^0 = 20.00 \times 10^{-4} \text{ M}$$

$$T_m^0 = 4.00 \times 10^{-4} \text{ M}$$

$$V^0 = 50 \text{ mL}$$

$$N = 0.1330 \text{ M}$$

$$\text{Temp.} = 26.5^\circ\text{C}$$

pH	V_2	V_3	$(V_3 - V_2)$	\bar{n}
3.00	2.00	2.01	0.01	0.0685
3.20	2.70	2.73	0.03	0.1995
3.40	3.60	3.65	0.05	0.3382
3.60	4.20	4.30	0.10	0.6577
3.80	4.50	4.63	0.13	0.8503
4.00	4.70	4.85	0.15	0.9776
4.20	4.70	4.90	0.20	1.3034
4.40	4.85	5.07	0.22	1.4338
4.60	4.85	5.10	0.25	1.6248
4.80	4.85	5.15	0.30	1.9489
5.00	4.85	5.18	0.33	2.1448

It could be seen from Table 7 that there is considerable difference between of UO_2 (II) are found to be greater than Th (IV), this is due to the fact of larger cation size of Th (IV) having less values of stability constants.

Table 7: Metal – ligand stability constants ($\log K_1$ and $\log K_2$)

System	Log K_1	Log K_2
UO_2 (II) – L_1	12.60	9.65
UO_2 (II) – L_2	10.00	8.35
Th (IV) – L_1	11.15	8.55
Th (IV) – L_2	9.15	8.30

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