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Stability Constants of UO_2(II) Complexes with Substituted 1,2,4-Triazoles

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The proton-ligand dissociation constants of certain substituted 1, 2, 4-triazoles and the stability constants of their metal complexes with UO_2(II) in 60% ethanol-water medium at 28°C using Bjerrum-Calvin pH titration technique as modified by Irving and Rossotti were reported.

INTRODUCTION

In continuation of our earlier work[1] on dissociation constants of structurally similar substituted 1,2,4-triazoles [3-(methyl phenyl)-5-mercapto-1, 2,4-triazole (A), 3-(phenyl)-5-mercapto 1,2,4-triazole (B), 4-amino-3-(*p*-chloro phenoxymethyl)-5-mercapto 1,2,4-triazole (C) and 4-amino-3-(phenoxy methyl)-5-mercapto-1,2,4-triazole (D)] stability constants of their metal complexes and validity of Irving William order, an attempt has been made with UO_2(II) metal complexes of these ligands in 60% ethanol-water medium at 28°C±0.1°C and 0·05M (KNO_3) ionic strength using the Bjerrum-Calvin pH metric method[2,3] as modified by Irving and Rossotti[4].

EXPERIMENTAL

All the chemicals such as sodium hydroxide, potassium nitrate and nitric acid were of AR grade. The ligands, 3-(methyl phenyl)-5-mercapto-1,2,4-triazole (A), 3-(phenyl)-5-mercapto-1,2,4-triazole (B), 4-amino-3-(*p*-chloro phenoxy methyl)-5-mercapto-1,2,4-triazole (C) and 4-amino-3-(phenoxy methyl)-5-mercapto-1,2,4-triazole (D) were prepared according to the literature methods[5–9]. Uranyl nitrate of AnalaR grade was supplied by Glaxo (India). Double distilled water and ethanol were used for the preparation of solutions and titrations.

The experimental procedure involved the titration of the following carbonate free solutions with sodium hydroxide of 0.1 M.

(1) 5 ml of (0.01 M) nitric acid + 30 ml of ethanol + 15 ml of water. (2) 1 ml of (0.01 M) ligand in pure organic solvent + 5 ml of (0.01 M) nitric acid + 29 ml ethanol + 15 ml water. (3) 1 ml of (0.001 M) UO_2(II) solution + 1 ml of (0.01 M) ligand + 5 ml of (0.01 M) nitric acid + 29 ml of ethanol + 14 ml of water.

RESULTS AND DISCUSSION

The dissociation constants (log K_L) of the ligands were obtained from the formation curves of the proton ligand systems by plotting $\bar{n}A$ Vs pH. From these plots the log K_L values are found to be 9.6, 9.2, 8.3 and 7.8 for the ligands (A), (B), (C) and (D), respectively. The $\bar{n}A$ values were obtained at various pH values from the titration curves using solutions (1) and (2). From the titration curves of solutions (2) and (3) $\bar{n}$ and PL values were calculated.[4] Metal-ligand formation constants of the metal complexes were calculated applying least square method[4], to the $\bar{n}$, PL data (Table 1). The data are represented graphically in Fig. 1. From the

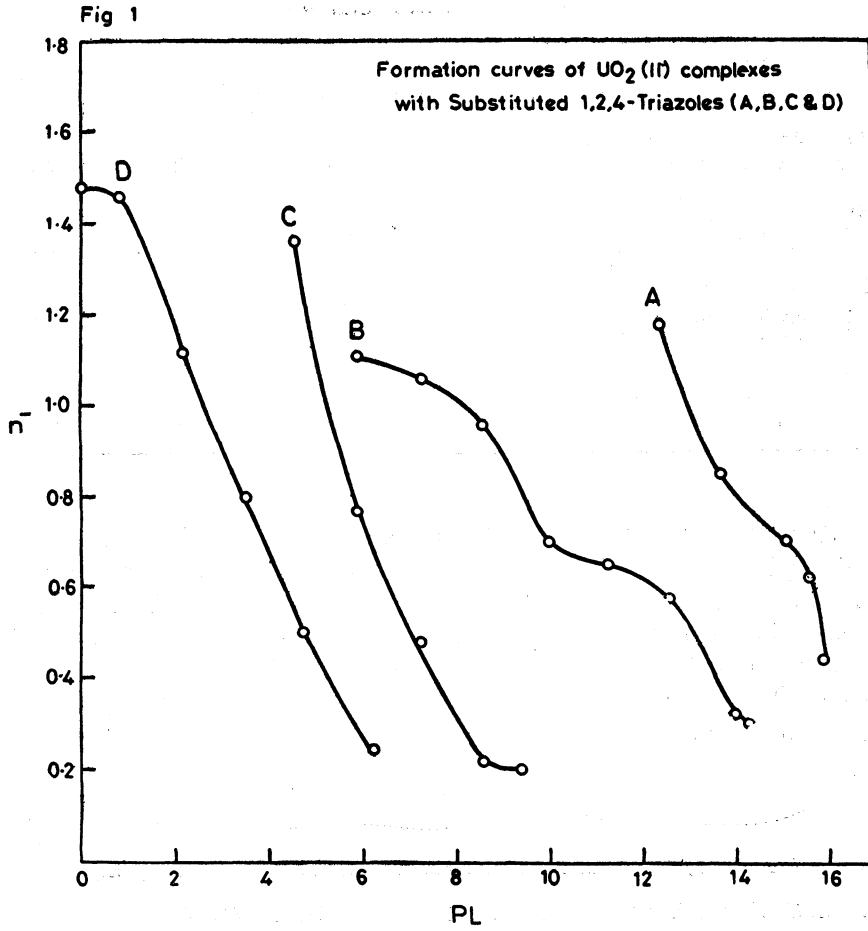

Fig. 1. Formation curves of UO_2(II) complexes with substituted 1, 2, 4-Triazoles (A, B, C & D)

results it is observed that the stability constants of UO_2(II) complexes with the structurally similar substituted 1,2,4-triazoles holds the same relation as it is observed in other metal complexes[1]. The stability constant values of these UO_2(II) complexes also decreased in the same order as it was observed in the dissociation constants of these structurally similar substituted 1, 2, 4-triazoles. The UO_2(II) complexes decrease in the order of A > B > C > D.

TABLE 1

STABILITY CONSTANTS OF UO_2(II) COMPLEXES WITH STRUCTURALLY SIMILAR SUBSTITUTED 1, 2, 4-TRIAZOLES

	Name of the ligand	Log K_1	Log K_2	Log β_2
(A)	3-(Phenyl methyl)-5-mercapto 1,2,4-Triazole	15.9	13.2	29.1
(B)	3-(Phenyl)-5-mercapto 1,2,4-triazole	13.1	8.1	21.2
(C)	4-Amino-3-(*p*-chloro-phenoxy methyl)-5-mercapto 1,2,4-triazole	7.2	5.3	12.5
(D)	4-Amino-3-(phenoxy methyl)-5-mercapto 1,2,4-triazole	4.8	2.7	7.5

From table 1, it is evident that there is a large difference in log K_1 and log K_2 values and also the value of log K_1/K_2 is positive for (A) and (B) which suggests the formation of two complexes ML^+ and ML_2, whereas in case of C and D these values are low. This suggests the equal tendency of formation of both ML^+ and ML_2 complexes with the ligands C and D with little or no steric hindrance by the addition of second ligand molecule.

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