

Hard-soft interaction of 2-mercaptobenzothiozol with Some metal ions

yahya Abdul Majid *

Nazic Mohammed Aziz **

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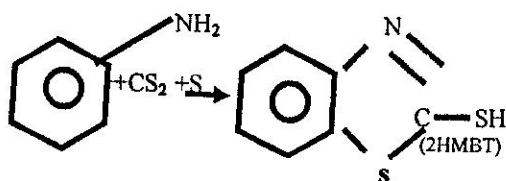
Abstract

Acid dissociation of 2-mercapto benzothiozol (2HMBT) in Dioxane –water mixture at 25 °c was obtained to be 8.3×10^{-8} . stability constants of complexes formed by (2HMBT) with Th^{4+} , UO_2^{++} and Pb^{++} ions were established.

Results obtained indicated that the organic ligand behave as hard base according to pearson's defination ,Hardness-softness parameters for ligand were calculated using Messono's equation,the order of Hardness could be arranged as follows:
 $\text{S}_2\text{O}_3^{-2} < \text{I}^- < \text{Br}^- < \text{phenol} < \text{2HMBT} < \text{Cl}^- < \text{NH}_3 < \text{OH}^-$

Introduction

The compound 2-Mercaptobenzothiozole abriviated as (2-HMBT),have been preparad⁽¹⁾ through the reaction between Aniline ,carben disulphide and sulpher at 250 °c and 450 P.S.I.



The compound (2HMBT) was used as a reagent forming coloured complexes useful for quantitative determination of $\text{Se}(\text{IV})^{2,3,4}$, $\text{Os}(\text{III})^5$, $\text{Hg}(\text{II})^6$. Nicked complexes were used in Industry in fixing the colour of Jut fabrics⁽⁷⁾, On the other hand ,Zinc complexes were used as an accelerators in rubber Industry^(8,9) and Tin complexes were used as an antibacterial agents⁽¹⁰⁾. Many other complexes of this ligand have been extensively studid⁽¹¹⁾ all of which were found to be stable at ordinary temperatures.

Pearson's Hard-soft interaction⁽¹²⁾ between the ligand (2HMBT) and

metal ions have not been investigated ,therefor it is the task of the present paper to clarify these aspects and therefor stability constants were suggested to do the task.

Experimental

Materials

B.D.H pure thorium nitrate,urany nitrate and lead nitrate ,Fluka (AG) 2-mercapto benzo thiozole (99.91. purity) were used. Dioxane was used after redistillation a B.D.H analar grade reagent . All solutions were made with deionized water and the carbonate free alkali solutions were standardized against pure potassium hydrogen phthalate¹³.

APPARATUS AND PROCEDURE

pH measurements were made using practironic pH –mater ,equiped with glass electrode and standared silver – silver chloride electrode. The pH – meter was standarized befor each run against buffer solutions of know pH values and was checked at the end of each run.

* Prof,Dr ,Chemistry department, college of science for women, University of Baghdad

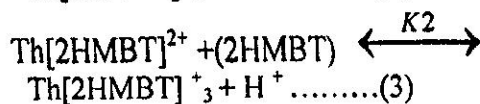
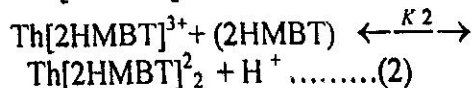
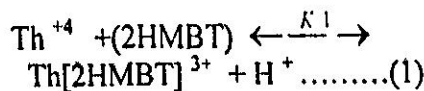
** Chemistry department, college of science for women, University of Baghdad

Titration were carried out in a closed vessel provided with magnetic stirrer. The titrant was delivered from a semimicro burette and the pH value was recorded as soon as it becomes steady. Temperature control of solutions was made with Townson and Mercer thermostated bath of 0.05 °C sensitivity. In 40 volume % dioxane, it was necessary to calibrate the pH meter, Van vitert and Hass¹⁴ have shown that a cell containing a glass electrode measures hydrogen ion activity in dioxane –water solutions as defined by the hydrogen electrode and that at a given salt concentration an empirical calibration $-\text{Log} [\text{H}^+] = B + \text{Log} U_H$ in solution, B is the meter reading and $\text{Log} U_H$ is the meter reading and $\text{Log} U_H$ is the correction factor. The pH meter was calibrated by titrating an aqueous solution of known nitric acid content with dioxane. The values obtained in this fashion were checked against a titration of dioxane with 0.10N nitric acid solution, The addition of -0.038 to the reading of the pH meter, in the case of 40% dioxane and $+0.039$ in the case of 60% dioxane. All calculations in this research were made using a special computer program.

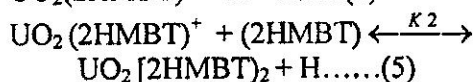
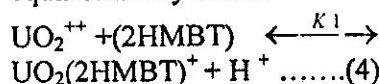
RESULTS

It is customary in using Bjerrum's method for the determination of stability constants of metal complexes to calculate two functions the concentration of the free chelating species (L) and the degree of formation (hⁿ), which is defined as the average number of ligand species bound per atom of metal.

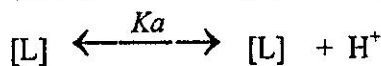
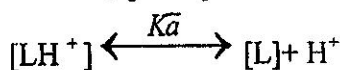
In the titration against a base, a solution of thorium (IV) ion and (2 HMBT) a (3:1) complex system. The following equilibria may occur :



The same type of equilibria occur between pH (II) ions and 2 HMBT a (3:1) complex system. As well, on the other hand titration against a base of solution of uranyl ions and 2HMBT a (2:1) complex system, the following equilibria may occur:



The free chelating species is the [2 HMBT] anion (L), which is, however in equilibria with its zwitter ion, and its cation [LH⁺] :-



In the case of thorium (IV) and lead(II)/ [2HMBT] systems, (n) must be between 0 and 3, and it is for Uranyl / [2HMBT] system between 0 and 2.

The precise relation between n and PH depends on the relative affinities of the ligand for the metal ion expressed by PK₁, PK₂ ...etc. and for the hydrogen ion expressed by pka.

In the present investigation the calculated value of pka for [2HMBT] (0.0125 M) in 40% Dioxane –water mixture was found to be equal to (7.007 ±0.1) at 25 °c at which the PK_w (40%Dioxane –water) is 16.5. Experimental data can be seen in table(1)

Representative titrations of metal ions –chelate mixtures with potassium hydroxide solutions are given in

table (II) for thoriom (IV) and lead ions and in table (III) for uranyl ions.

Calculations of stability constant were according to J. Bjerrum's summation equation¹⁵ and explained fully in previous papers¹⁶. Table (II),(III) and (IV) give detailed calculation for the two parameters(L') and (n') for the three complexes studied, from which values of stability constants were computed and given in table (VI).

Hard and soft parameter for the ligand (2HMBT) were calculated using Mesono's equation: $Pk = -\log K = \alpha x + \beta y + \delta$.

Where K is the instability constant, and were found to be:

$\alpha = 0.227$ and $\beta = 3.23$ respectively.

Table (1)

Determination of acid dissociations constant of (2HMBT) in 40% dioxane – water mixture

20ml 0.025M(2HMBT) dissolved in pure dioxane +27.5 ml deionized water, PH correction factor= -0.038, $PK_w(40\%dioxane) = 16.5$ Temperature $25^{\circ}c$

1 MI 0.1M KOH	2 PH Meter reading	3 Actual PH	4 Stoicheometric Concentration		6 [OH-]	7 [LH]+[OH]	8 PK=PH+Log column 7
			[LH]	[L]		[L]+[OH]	
0.00	5.27	5.232	0.01	0	-	-	-
0.50	6.22	6.182	0.009	0.001	4.8×10^{-11}	9	7.136
1.00	6.66	6.622	0.008	0.002		4	7.224
1.50	6.91	6.872	0.007	0.003		2.333	7.239
2.00	7.08	7.042	0.006	0.004		1.5	7.218
2.50	7.21	7.172	0.005	0.005		1.0	7.172
3.00	7.34	7.302	0.004	0.006		0.666	7.125
3.50	7.45	7.412	0.003	0.007		0.428	7.044
4.00	7.54	7.502	0.002	0.008		0.25	6.899
4.50	7.64	7.602	0.001	0.009		0.111	6.64
5.00	7.75	7.712	0.0	0.010	1.62×10^{-9}	-	-

Total=63.697

Pka. =7.077

average

$Ka=8.3 \times 10^{-8}$

Table (II)

Titration of (2HMBT-Pb⁺⁺) complexes

30 ml 0.023 M(2HMBT) in dioxane + 5 ml 0.05 M pb (NO₃)₂ + 12.5 ml deionized water , titrated with 0.1 M KOH , Temp = 25c , % Dioxane =60 , PH correction =+0.039 ,PKw (60%Dioxane)=17.76

1	2	3	4	5	6	7	8	9
ml 0.1M KOH	PH meter reading	Actual Ph	[L ⁻] _T	[Pb ⁺⁺] _T	[KOH]	Log[L ⁻]	[L]	H
0.00	3.62	3.659	0.01579	5.26x10 ⁻³	-	-5.219	-	-
0.10	3.67	3.709	0.01575	5.25x10 ⁻³	2.10x10 ⁻⁴	-5.176	6.659x10 ⁻⁶	0.0126
0.20	3.77	3.809	0.01572	5.24x10 ⁻³	4.193x10 ⁻⁴	-5.083	8.255x10 ⁻⁶	0.0519
0.30	3.85	3.889	0.01569	5.23x10 ⁻³	6.27x10 ⁻⁴	-5.010	6.769x10 ⁻⁶	0.092
0.40	3.94	3.979	0.01565	5.21x10 ⁻³	8035x10 ⁻⁴	-4.927	1.182x10 ⁻⁵	0.132
0.50	4.00	4.039	0.01562	5.20x10 ⁻³	1.041x10 ⁻³	-4.874	1.335x10 ⁻⁵	0.173
0.60	4.07	4.109	0.01559	5.19x10 ⁻³	1.247x10 ⁻³	-4.811	1.544x10 ⁻⁵	0.2127
0.70	4.12	4.139	0.01556	5.18x10 ⁻³	1.452x10 ⁻³	-4.768	1.703x10 ⁻⁵	0.254
0.80	4.18	4.219	0.01552	5.17x10 ⁻³	1.656x10 ⁻³	-4.716	1.923x10 ⁻⁵	0.293
0.90	4.22	4.259	0.01549	5.16x10 ⁻³	1.0859x10 ⁻³	-4.683	1.072x10 ⁻⁵	0.333
1.00	4.25	4.289	0.01546	5.15x10 ⁻³	1.061x10 ⁻³	-4.660	1.183x10 ⁻⁵	0.372

n=10 , pka=7.077 , ka =8.3 x10⁻⁸ , Temp = 25
 Log [L⁻] = (pH -Pka) + log [[L]_T - [KOH]_T]

$$\bar{n} = \frac{[L]_T - \{[H^+] + 1\} [L]}{ka [M]_T}$$

Table (III)
Titration of (2HMBT-Th⁺⁴) complexes

30 ml 0.025 M(2HMBT) in dioxane + 5 ml 0 .05 M Th (NO₃)₄ + 12.5 ml deionized water , titrated with 0.1 M KOH , Temp = 25° c ,
 % Dioxane =60 , PH correction =+0.039 .PKw (60%Dioxane) =17.76

1	2	3	4	5	6	7	8	9
ml 0.1M KOH	PH meter reading	Actual PH	[L] _r	[Th ⁺⁴] _r	[KOH]	Log[L]	[L]	\bar{n}
0.00	2.80	2.839	0.01579	5.26x10 ⁻³	-	-6.0396	9.128x10 ⁻⁷	-
0.10	2.81	2.849	0.01575	5.25x10 ⁻³	2.10x10 ⁻⁴	-6.0363	9.192x10 ⁻⁷	0.0132
0.20	2.81	2.849	0.01572	5.24x10 ⁻³	4.193x10 ⁻⁴	-6.0432	9.051x10 ⁻⁷	0.0533
0.30	2.82	2.859	0.01569	5.23x10 ⁻³	6.27x10 ⁻⁴	-6.0400	9.118x10 ⁻⁷	0.0936
0.40	2.083	2.869	0.01565	5.21x10 ⁻³	8.035x10 ⁻⁴	-6.0372	9.177x10 ⁻⁷	0.1343
0.50	2.084	2.879	0.01546	5.20x10 ⁻³	8.35x10 ⁻⁴	-6.0342	9.241x10 ⁻⁷	0.1746
1.00	2.86	2.899	0.01530	5.15x10 ⁻³	2.06x10 ⁻³	-6.0509	8.894x10 ⁻⁷	0.3762
1.50	2.87	2.909	0.01515	5.102x10 ⁻³	3.06x10 ⁻³	-6.080	8.312x10 ⁻⁷	0.578
2.00	2.90	2.939	0.015	5.05	4.04x10 ⁻³	6.0922	8.085x10 ⁻⁷	0.780
2.50	2.93	2.969	0.01485	5x10 ⁻³	5.00x10 ⁻³	-6.108	7.798x10 ⁻⁷	0.981
3.00	2.95	2.989	0.01456	4.95x10 ⁻³	5.94x10 ⁻³	-6.1381	7.275x10 ⁻⁷	1.1837
4.00	3.00	3.039	0.01428	4.854x10 ⁻³	7.76x10 ⁻³	-6.2038	6.224x10 ⁻⁷	1.587
5.00	3.06	3.099	0.01401	4.761x10 ⁻³	9.52x10 ⁻³	-6.3006	5.004x10 ⁻⁷	1.9910
6.00	3.16	3.199	0.01351	4.67x10 ⁻³	1.11x10 ⁻³	-5.7677	1.707x10 ⁻⁷	2.998

n = 12

Table (IV)

Titration of (2HMBT- UO_2^{++}) complexes

20 0ml 0.025 M(2HMBT) in dioxane + 5 ml 0.05 M $UO_2(NO_3)_2$ + 22.5 ml deionized water, titrated with 0.1 M KOH, Temp = 25 °C,
% Dioxane =40, PH correction = - 0.038, $PK_w = 16.5$

1	2	3	4	5	6	7	8	9
ml 0.1M KOH	PH meter reading	Actual PH	[L] _T	[UO_2^{++}] _T	[KOH]	Log[L]	[L]	n
0.00	3.47	3.432	0.01052	5.263×10^{-3}	0.00	-5.6229	2.38×10^{-6}	-
0.10	3.61	3.572	0.01050	5.752×10^{-3}	2.1×10^{-4}	-5.4925	3.216×10^{-6}	-
0.20	3.62	3.582	0.01048	5.24×10^{-3}	4.19×10^{-4}	-5.4923	3.128×10^{-6}	-
0.30	3.63	3.592	0.01046	5.23×10^{-3}	6.27×10^{-4}	-5.4923	3.128×10^{-6}	0.102
0.40	3.70	3.662	0.01044	5.219×10^{-3}	8.35×10^{-4}	-5.432	3.694×10^{-6}	0.1426
0.50	3.75	3.712	0.01041	5.208×10^{-3}	1.04×10^{-3}	-5.393	4.045×10^{-6}	0.182
1.00	3.91	3.872	0.01031	5.154×10^{-3}	2.06×10^{-3}	-5.288	5.014×10^{-6}	0.384
1.50	4.04	4.002	0.0102	5.102×10^{-3}	3.06×10^{-3}	-5.221	6.006×10^{-6}	0.586
2.00	4.16	4.122	0.0101	5.050×10^{-3}	4.04×10^{-3}	-5.172	6.721×10^{-6}	0.788
2.50	4.29	4.252	0.0100	5.0×10^{-3}	5.0×10^{-3}	-5.126	7.481×10^{-6}	0.989
3.00	4.42	4.382	9.90×10^{-3}	4.95×10^{-3}	5.94×10^{-3}	-5.097	7.99×10^{-6}	1.191
3.50	4.55	4.512	9.804×10^{-3}	4.901×10^{-3}	6.86×10^{-3}	-5.96	8.015×10^{-6}	1.392

n = 12

Table (VI)

Summary of the computed stability constants of [Metal: (2HMBT)] complexes

Metal ion	K_1	K_2	K_3	$K = K_1 \times K_2 \times K_3$
Th^{++}	1.683×10^8	2.852×10^4	1.043	5.01×10^{12}
UO_2^{++}	1.392×10^8	1.584×10^3	-	2.15×10^{11}
Pb^{++}	2.377×10^3	2.309×10^4	0.154	8.408×10^8

Table (VII)

Hard - soft parameters of some metal ions

Interaction parameter	Metal ions		
	Th^{++}	UO_2^{++}	Pb^{++}
x	8.93	20.32	4.15
y	2.75	1.86	3.58

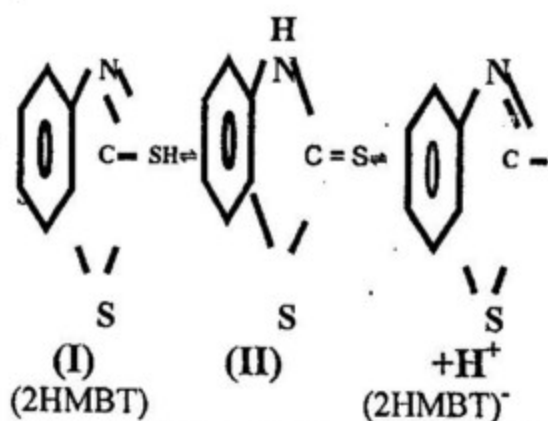
Table (VIII)

Comparison of hard and soft interaction parameters of (2HMBT) Ligands with other Ligands

Interaction parameter	Ligands						
	OH ⁻	NH ₂	Cl ⁻	(2HMBT)	Phenol	Br ⁻	I ⁻
α	1.58	0.83	0.6	0.227	0.16	1.19	0.99
β	0.40	1.08	2.49	3.23	3.46	5.58	7.17
γ	-	-	-	1.79	-4.17	-	-

Discussion

The compound 2HMBT could be written in different tautomeric forms under certain conditions of PH. The compound undergoes ionization as it can be seen from the equation below :



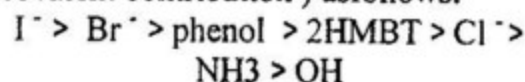
In order to evaluate proton affinity for the molecule - ion (2HMBT)⁻, it is necessary to calculate the acid constant of the molecule itself, this has been done in Dioxane –water system as can be seen in table (1). The obtained value of 8.3×10^{-8} is comparable with those of glycime¹⁷, dihydroxy benzenes¹⁸, 8-hydroxquinoline and others¹⁹.

It was shown²⁰ that the coordinating sites of 2HMBT molecule are the soft sulphur atom and the hard nitrogen atom of the thiozole moiety. Resultant Hard –soft interaction of the this ligand with metal ions is the overall interactions of Nitrogen and sulphur atoms involved.

Introducing stability constant values of (metal ion : 2HMBT) complexes, together with hard & soft

parameters of metal ions of table(VII)²¹ in Messon's equation²² gives the interaction parameters (α) and (β) for the ligand, this can be seen from table(VIII) .

Comparison of the softness parameter value (β) of (2HMBT)ligand ($\beta = 3.230$) with others as shown in table (VIII) will enable one to write softness interaction sequence (i.e the covalent contribution) as follows:



Again : comparison of the hardness parameter value (α) of

(2HMBT) Ligand ($\alpha = 0.227$) with corresponding values of phenol ($\alpha = 0.16$) and others will enable one to write hardness interaction sequence (i.e The ionic contribution) as follows:
 $OH^- > Br^- > I^- > NH_3 > Cl^- > 2\text{HMBT} > \text{Phenol}$

In conclusion, and from the above disussion, it is quite clear that Harder behavior of (2HMBT) Ligand is the predominant Interaction forming stable complexes with hard metal ions⁽²³⁾.

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التداخلات الصلدة والليونة لـ2- مركبتو بنزو ثايوزول مع بعض الأيونات الفلزية

يحيى عبد المجيد العبيدي * نازك محمد عزيز **

* قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد
** قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد

الخلاصة

تم تعيين ثابت تفكك الحامضي لليكاند العضوي 2-مركبتو بنزو ثايوزول في محاليل (دايوكزان-ماء) في درجة حرارة 25°C ، وكان يعادل 8.3×10^{-8} ، كذلك تمت دراسة ثوابت استقرارية معقدات الليكاند العضوي مع أيونات الثوريوم الرباعي واليورانييل وأيونات الرصاص في محاليل (دايوكزان-ماء) في درجة 25°C .
لقد اثبتت نتائج البحث ان الليكاند العضوي يتصرف وكأنه قاعدة صلدة (Hard-base) حسب تعريف بيرسون، ولقد امكن حساب معاملات الصلادة والنعومة لليكاند العضوي (2HMBT) باستعمال معادلة ميسونو وبذلك أمكن ترتيبها من حيث صلادتها كما يلي:

