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RESEARCH ARTICLE

DETERMINATION OF STABILITY CONSTANT OFSOME METAL IONCOMPLEXES WITH (N-TRIS [HYDROXYLMETHYL] METHYL (2-AMINO ETHANESULFONICACID)(TES)

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ABSTRACT

Ionization constant was been determined for N-tris [hydroxyl methyl] methyl (-2-amino ethane sulfonic acid)(TES) has been determined in 25^0C .The value of pka consider as7.5 and kais(3.1×10^{-8}) respectively, Measurement of stability constants for various complexes with Ag^{+1}, Co^{+2},Ni^{+2}, Cu^{+2} , Cd^{+2},Cr^{+3} metal ions was determined, And measured recommended have been performed. The result showed that (TES) behave as bi dentate lig and with complexes being formed was of (1:1) ratio. Measurement of hardness and softness parameters of (TES) have been hardness parameter (α) of (1.46) and softness of (β) was (5.93).

INTRODUCTION

N-tris[hydroxyl methyl] methyl (-2-amino ethane sulfonic acid)(TES) is one of amino and sulfonic acids group and its derivatives are an important class of bioactive molecular in the field of drugs and pharmaceuticals (RonniGamzu,1997).Test(TES (N-tris[hydroxymethyl]methyl-2-aminoethanesulfonic acid) and Trisyolk buffer (TYB) has recently been shown to improve the binding capacity of spermatozoa to zona pellucidae (Bulos, 2003). it's have wide applications immedical chemistry as uses the biochemical buffers. Sulphur donor atoms are one of the most important binding sites of metalloproteins. (Zeinab ,2005), thereforindicated that widespread investigations have been carried out to reveal thecoordination chemistry of amino acids and piptides containing sulphur donors one of the biologically important ligand of this type is the tripeptide glutathione like (N-[2-hydroxyethyl]iperazine-N-{2-ethanesulfonicacid) (HEPES) and (N-[2-Hydroxyethyl]piperazine-N-[2-Hydroxy-propanesulfonic acid (HEPPSO).(Hong ,2003) 3-[(O-carboxy nitrobenzene) azo] chromotropic acid (CNBAC) was also used as a ligand for selective determination of Cu^{+2} and Co^{+2} ions.

(Deosarkar,2009) the stability constants of4-amino-3-naphthol-sulphonicacid with Co(II) metal ions and3-amino 4-hydroxy 5-nitro benzene sulphonic acid with Cu^{+2}metal ions in differentpercentage of ethanol-water mixtures having varying dielectric constants and at constant ionic strength (**μ** a=0.01M) have been determined potentiometrically. Recently, a research mentioned that satability constants of macro molecular metal complexes of transition metal ions (Ag+ ,Cu^{2+},Ni^{+2},Fe^{+3}) with sulfonated polymers in water and aqueous HCl and NaCl solution (Pautov, 2007).

Basima (2012) prepared a (N-tris[hydroxyl methyl]methyl(2-amino ethane sulfonic acid)(TES) with of metal ions (Ag^{+} , VO^{+2},Co^{+2} , Ni^{+2} . Cu^{2+},Zn^{+2} .Hg^{+2} ,Cd^{+2} ,Cr^{+3}). in this stady we are interested mainly in measuring the stability constant (pKa)of complexes in aqueous solution of (N-tris[hydroxyl methyl]methyl(2-amino ethane sulfonic acid)(TES)(Pearson ,1963) , also to apply Pearsons hard-soft ,acid-base prostitute(HSAB) to explain the behavior of this ligand inters of misonos parameters(Misono,1967).

Location and duration of study

This study was conducted at the college pharmacy, Department of pharmaceutical chemistry, University of karbala, , lasted for a period of three months.

Experimental

Reagent

The ligand(TES)were used(B.D.H)analar grade.Standard solutionsof metal nitrate wereprepared from analar reagents. Solution of metal nitrate were made with distilled water and carbonate free alkali solution and were standardized against pure potassium hydrogen phthalate.

Apparatus and procedure

pH - Measurements were carried out with(3510 PH –meter – Jenway pH-Meter).PH-Meter was standardized before each run against buffer solutions of known pH values and was checked at the end of each run.

RESULTS AND CALCULATION

The acid dissociation constant of (TES) was calculated the detailed calculation can be seen in Table (1). In order to determine stability constant of metal complexes, Two

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functions must be calculated. The concentrations of the free chelating species (L^-) and the degree of formation (n^-) which is defined as the average of ligand species bound per atom of metal. concentration of free ligand species were calculated by equation previously used with thorium-glycinate(Majed, 1980) of the form :

$$\log [L'] = (PH - PKa) + \log ([L]_T - [KOH]_T) \ldots\ldots\ldots \quad (1)$$

An expression for the degree of formation (n-)was used of the form;-

$$n^- = \frac{[L]_T - [H^+ + 1][L']}{[M]_T} \ldots\ldots\ldots \quad (2)$$

Where $[L]_T$, $[L^-]$, $[M]_T$,are concentrations of total ligands,free ligands and total metal ion ,respectively .for the present systems ,the reported stability constants, β_1, β_2 and β_3 were computed using the well known

J.Bierum summation equation with $[L^-]$ an $[n^-]$ calculated at different PH values from equation (1) and (2) respectively .

$$\sum_{n=0}^{n=max} [n-n^-] \beta n [L]^{n-} = 0 \ldots\ldots\ldots\ldots\ldots \quad (3)$$

It can be shown after simple approximation that equation (3) may be written for present system as:

$$\frac{1}{\beta_3} + \frac{(n^- -1)(L)}{\beta_3}\beta_1 + (n^- -2)(L)^2\beta_2 + (3- n^-)(L)^3 = 0 \ldots\ldots\ldots \quad (4)$$

Where β_1, β_2 and β_3 are the corresponding stability constants equation (4) is of the form :

$$c + ax + by = z \ldots\ldots\ldots \quad (5)$$

Where

$$X = \frac{(n^- -1)(L)}{n^- n^- n^-}, \quad Y = \frac{(n^- -2)(L)_2}{n^- n^- n^-}, \quad Z = \frac{(3 - n^-)(L)_3}{n^- n^- n^-}$$

All being experimentally determined functions and

$$a = \frac{\beta_1}{\beta_3\beta_3\beta_3} \quad b = \frac{\beta_2}{\beta_3\beta_3\beta_3} \quad \text{and} \quad c = \frac{1}{\beta_3\beta_3\beta_3}$$

In each system. the functions X ,Y and Z were calculated from the experimental data and where fitted to aggression equation using crammer'ˢ rule for solving such equation. Typical titration results are summarized in Table (2,3,4,5,6,7 and 8)

Table 2 Titration of 30ml (0.025 M) of (TES) and 5ML(0.025 M)M(NO_3)n solution with(0.085 M KOH solution , Temp: 25^0C, Vol, 47.5ml , μ = 0.1

KOH 0.085M	Ag^{+1}	Co^{+2}	Ni^{+2}	Cu^{+2}	Cd^{+2}	Cr^{+3}
0.0	4.69	5.17	4.54	4.02	5.05	3.44
0.5	5,73	6	5.49	4.57	5.69	3.68
1.0	5.99	6.47	5.86	4.96	5.87	3.88
1.5	6.21	6.66	6.10	5.19	6,03	4.14
2.0	6.38	6,78	6,28	5.39	6.27	4.37
2.5	6.52	6.94	6.49	5.5	6.41	4.63
3.0	6.62	7.03	6.61	5.73	6.59	4.93
3.5	6.74	7.12	6.76	5.88	6.71	5.18
4.0	6,84	7.21	6.86	5.98	6,92	5.26
4.5		7.29	6.97	6	7.01	5.34
5.0		7.47	6.98	6.23	7.8	5.49

Stability constants metal TES complexes and hardness – softness parameter of TES are calculated using misonos equations (Pearson,1963). result are shown in table(9) .

DISCUSSION

The decrease in the pH value of solution of TES when a neutral salt solution of metal ions were added is a clear indication of complexes formation . the chemical equation representing the equllibrium could be written as follows .

N-tris[hydroxyl methyl] methyl (-2-amino ethane sulfonic acid)(TES)

R=(CH3OH)3-C- , M=Ag^{+1}, Co^{+2}, Ni+2, Cu+2 , Cd+2 , Cr +3

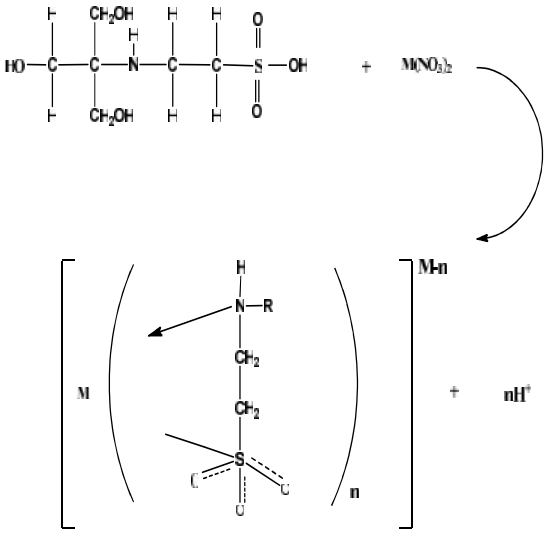

Table 1 Determination of the dissociation of(TES).20ML(0.025M)for(TES)+27.5ml of water temp:25C^0, μ = 0.1

$$HL \rightleftharpoons H+ + L^- PKa = PH + \log \frac{[HL]+[OH^-]}{[B] - [OH^-]}$$

1	2	3	4	5	6	7
KOH 0.085 M	**PH**	**Stoichiometric [B]**	**[HL]**	**$[OH^-]$**	**[HL]+[OH][B]-$[OH^-]$**	**PKa=PH^+ logCol 6**
0.00	5.85	0	1.05×10^{-2}	7×10^{-9}	-	-
0.5	6.49	$\times8.8510^{-4}$	1.04	3×10^{-8}	10.746	7.52
1	6.80	$\times1.7410^{-3}$	1.03	6.3	4.948	7.49
1.5	7.04	2.60	1.02	7.04×10^{-7}	2.934	7.50
2	7.21	3.43	1.01	7.21	11.929	7.495
2.5	7.36	4.25	1×10^{-3}	7.36	1.356	7.49
3	7.52	5.05	9.9	7.52	0.9623	7.50
3.5		5.83	9.80			
4		6.60	9.70			

Pka= 7.5 , Ka=3.1. 10^{-8}

Table 3 Titration of 30ml (0.025 M) of (TES) and 5ML(0.025 M)Ag NO_3 solution with (0.085 M KOH solution , Temp:25^0 C, Vol,47.5ml , μ = 0.1

KOH 0.085M	pH	$[KOH]_T$	$[M]_T$	$[L]_T$	H^+/ Ka	$[L]^-$	n^-
0.0	4.54	0	5.26×10^{-3}	1.57×10^{-4}	930.3	0	0
0.5	5.49	8.85×10^{-4}	5.21	1.56	104.38	1.43×10^{-4}	0.08566
1.0	5.86	$\times1.74\ 10^{-3}$	5.15	1.54	44.5	3.12	0.2255
1.5	6,1	2.60	5.10	1.53	25.6	5.05	0.3629
2.0	6.28	3.43	5.05	1.51	16,9	7.03	0.4976
2.5	6.49	4.25	5.00	1.50	10.43	1.05×10^{-3}	0.5984
3.0	6.61	5.05	4.95	1.48	7.9	1.25	0.7315
3.5	6.76	5.83	4.90	1.47	5.6	1.61	0.8259
4.0	6.86	6.60	4.85	1.45	4.45	1.8	0.9560
4.5	6.96	7.35	4.81	144	3.45	2.08	1.0688
5.0	6.98	8.09	4.76	142	3.37	1.84	1.2891

Table 4 Titration of 30ml (0.025 M) of (TES) and 5ML(0.025 M)Co(NO_3)$_2$ solution with (0.085 M KOH solution , Temp:25^0 C, Vol,47.5ml , μ = 0.1

KOH 0.085M	pH	$[KOH]_T$	$[M]_T$	$[L]_T$	H^+/ Ka	$[L]^-$	n^-
0.0	5.17	0	5.26×10^{-3}	1.57×10^{-4}	218.09	0	0
0.5	6	$\times8.8510^{-4}$	5.21	1.56	32.25	4.65×10^{-4}	0.0245
1.0	6.47	$\times1.7410^{-3}$	5.15	1.54	10.93	1.27×10^{-3}	0.03715
1.5	6.66	2.60	5.10	1.53	7.05	1.83	0.10246
2.0	6.78	3.43	5.05	1.51	5.35	2.22	0.1939
2.5	6.94	4.25	5.00	1.50	3.7	2.96	0.2176
3.0	7.03	5.05	4.95	1.48	3.01	3.3	0.3135
3.5	7.12	5.83	4.90	1.47	2.44	3.69	0.4041
4.0	7.21	6.60	4.85	1.45	1.98	4.05	0.5002
4.5	7.29	7.35	4.81	144	1.65	4.34	0.5985

Table 5 Titration of 30ml (0.025 M) of (TES) and 5ML(0.025 M)Ni(NO_3)$_2$ solution with(0.085 M KOH solution , Temp:25 ^{0}C, Vol,47.5ml , μ = 0.1

KOH 0.085M	pH	$[KOH]_T$	$[M]_T$	$[L]_T$	H^+/ Ka	$[L]^-$	n^-
0.0	4.54	0	5.26×10^{-3}	1.57×10^{-4}	930.3	0	0
0.5	5.49	$\times8.8510^{-4}$	5.21	1.56	104.38	1.43×10^{-4}	0.08566
1.0	5.86	$\times1.7410^{-3}$	5.15	1.54	44.5	3.12	0.2255
1.5	6.1	2.60	5.10	1.53	25.6	5.05	0.3629
2.0	6.28	3.43	5.05	1.51	16.9	7.03	0.4976
2.5	6.49	4.25	5.00	1.50	10.43	1.05×10^{-3}	0.5984
3.0	6.61	5.05	4.95	1.48	7.9	1.25	0.7315
3.5	6.76	5.83	4.90	1.47	.5.6	1.61	0.8259
4.0	6.86	6.60	4.85	1.45	4.45	1.8	0.9560
4.5	6.97	7.35	4.81	144	3.45	2.08	1.0688
5.0	6.98	8.09	4.76	142	3.37	1.84	1.2891

Table 6 Titration of 30ml (0.025 M) of (TES) and 5ML(0.025 M)Cu(NO_3)$_2$solution with (0.085 M KOH solution , Temp:25^0 C, Vol,47.5ml , μ = 0.1

KOH 0.085M	pH	$[KOH]_T$	$[M]_T$	$[L]_T$	H^+/ Ka	$[L]^-$	n^-
0.0	4.02	0	5.26×10^{-3}	1.57×10^{-4}	3080.6	0	0
0.5	4.57	$\times8.8510^{-4}$	5.21	1.56	868.23	1.7×10^{-4}	0.1098
1.0	4.96	$\times1.7410^{-4}$	5.15	1.54	353.7	3.93	0.2769
1.5	5.19	2.60	5.10	1.53	208.2	6.22	0.4485
2.0	5.39	3.43	5.05	1.51	131.41	9.05	0.6150
2.5	5.5	4.25	5.00	1.50	102	1.07×10^{-3}	0.7855
3.0	5.73	5.05	4.95	1.48	60.06	1.65	0.9474
3.5	5.88	5.83	4.90	1.47	42.5	2.12	1.11106
4.0	5.98	6.60	4.85	1.45	33.77	2.38	1.2827
4.5	6	7.35	4.81	144	32.25	2.22	1.4526
5.0	6.23	8.09	4.76	142	18.99	3.28	1.6052

However. calculation of acidity as can be seen in Table (1) (Ka= $3.1x10^{-8}$)indicate that TES behaves as an acid.

It is reasonable to expect a correlation between the stability of complex and the acidic dissociation constant of the conjugate acid of the ligand

$$nHL + M^{+m} \rightleftharpoons [ML_n]^{m-n} + nH^+$$

Considering the case of TES, the association which metal ions takes the following route :

$$n(TES) + M^{+m} \rightleftharpoons [M(TES)_n]^{m-n} + nH^+$$

where $[M(TES)_n]^{m-n}$ represents

From table (9)the following conclusion could be drown because of the negative values of (β_2, β_3, β_3)…… etc

Table 7 Titration of 30ml (0.025 M) of (TES) and 5ML(0.025 M)Cd(NO_3)$_2$ solution with (0.085 M KOH solution , Temp:25^0 C, Vol,47.5ml , μ = 0.1

KOH 0.085M	pH	$[KOH]_T$	$[M]_T$	$[L]_T$	H^+/ Ka	$[L]^-$	n^-
0.0	5.05	0	5.26×10^{-3}	1.57×10^{-4}	287.5	0	0
0.5	5.69	$\times8.8510^{-4}$	5.21	1.56	65.86	2.2×10^{-4}	0.06949
1.0	5.87	$\times1.7410^{-3}$	5.15	1.54	43.51	3.2	0.2246
1.5	6.03	2.60	5.10	1.53	30.10	4.3	0.3842
2.0	6.27	3.43	5.05	1.51	17.32	6.87	0.4971
2.5	6.41	4.25	5.00	1.50	12.54	8.73	0.6337
3.0	6.59	5.05	4.95	1.48	8.29	1.19×10^{-3}	0.7386
3.5	6.71	5.83	4.90	1.47	6.28	1.43	0.8627
4.0	6.92	6.60	4.85	1.45	3.87	2.0	0.9032
4.5	7.01	7.35	4.81	144	3.15	2.28	1.02661
5.0	7.8	8.09	4.76	142	2.68	2.3	1.1872

Table 8 titration of 30ml (0.025 M) of (TES) and 5ML(0.025 M)Cr(NO_3)$_3$ solution with (0.085 M KOH solution , Temp:25^0 C, Vol,47.5ml , μ = 0.1

KOH 0.085M	Ph	$[KOH]_T$	$[M]_T$	$[L]_T$	H^+/ Ka	$[L]^-$	n^-
0.0	3.44	0	5.26×10^{-3}	1.57×10^{-4}	11712.1	0	0
0.5	3.68	$\times8.8510^{-4}$	5.21	1.56	6739.6	2.2×10^{-6}	0.1127
1.0	3.88	$\times1.7410^{-3}$	5.15	1.54	4252.4	3.2	0.2839
1.5	4.14	2.60	5.10	1.53	2336.8	5.5	0.4587
2.0	4.37	3.43	5.05	1.51	1376.0	8.6	0.6311
2.5	463	4.25	5.00	1.50	756.2	1.45×10^{-5}	0.8039
3.0	4.93	5.05	4.95	1.48	378.9	2.6	0.9758
3.5	5.18	5.83	4.90	1.47	213.1	4.2	1.1449
4.0	5.26	6.60	4.85	1.45	177.2	4.54	1.3193
4.5	5.34	7.35	4.81	144	147.4	4.87	1.4889
5.0	5.49	8.09	4.76	142	104.38	5.97	1.6613

formation of (1:1)complex species between (TES)and metal ions may be considered as the only species existing in solution.

Hardness –Softness parameters

The relationship between stability constant of complexes and the characterstics properties of their constituents was established by pearson(Misono,1967) the forwarded the interpretation of hard interaction as eleactrostic and soft one as covalent.

later drago and way land put forward a two parameters equation to represent their acid–baseinteractions(Drago,1965),misano(Misono,1967)has introduced a quantitative relationships for coordination compounds which can be expressed as follows.

$PK= - Log K = \alpha X + \beta Y + \gamma$ ……. (6)

Where k is the stability constant of the complex,X and Y are parameters of metal ion ,(α) and (β) those of the ligand .the parameter (γ) is characteristic of ligand and used to adjust the PKs, so that all lie on the same scale, the (Y) parameter is

considered to be measure of softness and may be evaluated from atomic parameters including the radius of the ion from atomic parameters including the radius of the ion ,our results for the soft and hard parameters (Y)is complete agreement with those published by misono. Huheeg,(1978) the analogous ligand parameter (B) like wise shows the expected increase in values from hard to soft species HO^- = 0.4,NH_3 =1.08 ,Cl^- = 2.4 ,Br^- =5.58 , I^-=7.17,$S_2O_3^{=}$ =12.4(Misono ,1967).

Softness parameters (B) of (TES)ligand under investigation has value of (5.93)in reminiscent to between of glycine as ligand(Majid, 1996) (B= 5.58) and iodide as ligand (B= 7.17),The (α) and (X) parameters were interpreted by misono as hardness parameters of ligand and metal ion respectively although it includes the inherent acids-base strength of the ligand and metal ion.

Thus (X)is closely related to the electro negativity of the ion and measures the tendency of metal ion to accept electrons from the ligand. Calculated hardness parameter(α)for ligand (TES) was found tobe (α=1.46) a value comparable to(X) of the(N,N-bis(2-hydroxyl ethyle)Glycine(Sarhan, 2001), the weakly acidic ligand.

Table 9 Misano Metal -TES parameters calculation according to the equation Log k = α x +β y + γ , Where K being the first association (β_1)

Metal ion	β_1	Metal ion	
		X	Y
Ag^{+1}	1.49×10^6	4.80	3.99
Co^{+2}	3.38×10^5	4.39	2.59
Ni^{+2}	2.67×10^6	4.73	2.82
Cu^{+2}	3.66×10^6	5.31	2.80
Cd^{+2}	2.54×10^4	4.87	3.04
Cr^{+3}	4.88×10^4	8.39	2.70
Ligand parameters		α	1.46
		β	5.93
		γ	19.14-

*X is related to the electro negatively of the ion and is obtained from the equation.

$(10X)^{1/2} = X^0{}_m + (In)^{1/2}$ .Where $X^0{}_m$ is the electro negatively of the metal taken from(Gordy, 1956) Gordy and Thomas and (In) is the ionization energy (e.v)(Stockarg,1950).

** $Y=10 (In / In + 1)(r_i / \sqrt{n})$Where ($r_i$) is the ionic radius of metal ion and (n) is the formal charge .

***Schaum's,(1968) values of ligand parameters were calculated using the least squares solution of an over determined system of linear equations to derive the normal equation.

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