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Research paper



Effect of various ionic strengths on the stabilities of metal mediated ternary complexes

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Abstract

The stabilities of 1:1:1 ligand-metal-ligand complexes investigated at different ionic strength (KNO3) in the presence of mixed solvent (water50%+dioxane50%) system at temperature 250 centigrade by pH metric titration method. In this investigation copper, nickel, zinc and cobalt used as metal ions, Beta-Hydroxy ketone and Benzotriazole derivatives acted as ligands. Data of present investigation showed that Cu formed more stable complexes; it is followed by Zn and Ni complexes.Co formed less stable complexes. The stabilities of these 1:1:1 ligand-metal-ligand complexes are measured by Δ log K values, Percentage of stacking and intra molecular equilibrium constants.Due to overlapping of $–CH_2$ CH_3 ,2-methyl propyl and C6H5CH2- side chains of BHK ligands with aromatic ring of the BTAZ ligands these ligand-metal-ligand complexes attained extra stabilities. The values of Δ log K values for pair of (BHK-Alkyl)/ (BHK-Benzyl)-Metal (II)-(BTAZ-Alkyl-OH) and (BHK-Alkyl)/ (BHK-Benzyl)-Metal (II)-(BTAZ-Phenyl-OH) are alike. This indicates the side chain/aromatic ring of BHK is overlaying with the Benzotriazole ring, but not with the phenyl side chain/aromatic ring of the BTAZ ligand.

Keywords:*Intra Molecular Interactions; Ionization Constants; 1:1:1 Ligand-Metal-Ligand Complexes; Stability Constants; Stacking Interactions.*

1. Introduction

A metal ion interactions with various ligands is an extremely diversified field [1], because the interaction as well as the resulting complex can have different applications in the biological field[2], in color photography as color stabilizing agent, catalyst, luminescent materials development, therapeutic advantage[3], in the electronic display devices[4]or fluorescent probesand can also be used in the resin technology[5]. In all these cases, the utility of metal-ligand complex is directly related to the stability of the complex which is a tunable parameter.These stabilities of metal complexes directly depend on (i) metal ion nature ii) ligand structure iii) intra molecular interactions between two ligands which bonded to a single metal ion and iv) complex formation medium such as temperature, solvent or ionic strength etc[6]. In a simple model, a single metal ion binds to a single ligand in a 1:1 ratio; it is called a binary complex.If a single metal ion binds to a two different ligands then the complex is called mixed ligand complex or ternary complex. The stabilities of the multi-ligand complexes are very unpredictable, because the flexible side chains of bound ligands participate in the ligand-ligand interactions, which play a major role in the overall stability of the complexes. The interactions of metal ions with the ligands are measured in terms of formation constant or stability constants (log K). Number of atoms coordinated with ligand, chelate ring size and metal ion, coordinated atoms charges influence stability constants [7]. The Intramolecular interactions like hydrophobic interactions, hydrogen bonding, Ionic/ electrostatic interactions [8] and stacking interactions between the ligands of the complex also influence the stability of metal-ligand complexes. Because of Intramolecular interactions between the coordinated ligands in the metal complex the stabilities of metal ligand complexes differ from predicted stability constants values based on pK_a with the experimental values. Interactions of metal ligands(s) complexes in solution can be easily determined by using pH metric method [9]. In present research work to find stability constants of metal ligand complexes, beta-hydroxy ketone (BHK) derivatives and benzotriazole (BTAZ) derivatives selected as ligands, Copper (II), Nickle(II), Zinc(II) and Cobalt(II) selected as metal ions. $–CH_3$,$–CH_2CH_3$, 2-methyl propane and $C_6H_5CH_2$- flexible side participated in metal ion coordination. The other selected ligand is benzotriazole derivative (BTAZ). It has benzotriazole ring. This benzotriazole ring connected to C_2H_5-OH, C_6H_5-OH, C_2H_5-NH_2, and C_6H_5-NH_2 side chains. These side chains involved in thecoordination with the metal ion.
The main objective of present research work is to determine the effect of ionic strength on the stabilities of metal- ligand complexes and Intramolecular interactions and their contributions towards the overall stabilities of metal-ligand complexes. In present investigationit will be proved that the flexible side chains C_2H_5-OH, C_6H_5-OH, C_2H_5-NH_2, and C_6H_5-NH_2 ofbeta-hydroxy ketone (BHK) involves in the Intramolecular interaction with the benzotriazole ring, but not with benzotriazole ringconnectedC_2H_5-OH, C_6H_5-OH,C_2H_5-NH_2, and C_6H_5-NH_2 side chains.
In this investigation it will be proved that how the side chain groups from BHK interact with fixed aromatic moieties of bound BTAZ ligand to the metal ion and its effect on the overall stability of the ternary metal-ligand complexes in solution.

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2. Experimental

The ligands from the derivatives of the beta-hydroxy ketones (BHK) are shown in Fig 1 (a)-(d). At their terminal positions, the scheduled ligands differ from each other. The formula (a) is shown as BHK-Me, the formula (b) is shown as BHK-Et, the formula (c) is shown as BHK-Bu, and the formula (d) is shown as BHK-Ph, where BHK is CF3-C(OH)=CH-C(=O)-CH2-, Me is–CH3 , Et is $–CH_2CH_3$, Bu is  and Ph is C6H5CH2- group.
The ligands from benzotriazole (BTAZ) derivatives are shown in Fig1 (e)-(h). The listed ligands differed by substituted alcohol and amino group. The formula (e) is abbreviated as BTAZ-Alk-OH, the formula (f) is abbreviated as BTAZ-Ph-OH, the formula (g) is abbreviated as BTAZ-Alk-NH_2, the formula (h) is abbreviated as BTAZ-Ph-NH_2 where Alk is –CH2-CH2- and Ph is -phenyl group.

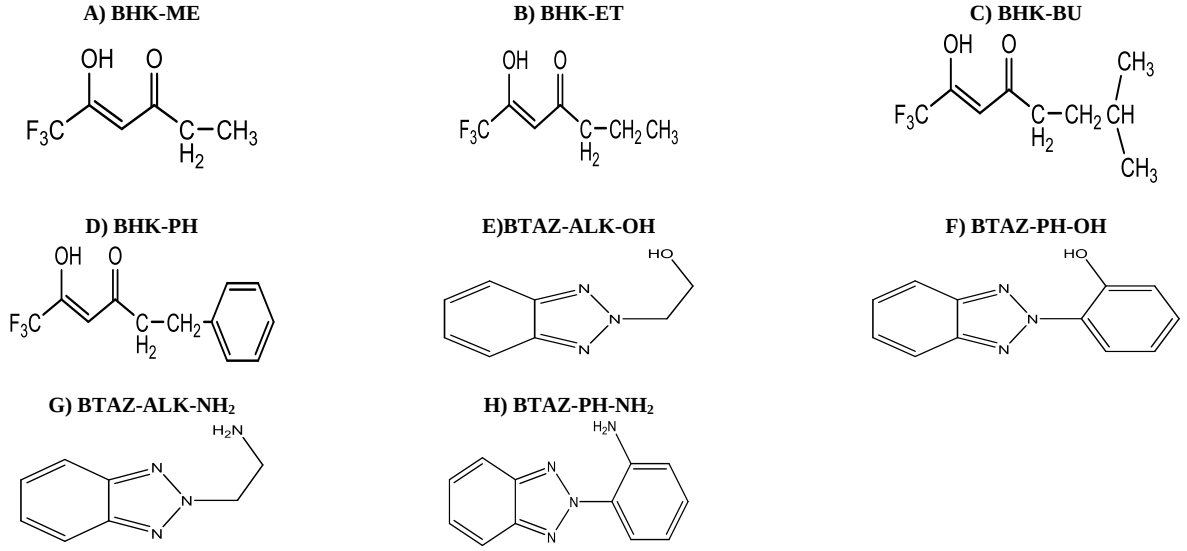


Fig. 1:. Beta-Hydroxy Ketone (BHK) Derivatives (A)-(D) and Benzotriazole(BTAZ) Derivatives (E)-(H).

The above ligands are synthesized and purified in our laboratory (unpublished data).
AR grade Cu (II), Ni (II), Co (II) and Zn (II) metal salts were used.Stock solutions of Cu (II), Ni (II), Co (II) and Zn (II)metal ions were prepared using double distilled water.The present investigation carried out by pH metric titration method. A digital pH meter with a combination electrode was used to determine the hydrogen ion concentration.

2.1. Calibration of PH meter

Two different buffer solutions pH4 and pH7 used for the calibration of pH meter.

2.2. Free ligand systems

The titrations were carried out in a double-wall reaction cell equipped with a magnetic stirrer. All these titration experiments were carried out using 0.1, 0.5 and 1M KNO_3 as a supporting electrolyte at three different ionic strengths in50:50 water: dioxane solvent system at 25^0C temperature. The ligand and metal ion concentrations were ($1x10^{-3}$M) maintained at moderately low concentrations.
To eliminate the effect of atmospheric CO_2 on titration a stream of N_2 gas passed over the solution. The efficiency of the thermostat was accurate to $\pm 0.1^0$C.The calibration was done before and after each experiment to avoid any errors that may arise from the faulty electrode system.

2.3. Binary systems

The experiment comprised of pH metric titration of ligands in an equimolar stoichiometric ratios using standard NaOH solution in the presence of metal ions likeCu (II), Ni (II), Zn (II) and Co (II).

2.4. Ternary systems

The experiments in this setup were done using ligands derived from individual beta-hydroxy ketone (BHK), ligands from benzotriozole derivatives (BTAZ) and metal ions in a 1:1:1 ratio. The other experimental conditions maintained for binary and ternary systems were similar to those described for free ligand systems.

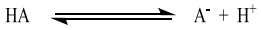
2.5. Calculations

Computer programme PKAS [10] used for the calculation of ionization constants of BHK and BTAZ ligands. Computer programme BEST used for the calculation of stability/ formation constants. The calculation of ionization constants of various ligands were achieved using the computer program PKAS. Entire pH range from the titration data has been given for the calculation of pKa values using the computer program. All the formation or stability constants were subjected to refinement using the computer program BEST [10].

3. Results and discussion

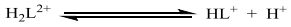
3.1. Dissociation constants of ligands

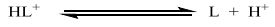
i) Beta-hydroxy ketone (BHK) derivatives:



Where HA is BHK ligand, A^- is dissociated BHK ligand and H^+ is proton

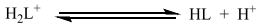
ii) Benzotriazole (BTAZ) derivatives containing amino group on the side chain





Where H_2L^{2+} is di-protonated BTAZ ligand, HL^+ is monoprotonated BTAZ ligand and L is fully deprotonated BTAZ ligand and H^+ is proton.

iii) Benzotriazole (BTAZ) derivatives having hydroxyl group on the side chain:





Where H_2L^+ is mono-protonated BTAZ ligand, HL is BTAZ ligand and L^- is dissociated BTAZ ligand and H^+ is proton.

3.2. Effect of ionic strength on the stabilities of metal ligand complexes

Another way to tune the properties of metal-ligand complexes is ionic strength of the medium. It is important to investigate the effect of ionic strength on the metal-ligand complexes under investigation.Specifically, these studies reveal the facts about the intramolecular interactions in the mixed ligand complexes and how these interactions change dynamically with the tunable conditions, such as various concentrations of ionic strength [11-13].

The dissociation constants for the ligands at various ionic strengths are shown in Tables 1 and Table 2. The pK_a values decrease with increase in the ionic strength in solution.In this case dissociated products have higher charge than the reactants.In general the charged particles are get stabilized by higher ionic strength in solution, and therefore, decrease in pK_a values are expected upon increase in the ionic strength.

The complete data which is presented in this paper collected by pH metric titration method at fixed 25^0C temperature, in the presence of mixed solvent (water50%+dioxane50%) system atdifferent ionic strengths i.e. 0.1, 0.5 and 1.0 mol dm^{-3} (KNO_3).

Table 1: Beta-Hydroxy Ketone (BHK) Derivatives Ionization Constants (Pk_a) Values in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ligand	Ionic Strengths	pK_a	pK_{2a}
	0.1M	9.88	----
BHK-Me	0.5M	9.35	----
	1.0M	9.13	----
	0.1M	9.99	----
BHK-Et	0.5M	9.44	----
	1.0M	9.22	----
	0.1M	10.16	----
BHK-Bu	0.5M	9.65	----
	1.0M	9.46	----
	0.1M	10.36	----
BHK-Ph	0.5M	9.85	----
	1.0M	9.64	----

Table 2: Ionization Constants (Pk_a) of Benzotriazole(BTAZ) Derivatives in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ligand	Ionic Strengths	pK_a	pK_{2a}
	0.1M	6.55	9.82
BTAZ-Alk-OH	0.5M	6.04	9.32
	1.0M	5.85	9.03
	0.1M	6.74	10.22
BTAZ-Ph-OH	0.5M	6.25	9.71
	1.0M	6.06	9.52
	0.1M	6.51	9.22
BTAZ-Alk-NH_2	0.5M	6.01	8.71
	1.0M	5.83	8.53
	0.1M	6.72	9.33
BTAZ-Ph-NH_2	0.5M	6.21	8.82
	1.0M	6.03	8.64

3.3. Stabilities of binary complexes

The stability constants for the binary systems (1:1) in various ionic strengths are listed in Tables 3 and 4. It appears that the stability constants for the binary systems of BHK derivatives decrease with increase in the ionic strength of the system, See Table 3.This is expected because total charge decreases from reactants to the products.In this case, the reactant viz., BHK has two negative charges, when it gets dissociated in solution and whereas the total charge of the product, viz., metal-ligand complex is zero.
BTAZ has two types of donor atoms, viz., N-O and N-N donor atoms which participate in the complex formation with the metal ions.
Due to no overall change in the charge from the reactants to the product the stabilities of metal-ligand complexes for theBTAZ with N-O and N-N donors atoms, increased by increasing the ionic strength from 0.1 M to 1 M KNO_3. These stability constants are listed in Tables 4.

Table 3: Stability Constants (Log K) for the Interaction of Metal Ions with Beta-Hydroxy Ketone (BHK) Derivatives in 1:1 Ratio in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ligand	Ionic strengths	Cu(II)	Ni(II)	Zn(II)	Co(II)
	0.1M	6.62	4.45	3.62	3.56
BHK-Me	0.5M	6.52	4.35	3.52	3.46
	1.0M	6.45	4.25	3.51	3.36
	0.1M	6.33	4.24	3.33	3.25
BHK-Et	0.5M	6.23	4.05	3.19	2.93
	1.0M	6.16	4.04	3.14	2.85
	0.1M	6.03	3.92	3.13	2.89
BHK-Bu	0.5M	5.93	3.82	3.03	2.79
	1.0M	5.83	3.65	2.93	2.62
	0.1M	6.01	3.81	3.12	2.92
BHK-Ph	0.5M	5.91	3.71	3.02	2.82
	1.0M	5.85	3.68	2.95	2.75

Table 4: Stability Constants (Log K) for the Interaction of Metal Ions with Benzotriazole(BTAZ) Derivatives in 1:1 Ratio in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ligand	Ionic strengths	Cu(II)	Ni(II)	Zn(II)	Co(II)
	0.1M	8.71	5.98	6.28	5.83
BTAZ-Alk-OH	0.5M	8.81	6.08	6.38	5.93
	1.0M	8.85	6.11	6.42	5.99
	0.1M	8.65	5.78	6.01	5.63
BTAZ-Ph-OH	0.5M	8.75	5.88	6.11	5.73
	1.0M	8.82	5.93	6.15	5.79
	0.1M	8.92	6.19	6.47	6.03
BTAZ-Alk-NH_2	0.5M	9.02	6.29	6.57	6.13
	1.0M	9.12	6.3	6.67	6.16
	0.1M	8.68	5.98	6.28	5.93
BTAZ-Ph-NH_2	0.5M	8.78	6.08	6.38	6.03
	1.0M	8.88	6.14	6.48	6.13

3.4. Stabilities of ternary complexes

The stability constants for the ternary systems (1:1:1) in various Ionic strengths are listed in Tables 5, 6, 7 and 8.There are two types of ternary complexes based on the donor atoms on BTAZ derivatives.The first one is BTAZ with N-O donor atoms and the second one is BTAZ with N-N donor atoms in the formation of ternary complexes with BHK derivatives in the presence of metal ions.
In the first type, where BTAZ with N-O donor atoms participate in the ternary complex formation with BHK derivatives in the presence of metal ions, the stabilities increased with increase in the ionic strength. This is because there is no change in the overall charge from the reactants to the product.Typically, if there is no change in the charge from reactants to products, the complex formation results in the higher stabilities with the increase in ionic strength.The stability data is listed in the Tables 5-8.
In the second type, where BTAZ with N-N donor atoms coordinate with the metal ion in the formation of ternary complexes with BHK derivatives, the stabilities decreased with increase in the ionic strength.In this case, the total charge from the reactants to product decreased, and therefore the stabilities decreased upon increase in the ionic strength.The stability constants data listed in the Tables 5-8.

Table 5: Stability Constants (Log K) for the Interaction of Metal Ions with BHK-Me and BTAZ Derivatives in (1:1:1) Ratio in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ternary Complex	Ionic strengths	Metal ion			
		Cu(II)	Ni(II)	Zn(II)	Co(II)
	0.1M	14.98	9.82	9.52	8.68
(BHK-Me)-(Metal ion)- (BTAZ-Alk-OH)	0.5M	15.03	9.87	9.57	8.73
	1.0M	15.08	9.92	9.62	8.78
	0.1M	14.91	9.72	9.42	8.67
(BHK-Me)-(Metal ion)- (BTAZ-Ph-OH)	0.5M	14.96	9.77	9.47	8.71
	1.0M	15.01	9.82	9.52	8.76
	0.1M	15.13	9.99	9.72	8.78
(BHK-Me)-(Metal ion)- (BTAZ-Alk-NH_2)	0.5M	15.03	9.89	9.62	8.68
	1.0M	14.93	9.79	9.52	8.58
	0.1M	15.01	9.89	9.61	8.71
(BHK-Me)-(Metal ion)- (BTAZ-Ph-NH_2)	0.5M	14.91	9.79	9.51	8.61
	1.0M	14.81	9.69	9.41	8.51

Table 6: Stability Constants (Log K) for the Interaction of Metal Ions with BHK-Et and BTAZ Derivatives in (1:1:1) Ratio in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ternary Complex	Ionic strengths	Metal ion			
		Cu(II)	Ni(II)	Zn(II)	Co(II)
	0.1M	14.82	9.71	9.38	8.38
(BHK-Et)-(Metal ion)- (BTAZ-Alk-OH)	0.5M	14.97	9.92	9.45	8.69
	1.0M	15.01	9.98	9.48	8.75
	0.1M	14.72	9.62	9.22	8.29
(BHK-Et)-(Metal ion)- (BTAZ-Ph-OH)	0.5M	14.91	9.83	9.21	8.56
	1.0M	14.94	9.88	9.42	8.59
	0.1M	14.92	9.93	9.52	8.62
(BHK-Et)-(Metal ion)- (BTAZ-Alk-NH_2)	0.5M	14.82	9.83	9.42	8.52
	1.0M	14.72	9.73	9.32	8.42
	0.1M	14.79	9.82	9.42	8.52
(BHK-Et)-(Metal ion)- (BTAZ-Ph-NH_2)	0.5M	14.69	9.72	9.32	8.42
	1.0M	14.59	9.62	9.22	8.32

Table 7: Stability Constants (Log K) for the Interaction of Metal Ions with BHK-Bu and BTAZ Derivatives in (1:1:1) Ratio in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ternary Complex	Ionic strengths	Metal ion			
		Cu(II)	Ni(II)	Zn(II)	Co(II)
	0.1M	14.91	9.88	9.52	8.75
(BHK-Bu)-(Metal ion)- (BTAZ-Alk-OH)	0.5M	14.96	9.96	9.57	8.8
	1.0M	15.19	9.99	9.62	8.85
	0.1M	14.83	9.74	9.28	8.55
(BHK-Bu)-(Metal ion)- (BTAZ-Ph-OH)	0.5M	14.88	9.79	9.33	8.65
	1.0M	14.93	9.81	9.38	8.7
	0.1M	15.29	10.22	9.82	9.04
(BHK-Bu)-(Metal ion)- (BTAZ-Alk-NH_2)	0.5M	15.19	10.12	9.72	8.94
	1.0M	15.09	10.02	9.62	8.84
	0.1M	15.04	10.02	9.62	8.93
(BHK-Bu)-(Metal ion)- (BTAZ-Ph-NH_2)	0.5M	14.94	9.92	9.52	8.83
	1.0M	14.84	9.84	9.42	8.78

Table 8: Stability Constants (Log K) for the Interaction of Metal Ions with BHK-Ph and BTAZ Derivatives in (1:1:1) Ratio in Various Ionic Strengths Mol Dm^{-3} (KNO_3)

Ternary Complex	Ionic strengths	Metal ion			
		Cu(II)	Ni(II)	Zn(II)	Co(II)
	0.1M	15.39	9.92	9.79	8.88
(BHK-Ph)-(Metal ion)- (BTAZ-Alk-OH)	0.5M	15.44	9.97	9.84	8.93
	1.0M	15.49	10.02	9.89	8.98
	0.1M	15.34	9.75	9.54	8.71
(BHK-Ph)-(Metal ion)- (BTAZ-Ph-OH)	0.5M	15.39	9.8	9.59	8.76
	1.0M	15.44	9.85	9.64	8.81
	0.1M	15.74	10.26	10.14	9.24
(BHK-Ph)-(Metal ion)- (BTAZ-Alk-NH_2)	0.5M	15.64	10.16	10.04	9.14
	1.0M	15.54	10.1	9.94	9.08
	0.1M	15.51	10.04	9.92	9.12
(BHK-Ph)-(Metal ion)- (BTAZ-Ph-NH_2)	0.5M	15.41	9.94	9.82	9.02
	1.0M	15.31	9.90	9.72	8.98

3.5. Quantification of the stabilities of ternary complexes

The stabilization or destabilization in the formation of ternary complex by various ionic strengths are quantified in terms of Δ log K values and are listed in Tables 9, 10, 11 and 12.

Table 9: In Terms of Δlogk Values Quantification of Stabilities of (BHK-Me)-Metal (II)-BTAZ (1:1:1) Ternary Complexes at Various Ionic Strengths

Ternary Complex	Metal ion			
	Cu(II)	Ni(II)	Zn(II)	Co(II)
In 0.1 mol dm^{-3} (KNO_3)				
(BHK-Me)-(Metalion)- (BTAZ-Alk-OH)	-0.35	-0.61	-0.38	-0.71
(BHK-Me)-(Metalion)- (BTAZ-Ph-OH)	-0.36	-0.51	-0.21	-0.52
(BHK-Me)-(Metalion)- (BTAZ-Alk-NH_2)	-0.41	-0.65	-0.37	-0.81
(BHK-Me)-(Metalion)- (BTAZ-Ph-NH_2)	-0.29	-0.54	-0.29	-0.78
In 0.5 mol dm^{-3} (KNO_3)				
(BHK-Me)-(Metalion)- (BTAZ-Alk-OH)	-0.15	-0.29	-0.13	-0.41
(BHK-Me)-(Metalion)- (BTAZ-Ph-OH)	-0.16	-0.30	-0.01	-0.33
(BHK-Me)-(Metalion)- (BTAZ-Alk-NH_2)	-0.51	-0.75	-0.47	-0.91
(BHK-Me)-(Metalion)- (BTAZ-Ph-NH_2)	-0.39	-0.64	-0.39	-0.88
In 1.0 mol dm^{-3} (KNO_3)				
(BHK-Me)-(Metalion)- (BTAZ-Alk-OH)	-0.13	-0.04	-0.04	-0.16
(BHK-Me)-(Metalion)- (BTAZ-Ph-OH)	-0.04	-0.11	-0.13	-0.13
(BHK-Me)-(Metalion)- (BTAZ-Alk-NH_2)	-0.64	-0.76	-0.68	-0.94
(BHK-Me)-(Metalion)- (BTAZ-Ph-NH_2)	-0.52	-0.7	-0.6	-0.98

Table 10: In Terms of Δlogk Values Quantification of Stabilities of (BHK-Et)-Metal (II)-BTAZ (1:1:1) Ternary Complexes at Various Ionic Strengths

Ternary Complex	Metal ion			
	Cu(II)	Ni(II)	Zn(II)	Co(II)
In 0.1 mol dm^{-3} (KNO_3)				
(BHK-Et)-(Metalion)- (BTAZ-Alk-OH)	-0.22	-0.51	-0.23	-0.7
(BHK-Et)-(Metalion)- (BTAZ-Ph-OH)	-0.26	-0.40	-0.12	-0.59
(BHK-Et)-(Metalion)- (BTAZ-Alk-NH_2)	-0.33	-0.5	-0.28	-0.66
(BHK-Et)-(Metalion)- (BTAZ-Ph-NH_2)	-0.22	-0.4	-0.19	-0.66
In 0.5 mol dm^{-3} (KNO_3)				
(BHK-Et)-(Metalion)- (BTAZ-Alk-OH)	0.08	0.06	0.07	0.08
(BHK-Et)-(Metalion)- (BTAZ-Ph-OH)	0.08	0.06	0.06	0.05
(BHK-Et)-(Metalion)- (BTAZ-Alk-NH_2)	-0.43	-0.6	-0.38	-0.76
(BHK-Et)-(Metalion)- (BTAZ-Ph-NH_2)	-0.32	-0.5	-0.29	-0.76
In 1.0 mol dm^{-3} (KNO_3)				
(BHK-Et)-(Metalion)- (BTAZ-Alk-OH)	0.09	0.06	0.09	0.05
(BHK-Et)-(Metalion)- (BTAZ-Ph-OH)	0.08	0.06	0.06	0.05
(BHK-Et)-(Metalion)- (BTAZ-Alk-NH_2)	-0.56	-0.61	-0.59	-0.79
(BHK-Et)-(Metalion)- (BTAZ-Ph-NH_2)	-0.45	-0.56	-0.5	-0.86

Table 11: In Terms of Δlogk Values Quantification of Stabilities of (BHK-Bu))-Metal (II)-BTAZ (1:1:1) Ternary Complexes at Various Ionic Strengths

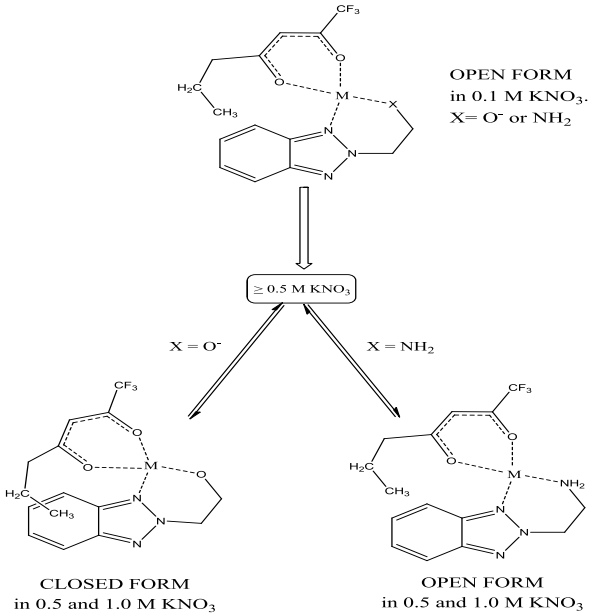
Ternary Complex	Metal ion			
	Cu(II)	Ni(II)	Zn(II)	Co(II)
In 0.1 mol dm^{-3} (KNO_3)				
(BHK-Bu)-(Metalion)- (BTAZ-Alk-OH)	0.17	0.02	0.11	0.03
(BHK-Bu)-(Metalion)- (BTAZ-Ph-OH)	0.15	0.04	0.14	0.03
(BHK-Bu)-(Metalion)- (BTAZ-Alk-NH_2)	0.34	0.11	0.22	0.12
(BHK-Bu)-(Metalion)- (BTAZ-Ph-NH_2)	0.33	0.12	0.21	0.11
In 0.5 mol dm^{-3} (KNO_3)				
(BHK-Bu)-(Metalion)- (BTAZ-Alk-OH)	0.37	0.33	0.35	0.33
(BHK-Bu)-(Metalion)- (BTAZ-Ph-OH)	0.35	0.25	0.34	0.28
(BHK-Bu)-(Metalion)- (BTAZ-Alk-NH_2)	0.24	0.07	0.12	0.06
(BHK-Bu)-(Metalion)- (BTAZ-Ph-NH_2)	0.23	0.05	0.11	0.03
In 1.0 mol dm^{-3} (KNO_3)				
(BHK-Bu)-(Metalion)- (BTAZ-Alk-OH)	0.6	0.53	0.54	0.55
(BHK-Bu)-(Metalion)- (BTAZ-Ph-OH)	0.5	0.48	0.38	0.49
(BHK-Bu)-(Metalion)- (BTAZ-Alk-NH_2)	0.14	0.01	0.02	0.02
(BHK-Bu)-(Metalion)- (BTAZ-Ph-NH_2)	0.13	0.02	0.01	0.01

Table 12: In Terms of Δlogk Values Quantification of Stabilities of (BHK-Ph))-Metal (II)-BTAZ (1:1:1) Ternary Complexes at Various Ionic Strengths

Ternary Complex	Metal ion			
	Cu(II)	Ni(II)	Zn(II)	Co(II)
In 0.1 mol dm^{-3} (KNO_3)				
(BHK-Ph)-(Metalion)- (BTAZ-Alk-OH)	0.67	0.13	0.39	0.13
(BHK-Ph)-(Metalion)- (BTAZ-Ph-OH)	0.68	0.16	0.41	0.16
(BHK-Ph)-(Metalion)- (BTAZ-Alk-NH_2)	0.81	0.26	0.55	0.29
(BHK-Ph)-(Metalion)- (BTAZ-Ph-NH_2)	0.82	0.25	0.52	0.27
In 0.5 mol dm^{-3} (KNO_3)				
(BHK-Ph)-(Metalion)- (BTAZ-Alk-OH)	0.82	0.45	0.63	0.43
(BHK-Ph)-(Metalion)- (BTAZ-Ph-OH)	0.84	0.37	0.61	0.36
(BHK-Ph)-(Metalion)- (BTAZ-Alk-NH_2)	0.71	0.16	0.45	0.19
(BHK-Ph)-(Metalion)- (BTAZ-Ph-NH_2)	0.72	0.15	0.42	0.17
In 1.0 mol dm^{-3} (KNO_3)				
(BHK-Ph)-(Metalion)- (BTAZ-Alk-OH)	0.87	0.53	0.66	0.5
(BHK-Ph)-(Metalion)- (BTAZ-Ph-OH)	0.88	0.39	0.65	0.38
(BHK-Ph)-(Metalion)- (BTAZ-Alk-NH_2)	0.41	0.09	0.15	0.02
(BHK-Ph)-(Metalion)- (BTAZ-Ph-NH_2)	0.42	0.08	0.12	0.02

The ΔlogK values are negative for the interaction of BHK-Me with BTAZ derivatives in the presence of metal ion. It appears that increase in ionic strength from 0.1 M to 1 M KNO_3 slightly lower the negative Δ log K values. The Δ log K values, for the interaction of BHK-Et with BTAZ derivatives in the presence of metal ion, showed different trend from that of BHK-Me. The Δ log K values are negative for the ternary complexes of BHK-Et at 0.1 M KNO_3 with both BTAZ with N-O and N-N donor atoms, but Δ log K values are positive at 0.5 M and does not change when ionic strength is increased to 1 M KNO_3 for BTAZ with N-O donor atoms. However, Δ log K values are negative for the ternary complexes when BTAZ with N-N donor atoms participate in the coordination at all ionic strengths used in this investigation. The positive Δ log K values for the interaction of BHK-Et with BTAZ having N-O donor atom ligands in the presence of metal ions suggests possibility of ligand-ligand interactions in the ternary complex. One possibility is that the ethyl group side from BHK may interact with the aromatic moiety of BTAZ derivative. This intramolecular interaction may contributes extra stability for the ternary complex and which results in the positive Δ log K values for the BHK-Et ternary complexes with BTAZ having N-O donor atoms.

The above mentioned intramolecular interactions, which are dependent on ionic strength, can be summarized with the following reaction schemes:



It is clear from the above reaction scheme that these intramolecular interactions are sensitive to change in the ionic strength.The open form for the complex (BHK-Et)-M-(BTAZ-NH_2) can be explained based on the destabilization factors in the formation of ternary complex.There are two destabilization factors, viz., (i) the net charge is decreased in the ternary complex and (ii) the net charge is also decreased in the binary complex of BHK-Et with metal ions.In case of closed form, there is no change in the net charge in the formation of ternary complex, which dominates and favors the formation ternary complex and also facilitates the intramolecular interactions, which result in the CLOSED FORM.

The above equilibrium can be quantified in terms of K_I and percentage of stacking.

$K_I = (10^{\Delta \log K}) - 1$

% of (Ternary Complex) stacking = (KI/(1+KI))*100

The K_I is intra-molecular equilibrium constant, which is a dimensionless constant [14-15]. The quantified data for the above equilibrium is listed in the Table 13.

Table 13: In Terms of Intra-Molecular Equilibrium Constant (K_I) and Percentage of Stacking¥ Quantification of Ligand-Ligand Interactions in (BHK-Et)-Metal (II)-BTAZ (1:1:1) Ternary Complexes

Ternary Complex	K_I and % of Stacking	Metal ion			
		Cu(II)	Ni(II)	Zn(II)	Co(II)
In 0.5 M KNO_3					
(BHK-Et)-(Metalion)- (BTAZ-Alk-OH)	K_I	0.20	0.15	0.17	0.15
	% of Stacking	16.67	13.04	14.89	13.04
(BHK-Et)-(Metalion)- (BTAZ-Ph-OH)	K_I	0.20	0.15	0.15	0.12
	% of Stacking	16.67	13.04	13.04	10.71
In 1 M KNO_3					
(BHK-Et)-(Metalion)- (BTAZ-Alk- OH)	K_I	0.23	0.15	0.23	0.12
	% of Stacking	18.70	13.04	18.70	10.71
(BHK-Et)-(Metalion)- (BTAZ-Ph-OH)	K_I	0.20	0.15	0.15	0.12
	% of Stacking	16.67	13.04	13.04	10.71

KI ± 0.05, % of stacking ±2

¥overlap between the ethyl side chain of BHK over the heterocyclic ring of benzotriazole.

According to the data from Table 13, the intra-molecular equilibrium constant is high for copper and zinc complexes compared to other metal ternary complexes. The percentage of stacking is also high for copper and zinc complexes, and about the same for nickel and cobalt complexes.It appears that increase in the ionic strength from 0.5 to 1 M does not effect on the overall KI and percentage of ligand-ligand interactions.

The Δ log K values for the ternary systems, viz., for the interaction of BHK-Bu with BTAZ derivatives in the presence of metal ions, are listed in Table 11 and showed positive at all the ionic strengths.The Δ log K values increased with increase in the ionic strength from 0.1 to 0.5 M KNO_3, and remains same or slightlyincreased by increasing the ionic strength from 0.5 M to 1 M KNO_3 for the BTAZ with N-O donor atoms. This can be explained based on the fact that there is no change in the net charge in the formation of ternary complex, so increase in the ionic strength increases the stabilities and intramolecular interactions, which result in the increase in the Δ log K values.In the ternary complexes with BTAZ having N-N donor atoms, the Δ log K values decreased with increase in the ionic strength.This can be explained based on the fact that the net charge decreased in the formation of ternary complex, so increase in the ionic strength decreases the stabilities and then intramolecular interactions, which result in the decrease in the Δ log K values.

Similar pattern is noticed for the Δ log K values for the ternary systems of BHK-Ph with BTAZ derivatives in the presence of metal ions, see Table 12 Same reasoning can be applied to explain the different trends in the Δ log K values towards BTAZ with N-O or N-N donor atoms.

The further analysis of ionic strength effect on the side chain on BHK ligand towards the aromatic moieties of BTAZ ligand has been explored.It appears that Δ log K values for both BTAZ having either –Alk-OH or –Ph-OH systems are about the same. That means ethyl

or butyl or phenyl side chain of BHK ligand is overlapping with the heterocyclic ring, but not the phenyl ring of the BTAZ ligand.This also suggests that there is no effect of ionic strength on the side chain of BHK towards the aromatic moieties of BTAZ ligand, in other words increase in the ionic strength does not change the interaction of side chain of BHK towards the heterocyclic ring of BTAZ.
In a further analysis of the above data, the intra-molecular equilibrium constants (K_I) and percentage of stacking interactions, if present, have been explored.Both K_I and percentage of stacking interactions increased upon increase in the ionic strength for the ternary systems, in which BTAZ having N-O donor atoms.However, reverse trend is noticed in the ternary systems, in which BTAZ having N-N donor atoms.
According to the data from the tables, the stability constants decrease in the order Zn < Cu > Ni > Co,which is the natural order of stability.

4. Conclusion

Stabilities of 1:1:1 ligand-metal-ligand complexes in different ionic strengths investigated. From this investigation it is found that Copper(Cu) forms more stable complexes with BTAZ and BHK ligands. Cobalt (Co) forms more unstable complex than other three metal complexes. The stabilities of these 1:1:1 ligand-metal-ligand complexes are measured in terms of ΔlogK values, percentage of stacking and intra molecular equilibrium constants. The positive ΔlogK values indicates thatside chains $–CH_2CH_3$, 2-methyl propyl and $C_6H_5CH_2$- of BHK ligands overlapping with the aromatic ring of the BTAZ ligands due to this reason (BHK-Alkyl)/ (BHK-Benzyl)-Metal(II)-(BTAZ) showed extra stabilities.
The ΔlogK values for both (BHK-Alkyl)/(BHK-Benzyl)-Metal(II)-(BTAZ-Alkyl-OH) and (BHK-Alkyl)/(BHK-Benzyl)-Metal(II)-(BTAZ-Phenyl-OH) are similar. This indicates the side chain/aromatic ring of BHK is overlapping with the triazole ring, but not with the phenyl side chain/aromatic ring of the BTAZ ligand.
From this investigation it is found that due to intramolecular interaction of 1:1:1 ligand-metal-ligand complexes attained more stabilities. The results of present investigation are useful to develop more stable metal-complexes which have varies applications in chemical field.

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