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Studies in Formation Constant of transition metal ions with Peptides, pH-metrically, spectrophotometrically and polarizability constant by Refractometry

G.B. Pethe[1], S.M. Maskey[2], N.D. Vilayatkar[3], U.P. Meshram[1]*
[1]Department of Chemistry, N.K.S Model College, Karanja (Ghadge), Dist. Wardha
[2]Yashwantrao Chawhan Art, Commerce and Science College, Lakhandur-441803, India
[3]S.S. Jaiswal College, Arjuni/Morgoan 441701, India
E-mail: gaurav.pethe@gmail.com

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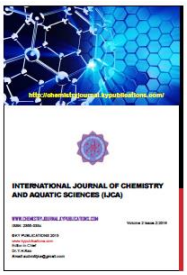

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ABSTRACT

The Spectrophotometric study of Cr(II), Fe(II). Al(II) and Zn(II) complexes with Carnosine (L_1), Glutathione (L_2), DL-phenylamine (L_3) and Pentaglycine (L_4) showed 1:1 and 1:2 complex formation between the pH range of 3.0 to 6.0 studied by Job's variation method at 0.1M ionic strength and 30°C 11°C spectrophotometrically. The conditional stability constants are determined for 1:1 complexes at about pH 3.0 and molar refraction and polarizability constant for L_1. L_2, L_3 & L_4 at different percentages of dioxane are calculated. The molar refraction and polarizability constant in different percentages of dioxane-water mixture are studied.

Keywords: Carnosine, Glutathione, DL-phenylamine, Pentaglycine, 1,4-Dioxane solvent, Spectrophotometer, Refractometry.

Introduction

Dipeptide like Carnosine is a naturally occurring (*β*-alanine and L-histidine), widely distributed in muscular and nervous tissues of vertebrates in the medical field. [1-2]. In view of analytical applications as carnosine, glutathione, Dl-phenylamine and pentaglycine which act as a ligand and are selected in the present investigation. The stability of transition metal complexes in solution has been extensively investigated and number of crystal structure have been determined [3-6]. The optimized geometries of 1:1 complex of a-alamine with Gi" and Ni" have been confirmed[7]. The formation constants of La(III), Pm(III) and Nd(III) complexes with glycine are known Stabilities and of Uranly(II) & Thorium(IV) complexes of DL-nor-leucine have been studied. The complex formation of Uranyl(II) and Vanady(II) with DL-tryptophane have been studied employing potentiometric technique and overall changes in thermodynamic functions have been calculated [8]. Stabilities constants of Mg(II), Co(II), Al(III). Nd(11), UO_2(II). Th(IV) complexes such as Glycine, DL-Alanyl-DL-

Phenyl Alanic & DL-Alanyl Glycine have been studied[9]. The extensive work in coordination complexes has been made possible with the help of various experimental techniques and has led to a number of empirical conclusions [9-11]. The properties of liquid such as viscosity, refractive index and ultrasonic speed of binary mixtures are studied by many workers [9].

The study of conditional stability constant of Cr(II), Fe(II). Al(II) and Zn(II) with carnosine, glutathione, DL-phenylamine and pentaglycine is still lacking, therefore, the present work has been undertaken to study the complex formation and their confirmation by carried out using pH metry and spectrophotometric method and also study of molar refraction and polarizability constant in different percentages of dioxane-water mixture was carried out.

Experimental:

The peptide Carnosine, glutathione, DL-phenylamine and pentaglycine having many applications for living things, which are used as a ligand. The Nitrate salts of Cr(II), Fe(II). Al(II) and Zn(II) were used and their solutions were prepared in double distilled water (0.01 M). The solutions of potassium nitrate were prepared (0.1 M) and used for maintaining ionic strength constant. Systronic Spectrophotometer No. 108 was used for measuring absorption of solution. The solution of ligand L_1, L_2, L_3 and L_4 in different percentages of dioxane-water mixture were prepared by weight. The accuracy of density measurements was within 0.1% kgm. The refractive indices of solvent mixture and solutions were measured by Abbe's refractometer. The accuracy of Abbe's refractometer was within ±0.001 unit. The temperature of the prism box was maintained constant by circulating water from thermostat maintained at 30 (+0.1°C). Initially, the refractometer was calibrated with glass piece (n = 1.5220) provided with the instrument.

The molar refraction of solvent, dioxane-water mixtures are determined from -

$R_{D\text{-}W} = X_1R_1 + X_2R_2$

where, R_1 and R_2 are molar refraction of dioxane and water respectively.

The molar refraction represents actual or true volume of the substance molecules in 1 mole. The molar refraction of solutions of ligand in dioxane-water mixture is determined from -

$R_{Mixture} = [(n^2-1)/(n^2+2)] \{[X_1M_1 + X_2M_2 + X_3M_3]/d\}$

where, n is the refractive index of solution, X, is mole fraction of dioxane, X_2 is mole fraction of water, X, is mole fraction of solute, M_1, M_2 and M3 are molecular weights of dioxane, water and solute respectively. 'd' is the density of solution.

The molar refraction of ligand is calculated as -

$R_{Lig} = R_{Mixture} - R_{D\text{-}w}$

Results and Discussion:

pH-Metric method

The dependences of pH on volume of NaOH are investigated. The same dependences were received for other systems from Table 1. The pH-Metric work has been done with a limited aim to compare the formation constant value obtained spectrophotometrically. It could be seen from table 1 that there is good agreement of proton-ligand stability constant between half integral method and point wise calculation method the pk value for L_1 is found to be greater as compare to other ligand L_2, L_3 and L_4. The $logk_1$ and $logk_2$ value obtained are found to be good agreement with half integral method and pointwise calculation method that shown in table 1 for each system the pH value at which metal complex formation started and hydrolysis commenced have been tabulated and data are presented in table 2.

Spectrophotometric measurement by Jobs method

The spectrophotometric studies has been done with limited aim of comparing the results obtained by this techniques with those of pH-metric techniques pk and log k value are determined at 0.1M ionic strength which is maintained constant by addition of appropriate amount of 1M potassium nitrate solution (table 3). Equimolar solution of Cr(II), Fe(II). Al(II) and Zn(II) with L_1, L_2, L_3 and L_4 (1.00x10-2m) were mixed in different ratios to prepare jobs solution final volume of each solution made up to 10ml after adjusting the appropriate pH and maintaining constant ionic strength μ=0.1M. In addition to wavelength of maximum λmax same other wavelength were selected. The absorption for all the composition was recorded at a constant wavelength λmax the data of absorption and percentage composition of metal ion and ligand solution at constant pH can be used and curves were constructed. It is observed that 1:1 complex formation curves occurs in pH range 4 to5 and 1:2 complex formation in the range of 3 to 6 each solution is diluted up to 15 ml and recorded absorption at same max conditional stability constant of metal-ligand complexes were calculated for all the system using following equation.

$$K = \frac{x}{(a_1 - x)(b_1 - x)(a_2 - x)(b_2 - x)}$$

Where:

- x is the amount of complex formed,
- a_1 and b_1 are the initial concentrations of the metal and ligand in the 1:1 complex system,
- a_2 and b_2 are the initial concentrations of the metal and ligand in the 1:2 complex system.

Conditional stability constants are found to be smaller than real stability constant. The agreement between the values obtained by both techniques is fairly good (table 4).

Refractometry study:

The values of molar refractivity of solution, solvent, peptides L_1, L_2, L_3, L_4 and polarizability constant of peptides solution represented in Tables 5 to 6 shows that, with increase in percentage of DMSO, the molar refractivity (true molar volume) as well as the polarizability constant of peptides decreases or increases. This may be attributed to the fact that the dipole in peptides lies perpendicular to the longer axis of the molecule and with increase in percentage of DMSO causing decrease in dielectric constant of medium, considerable dipole association (inter molecular attraction) takes place which would be accompanied by decrease in polarizability as well as molar refractivity because of mutual compensation of the dipoles.

Table 1: Metal-Ligand Stability Constants by Different Methods

			Method	
S.No	System	Constants	Half Integral	Pointwise
1	Cr(II)-Ligand (L_1)	log K_1	2.1268	3.2364
		log K_2	3.2654	5.3648
2	Fe(II)-Ligand (L_1)	log K_1	2.1684	3.2556
		log K_2	2.6983	2.0365
3	Al(II)-Ligand (L_1)	log K_1	2.6598	2.6255
		log K_2	2.3657	3.2365
4	Zn(II)-Ligand (L_1)	log K_1	2.3657	2.6348
		log K_2	2.8865	2.3654
5	Cr(II)-Ligand (L_2)	log K_1	4.3652	4.2646
		log K_2	4.2873	4.04829
6	Fe(II)-Ligand (L_2)	log K_1	3.3265	3.2698

		log K_2	3.3658	3.6512
7	Al(II)-Ligand (L_2)	log K_1	3.23658	3.2654
		log K_2	5.14178	3.01328
8	Zn(II)-Ligand (L_2)	log K_1	4.2361	4.3651
		log K_2	4.3621	4.3265
9	Cr(II)-Ligand (L_3)	log K_1	3.2364	3.3648
		log K_2	4.2365	4.3265
10	Fe(II)-Ligand (L_3)	log K_1	4.3264	4.3658
		log K_2	4.9625	4.6984
11	Al(II)-Ligand (L_3)	log K_1	3.6513	3.6954
		log K_2	3.2691	3.6254
12	Zn(II)-Ligand (L_3)	log K_1	4.3215	4.3265
		log K_2	3.6651	3.2555
13	Cr(II)-Ligand (L_4)	log K_1	4.8894	4.8461
		log K_2	3.2486	6.2547
14	Fe(II)-Ligand (L_4)	log K_1	4.3264	4.6568
		log K_2	5.3655	3.5129
15	Al(II)-Ligand (L_4)	log K_1	3.3265	4.2157
		log K_2	4.3587	4.2137
16	Zn(II)-Ligand (L_4)	log K_1	3.2001	3.0215
		log K_2	3.2445	4.6988

Table 2: Commencement of the hydrolysis and complete formation

S.No	Metal Ion	pH at the commencement of the Hydrolysis	pH at the commencement of complete formation			
			L_1	L_2	L_3	L_4
1	Cr(II)	8.23	2.26	2.93	2.64	2.14
2	Fe(II).	8.97	2.67	2.45	2.82	2.73
3	Al(II)	8.67	2.94	2.84	2.34	2.51
4	Zn(II)	9.06	2.66	2.41	2.77	2.91

Table 3: Determination of conditional stability of metal-ligand complex by Jobs method

S.No	**System**	**Concentration complex (x) mole lit^{-1}**	**Conditional stability constant (K)**	**log K**
1	Cr(II) –L_3	3.3486	2.3648	0.2368
2	Fe(II) - L_3	2.3654	1.6542	0.1325
3	Al(II) –L_1	2.2648	2.3154	0.2541
4	Cr(II) –L_1	3.0358	2.3641	0.2158
5	Zn(II) –L_2	3.2547	1.0247	0.1542
6	Zn(II) –L_2	3.0152	1.9984	0.1548
7	Fe(II) –L_4	3.0157	2.5487	0.2143

Table: 4 Comparison of log K values between pH-metry and spectrophotometry techniques

S.N.	System	pH-metric log K	Spectrophotometric log K
1	Fe(II) – L_1	5.2164	4.3785
2	Al(II) –L_2	4.3125	4.2457
3	Cr(II) –L_1	3.9846	4.3548
4	Zn(II) –L_2	2.2364	3.2541
5	Cr(II) – L_4	3.2011	2.3698

Table 5: Molar Refraction and polarisability Constant for L_1, L_2 at Different Percentage of DMSO

S.N	% of DMSO	Ligand – L_1		Ligand – L_2	
		[R]cm^3 $mole^{-1}$	α x 10^{-23} $mole^{-1}$	[R]cm^3 $mole^{-1}$	α x 10^{-23} $mole^{-1}$
1	60	3.2687	0.2154	3.3648	0.2483
2	65	3.6489	0.1254	3.6548	0.2148
3	70	3.6712	0.1548	3.5587	0.1458
4	75	3.0214	0.1254	3.2448	0.1684
5	80	3.2487	0.0214	3.2649	0.2145
6	85	3.3548	0.2487	3.2948	0.1486
7	90	1.2365	0.2654	3.2588	0.1289
8	95	1.8461	0.2146	3.9964	0.2785

Table 6: Molar Refraction and Polarisability Constant for L_3, L_4 at Different Percentage of DMSO

S.No.	% of DMSO	Ligand – L_3		Ligand – L_4	
		[R]cm^3 $mole^{-1}$	α x 10^{-23} $mole^{-1}$	[R]cm^3 $mole^{-1}$	α x 10^{-23} $mole^{-1}$
1	60	3.2548	0.2148	3.6548	0.2474
2	65	3.6984	0.2481	3.2189	0.2178
3	70	3.2684	0.2854	3.2546	0.3541
4	75	3.3698	0.2548	3.9964	0.2584
5	80	3.2548	0.1694	3.9548	0.2158
6	85	3.9547	0.2487	3.2648	0.2456
7	90	3.6948	0.2166	3.2696	0.2673
8	95	3.3269	0.1238	3.6947	0.2196

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