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Calculation of stability constants of binary and ternary complexes of Zinc ion in DMSO-Water medium

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Abstract : *Calculatuon of the stability constants of binary and ternaty complexes of zinc ion with the ligands Bis-(pyridyl)benzilidene (BPB) (primary ligand); Glycine (Gly), L-Alanine (Ala) , L- Phenylalanine (Phe), L-Leucine (Leu) and L-Valine (Val) (secondary ligands) in DMSO-water medium. The stability of the complexes is discussed in terms of medium and the nature of the secondary ligands. The computer programme, SCOGS[5] (Stability Constants of Generalized Species) employs the conventional non-linear least square approach.*

Key Words: ***Z****inc ion, Bis-(pyridyl) benzilidene, Glycine, Alanine, Phenylalanine, Leucine, Valine, DMSO and SCOGS*

Introduction

Co-ordination compounds have always been a challenge to the inorganic chemists. Co-ordination chemistry pertains to the complexity of the compounds, which do not exist as individual, but as related groups often surrounding a metal ion in the center. The groups that are bound to the central metal ion in a symmetrically oriented fashion are called ligands. For instance, in the conversion of carbon dioxide and water into carbohydrate in the plants, a co-ordination compound called chlorophyll [Mg^{2+} complex][1, 2] plays an important role. A similar iron complex known as haemoglobin[3, 4] operates in the red blood cells as carrier of oxygen.

Stability constants

In solution, complex results from the reversible association of one or more metal ions and ligands. The chelate compound in which a metal is joined to two or more donor groups of a single molecule or ion are particularly important since they have exceptionally high stability and in many cases they possess remarkable properties.

Two kinds of stabilities are recognized for the complexes.

1. Thermodynamic stability

2. Kinetic stability

The metal ion, the ligands and the complexes are solvated to different extents in solution. However, the solution of the metal ion is of considerable importance; infact, complex formation in solution involves stepwise displacement of solvent molecules from the inner co-ordination sphere of the metal ion by the ligand groups:

$$M(solvent)_n + L \rightleftharpoons M(solvent)_{n-1}L + solvent$$

Evaluation of stability constants using the computer programme SCOGS[5]

The computer programme, SCOGS[5] (Stability Constants of Generalized Species) employs the conventional non-linear least square approach. The programme written in FORTRAN is capable of calculating simultaneously or individually the association constants for any of the species formed in systems containing upto two metals and two ligands, provided that the degree of complex formation is pH dependant. SCOGS may be used[6] to analyse appropriate pH titration data to yield acid association constants (pK^H values) of ligands and also of metal complexes, metal ion hydrolysis constants, stability constants of simple binary complexes (ML, ML_2 etc.), polynuclear species (M_2L_3, M_3L_4H, $M_2L_2(OH)_2$ etc.).

Scope of the work

From the literature survey no works have been made to study the stability of the mixed ligand metal complexes are determined by potentiometric method in DMSO-water medium. The stability of the complexes is discussed in terms of medium and the nature of the secondary ligand.

Experimental

E. Merck sample of sodium hydroxide was dissolved in double distilled water in a pyrex flask. The layer of carbondioxide on the sodium hydroxide pellets was washed away previously. The solution was standardized potentiometrically against a standard oxalic acid solution. The stock solution of nitric acid was prepared by diluting AR BDH sample to required concentration and this was titrated potentiometrically against standard alkali solution. Dimethyl sulphoxide (DMSO) was purified by standard method.[7] An AR, BDH sample of potassium nitrate (KNO_3) was dissolved in double distilled water to make the stock solution of strength 1 mol dm^{-3}.

Metal ion solution

Approximately 0.004224 mol dm^{-3} stock solution of zinc ion(II) and the metal solution was

standardized using reported procedure.[8]

Apparatus

A digital pH / mv meter, DPH-14 and accessories having a combined glass – calomel electrode assembly was employed in the present investigation. The calomel electrode (supplied with the instrument) was replenished with potassium chloride solution (AR, BDH). The pH meter was calibrated with buffer solution (0.05 mol dm^{-3} potassium hydrogen phthalate) before starting a titration and the calibration was checked again after completion of the titration.

Conditions of Studies

The experiments in the present investigation were performed in a thermostat bath at 30°C $\pm$ 0.1°C. The ionic strength of the mixture kept at 0.1 mol / dm^3 by adding required amount of potassium nitrate solution. The total initial volume of the mixture was made upto 30 mL.

Calibration of pH meter in DMSO – Water medium

A mixture of 56% (v/v) DMSO – water medium was used since the chelates formed are relatively insoluble in water. Therefore, it is necessary to calibrate the pH meter in DMSO – water medium[9]. To accomplish that the following concentrations of nitric acid in 56% (v/v) DMSO – water medium were prepared (total volume 30 mL) and the pH meter readings (B values) were measured in all cases (Table 1).

Table 1: Calculated and observed values of pH

Conc. Of $[H^+]$	Calculated pH	Observed pH
1.48×10^{-3}	2.83	3.07
2.884×10^{-3}	2.54	2.84
3.981×10^{-3}	2.40	2.69
5.370×10^{-3}	2.27	2.60
6.456×10^{-3}	2.19	2.53
7.586×10^{-3}	2.12	2.48

Intercept = - 0.81, r = 0.998

Experimental conditions

The following mixture is prepared for each system and titrated against standard alkali solution using Bjerrum Calvin pH titration technique.

a. 3 mL of nitric acid (0.0439 mol. dm^{-3}) + 3mL of potassium nitrate (1 mol dm^{-3}) + 3 mL of primary ligand (0.015 mol dm^{-3}) + 1.5 mL of secondary ligand (0.015 mol dm^{-3}) + 3mL of zinc (0.004224 mol dm^{-3}) + appropriate amount of DMSO and water.

Results and Discussion

Stability constants of binary and ternary complexes

When a metal ion is in equilibrium with two different ligands, here BPB (primary) and α - amino acids (secondary) which can form ternary complexes with metal ion, equilibria (1-5) forming simple non-protonated *bis* complexes will be represented in the following equations

$$Zn(BPB) + BPB \rightleftharpoons [Zn(BPB)_2] \quad (1)$$

$$Zn(BPB) + gly \rightleftharpoons [Zn(BPB)(gly)] \quad (2)$$

$$Zn(BPB)(gly) + gly \rightleftharpoons [Zn(BPB)(gly)_2] \quad (3)$$

$$Zn(gly) + BPB \rightleftharpoons [Zn(BPB)(gly)] \quad (4)$$

$$Zn(BPB)(gly) + gly \rightleftharpoons [Zn(BPB)(gly)_2] \quad (5)$$

Sigel[10] defined the two equilibrium constants involved in ternary complexes as

$$\Delta \log K = \log K^{Zn(BPB)}_{Zn(BPB)(Gly)_2} - \log K^{Zn}_{Zn(Gly)_2}$$

$$= \log K^{M(gly)}_{Zn(BPB)(Gly)_2} - \log K^{Zn}_{Zn(BPB)_2}$$

The pH metric titration data shown in table 2 and pH verses volume of NaOH curves are figures from 1 to 6

Table 2: pH titration data of BPB + Glycine, alanine, phenylalanine, leucine and valine with Zn^{2+} at 30 ± 0.1°C in DMSO - water (56% v/v)

Ionic Strength [I] = 0.1 mol dm^{-3} $[HNO_3]$ = 0.004390 mol dm^{-3}
[NaOH] = 0.1219 mol dm^{-3} [*gly*] = 0.0014919 mol dm^{-3}
[*ala*] = 0.0014928 mol dm^{-3} [*phe*] = 0.015013 mol dm^{-3}
[*leu*] = 0.001494 mol dm^{-3} [*val*] = 0.01494 mol dm^{-3}
[*BPB*] = 0.0015 mol dm^{-3} $[Zn^{2+}]$ = 0.0042224 mol dm^{-3}
Initial Volume = 30 mL

Volume of NaOH (mL)	pH (corrected)				
	gly	ala	phe	leu	val
0	3.56	3.55	3.26	3.26	3.63
0.02	3.6	3.57	3.28	3.27	3.64
0.04	3.63	3.57	3.3	3.28	3.66
0.06	3.68	3.61	3.33	3.29	3.68
0.08	3.7	3.63	3.35	3.32	3.69
0.1	3.74	3.65	3.38	3.33	3.71
0.12	3.77	3.67	3.4	3.36	3.74
0.14	3.79	3.69	3.42	3.39	3.78
0.16	3.81	3.72	3.45	3.42	3.82
0.18	3.84	3.75	3.48	3.45	3.85
0.2	3.86	3.78	3.51	3.48	3.87
0.22	3.89	3.81	3.53	3.51	3.9
0.24	3.92	3.84	3.58	3.54	3.94
0.26	3.95	3.87	3.62	3.56	3.97
0.28	3.98	3.9	3.66	3.61	4
0.3	4.01	3.93	3.71	3.67	4.03
0.32	4.04	3.96	3.74	3.71	4.07
0.34	4.07	3.99	3.8	3.75	4.11
0.36	4.11	4.04	3.86	3.79	4.15
0.38	4.14	4.08	3.95	3.83	4.18
0.4	4.17	4.11	4.02	3.88	4.21
0.42	4.22	4.15	4.04	3.92	4.25
0.46	4.28	4.19	4.08	3.96	4.29
0.48	4.35	4.23	4.1	4	4.34
0.5	4.42	4.28	4.1	4.05	4.38
0.52	4.47	4.37	4.11	4.1	4.42
0.54	4.53	4.37	4.15	4.15	4.47
0.56	4.58	4.42	4.19	4.2	4.52
0.58	4.63	4.46	4.24	4.25	4.57

0.6	4.68	4.51	4.3	4.3	4.62
0.62	4.74	4.56	4.36	4.35	4.67
0.64	4.8	4.62	4.42	4.4	4.72
0.66	4.86	4.67	4.48	4.44	4.78
0.68	4.92	4.73	4.56	4.49	4.84
0.7	4.99	4.81	4.58	4.55	4.89
0.72	5.05	4.87	4.63	4.61	4.96
0.74	5.11	4.92	4.7	4.67	5.01
0.76	5.17	4.97	4.76	4.74	5.07
0.77	5.20	4.99	4.79	4.78	5.1
0.78	5.24	5	4.82	4.82	5.14
0.8	5.32	5.1	4.88	4.89	5.21
0.82	5.4	5.2	4.97	4.98	5.28
0.84	5.48	5.27	5.05	5.04	5.34
0.86	5.56	5.34	5.11	5.1	5.4
0.88	5.62	5.41	5.17	5.17	5.46
0.9	5.69	5.48	5.24	5.27	5.53
0.92	5.77	5.57	5.35	5.33	5.62
0.94	5.86	5.65	5.46	5.44	5.69
0.96	5.94	5.73	5.6	5.54	5.78
0.98	6.02	5.81	5.72	5.64	5.87
1	6.1	5.88	5.86	5.82	5.96
1.02	6.18	6.02	6.05	6.33	6.06
1.04	6.26	6.21	6.44	6.77	6.18
1.06	6.34	6.32	6.84	7.8	6.3
1.08	6.44	6.44	7.86	8.74	6.46
1.1	6.52	6.57	8.22	9.08	6.56
1.12	6.64	6.67	8.45	9.31	6.67
1.14	6.68	6.77	8.78	9.44	6.76
1.16	6.76	6.87	8.88	9.57	6.85
1.18	6.84	6.96	9.07	9.7	6.92
1.2	6.92	7.14	9.19	9.94	7
1.22	6.99	7.24	9.27	10.2	7.09
1.24	7.07	7.32	9.35	10.6	7.2
1.26	7.15	7.4	9.43	11.3	7.3
1.28	7.26	7.47	9.51	12.6	7.36
1.3	7.34	7.53	9.6		7.42
1.32	7.42	7.61	10.06		7.48
1.34	7.52	7.65	10.49		7.56
1.36	7.63	7.69	10.58		7.65

1.38	7.74	7.73	10.63	7.71
1.4	7.8	7.79	10.76	7.76
1.42	7.87	7.81	10.81	7.81
1.44	7.9	7.83		7.83
1.46	7.94	7.84		7.86
1.48	7.96	7.85		7.88
1.5	7.98	7.86		7.9
1.52	7.99	7.88		7.92
1.54	8	7.99		7.94
1.56	8.01	7.9		7.96
1.58	8.02	7.91		7.97
1.6	8.02	7.92		7.98
1.7	8.09	7.93		7.98
1.8	8.18	7.95		7.99
1.52	7.99	7.97		8.01
1.54	8	7.98		8.03
1.56	8.01	7.99		8.05
1.58	8.02	8.01		8.06
1.6	8.02	8.02		
1.7	8.09	8.04		
1.8	8.18	8.05		

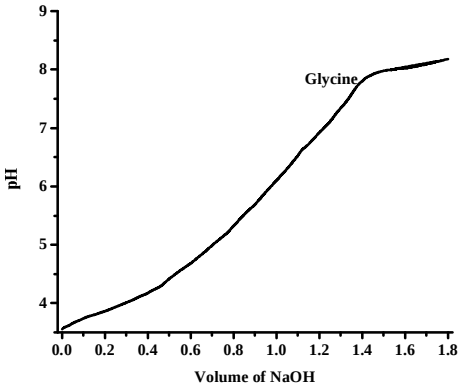

Figure 1: Curve of pH verses volume of NaOH for Glycine

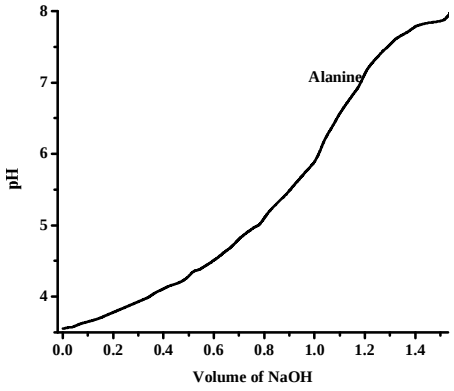

Figure 2: Curve of pH verses volume of NaOH for Alanine

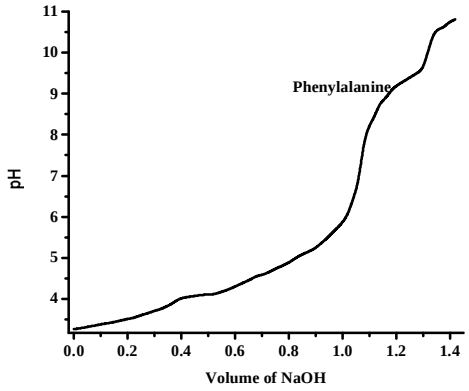

Figure 3: Curve of pH verses volume of NaOH for Phenylalanine

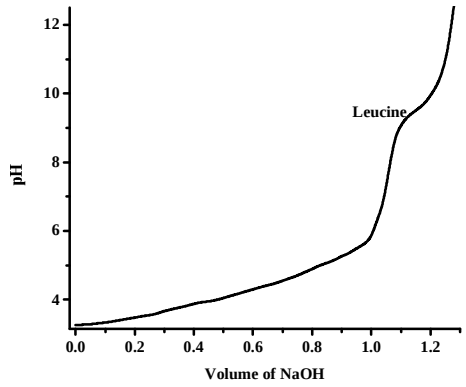

Figure 4: Curve of pH verses volume of NaOH for Leucine

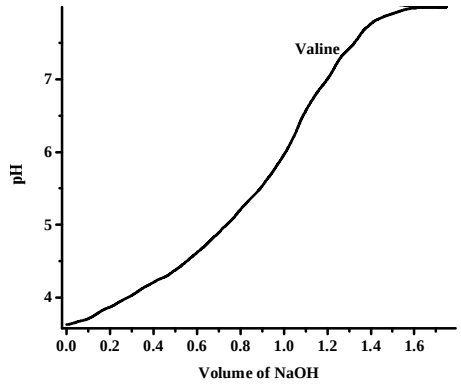

Figure 5: Curve of pH verses volume of NaOH for Valine

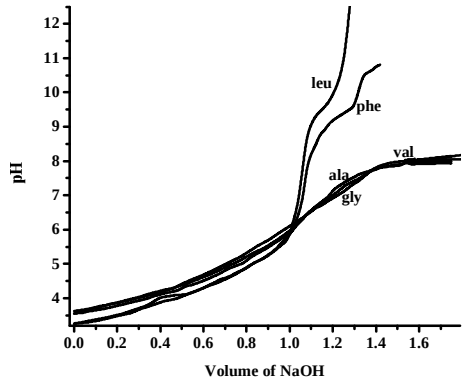

Figure 6: Curve of pH verses volume of NaOH for gly, ala, phe, lue and val

Protonation-ligand and metal-ligand stability constants of binary Zn(II) complexes in aqueous-DMSO medium are in table 3, protonation-ligand and stability constants of binary Zn(II) complexes in aqueous medium are in table

4 and stability constants of ternary complexes of Zn(II) complexes in DMSO-water medium are in table 5.

Table 3: Protonation-ligand and metal-ligand stability constants of binary Zn(II) complexes in aqueous-DMSO medium

[I] = 0.1 (KNO_3); Temp = 30 ± 0.1°C; 56% DMSO-WATER

Ligand	pK_1	pK_2	$\log K^{Zn}_{K_{ZnA/B}}$	$\log K^{Zn}_{ZnA_2/ZnB_2}$
BPB	4.94	-	2.79	4.76
glycine	9.89	2.95	-	13.48
L-alanine	9.71	3.62	-	13.48
L-phenylalanine	9.05	3.30	-	15.41
L-leucine	9.66	3.62	-	10.23
L-valine	9.78	3.53	-	13.56

All the values are ± 0.02 log K unit accuracy

Table 4: Protonation-ligand and stability constants of binary Zn(II) complexes in aqueous medium*

[I] = 0.2M ($NaClO_4$); Temp = 25 ± 0.1°C

Ligand	pK_1	pK_2	$\log K^{Zn}_{ZnL}$	$\log K^{Zn_2}_{ZnL_2}$	$\log \beta_{znL_2}$
glycine	9.60	2.31	5.22	4.37	9.59
L-alanine	9.76	2.31	5.17	4.10	9.21
L-leucine	9.67	2.83	4.74	4.16	9.10
L-phenylalanine	8.80	2.20	4.70	3.72	8.42
L-valine	9.60	2.31	4.74	4.24	8.98

* M.R. Patel, Nitin Patel, Mohan Patel and J.D. Joshi, *J. Indian Chem. Soc.,* **70,** 569-572 (1993).

Table 5: Stability constants of ternary complexes of Zn(II) complexes in DMSO-water medium

[I] = 0.1 mol dm^{-3} (KNO_3)]; Temp = 30 ± 0.1°C

A = *bis*(pyridyl)benzilidene

B (Secondary)	$\log K^{ZnA}_{ZnAB_2}$	$\log K^{ZnB_2}_{ZnAB_2}$	$\log \beta^{Zn}_{ZnAB_2}$	Δlog K
glycine	12.81	2.22	15.60	-4.55
L-alanine	15.81	5.12	18.60	-1.62
L-phenylalanine	20.14	7.52	22.93	+0.23
L-leucine	18.39	10.85	21.18	-5.75
L-valine	14.28	3.51	17.07	-3.27

All the values are ± 0.02 log K unit accuracy

Conclusions

1. The protonation constants, stability constants of binary and ternary systems are calculated by SCOGS computer program. The reported values are ± 0.02 log unit accuracy.
2. Solvent composition influences the formation constants of binary system, because amino acid-Zn complex has higher stability constant in aqueous-DMSO medium than that of in aqueous medium.
3. Among the ternary systems, phenylalanine ternary system has higher stability constant than other ternary systems employed under this investigation, because stacking interaction is predominant (phenyl ring of phenylalanine and phenyl ring of primary ligand).
4. The overall stability constants of ternary systems reveal that ternary complex formation is more favoured than binary complex formation.
5. The order of stability constant of ternary systems is

   Zn(BPB)(*phe*)$_2$ > Zn(BPB)(*leu*)$_2$ > Zn(BPB)(*val*)$_2$ > Zn(BPB)(*ala*)$_2$ > Zn(BPB)(*gly*)$_2$.

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