STUDIES OF THERMODYNAMIC STABILITY CONSTANT OF AMINO ACID WITH GD (III), YB (III) AND DY (III) COMPLEXES

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ABSTRACT

The formation of complexes has been studied by Job's method. The results obtained of stability constant were good agreement with other mathod. The metal-ligand and proton-ligand stability constant of Yb(III), Dy(III) and Gd(III) with amino acid (DL-methionine)were determined at various ionic strength by pH metric titration. $NaClO_4$ was used to maintain ionic strength of solution. The results obtained were extrapolated to the zero ionic strength using an equation with one individual parameter. The thermodynamic stability constant of the complexes were also calculated.

KEYWORD: Stability constant, ionic strength, amino acid.

INTRODUCTION

Amino acids are common components of all organisms. Protein of all species made from the amino acids. Protein plays many different biological roles in living systems. Methionine is an essential amino acid in humans. Methionine is important in angiogenesis, the growth of new blood vessels, and supplementation may benefit those suffering from Parkinson's, drug withdrawal, schizophrenia, radiation, copper poisoning, asthma, allergies, alcoholism, or depression.[1-3] Methionine is coded for by the initiation codon, meaning it indicates the start of the coding region and is the first amino acid produced in a nascent polypeptide during mRNA translation.[4] The effect of ionic strength of medium on stability constant of cu (II) complex of 2-amino-5-Chloro benzene sulphonic acid at 301K.[5] The stability constant of Co (III) with 1-Amidino-0-methylurea as primary ligand at different ionic strength.[6] The influence of ionic strength of medium on complex equilibria.[7] Association and dissociation constant of Pr (III) complexes with 3-(2-hydroxy-3-Iodo-5-methyl phenyl) 1, 5 diphenyl pyrazoline at different ionic strength.[8] Stability constant of vanadium with glycene at various ionic strength by potentiometric titration technique.[9] The stability constant of Mo (IV) with Iminodiacetic acid at different ionic strength maintain by using sodium per chlorate was investigated.[10] Effect of ionic strength and solvent effect on thermodynamic parameters.[11] They have also studied the mechanism of protonation and complex formation of binary complexes of La (III), Ce (III), Pr (III) and Nd(III) with aminopyridines. The apparent metal-ligand stability constants and confirmation of complexes studied.[13] The composition of complexes were confirmed by Job's method as modified by Vasburgh and Gold.[14]

In present work, determined the pK, metal-ligand stability constant at different ionic strength. We have studied at the 20% Dioxane-water mixture. Author thought of interest to study the effect of ionic strength on thermodynamic parameters of complexes of DL-methionine with Dy(III), Gd(III) and Yb(III) metals in 20% Dioxane-water mixture by pH metrically and spectrophotometrically.

Experimental

The pH measurements were carried out with equip-tronic EQ-610 pH meter (accuracy ± 0.01 units) using combine glass electrode at 208.15 K. Pure rare earth nitrates (99.9% Pure) was used. All metal nitrates available from Sigma Aldrich Chem. Co., U.S.A. Metal nitrate was prepared in triply distilled water and concentration was estimated by standard method. The solution of drugs was prepared in 20% 1, 4 dioxane. The pH metric readings in 20% 1, 4 dioxane–water mixture were converted to $[H^+]$ value by applying the correction proposed by Van Uitert Haas. The 1, 4 dioxane was purified by the method described by Vogel.[12] The overall ionic strength of solution was constant maintains by adding $NaClO_4$. All the solutions were titrated with standard carbonate free NaOH (0.2N) solution at different ionic strength. The titration was carried out at ionic strength by adding $NaClO_4$ (0.02 to 0.08 M).

The experimental procedure involved pH metric titrations of solutions of
1) Free $HClO_4$ (A)
2) Free $HClO_4$ + Ligand (A+L)
3) Free $HClO_4$ + Ligand +Metal ion (A+L+M)

Data obtained from each titration is plotted as pH Vs volume of NaOH added and corresponding volume at successive pH for each set is determined and calculated.

The metal-ligand stability constant of lanthanide metals complexes with DL-methionine were investigated spectrophotometrically. The absorbances measured were carried out with Shimadzu UV-1800 ENG 240V, Japan spectrophotometer. The solutions of metal nitrates were prepared in 20% dioxane–water mixture. $NaClO_4$ was used for maintaining the constant ionic strength. The different composition of metal ion (1×10^{-4}M) and ligand ion (1×10^{-4}M) were prepared in ten series. For determination of $\lambda_{max,}$ 50% metal ion solution at which maximum absorbance observed. The absorption of all composition was measured at constant wave length (λ_{max}) and at constant pH.

RESULT AND DISCUSSION
In the present investigation the determination of proton-ligand stability constant and metal-ligand stability constant on ionic strength of medium was examined by taking fix concentration of metal nitrates and ligand solution during pH metric titration. The system has been studied at 0.02, 0.04, 0.06, 0.08M ionic strength by varying the concentration of sodium per chlorate. The total ionic strength of medium is calculated by equation.

$\mu = \Sigma\ 1/2\ X_t Z_t^2$
C_i , Z_i are the concentration and valences of ith ion respectively.

The values of proton–ligand and metal-ligand constant of Yb(III), Dy(III) and Gd(III) complexes at different ionic strength 0.02,0.04,0.06 and 0.08M determined. These values were determined by using Irving-Rossotties method. From table-1, it was seen that the values of proton–ligand stability constant (P^K) decreases with increasing ionic strength of medium. The metal-ligand stability constant (logK) also decrease with increasing ionic strength.

For determination of stability constant at zero ionic strength the Bronsted equarion is used.

$logK = logK^0 + A\ \Sigma\ \Delta\ Z^2 \sqrt{\mu}$
$pK =\ pK^0 - A\ \Delta\ Z^2\ \sqrt{\mu}$

Where K^0 is the formation constant at zero ionic strength. pK^0 is proton-ligand stability constant at zero ionic strength . 'A' is the Debye-Huckel constant. $\Delta\ Z^2$ is the difference in square of the changes of product and reactant ion. The pK^0 and $logK^0$ values were calculated by plotting the graph of pK, $logK_1$, $logK_2$ versus $\sqrt{\mu}$.

From table-2, it was seen that the good agreement among thermodynamic constant obtained from different plots. The plots pK, $logK_1$, $logK_2$ versus $\sqrt{\mu}$ gives straight line over the entire range of ionic strength for both systems. It shows that the bronsted relationship is valid for dissociation equilibrium. Stability constant of different metal complexes with substituted acetophenone oxime at 0.1, 0.05, and 0.01M ionic strength in 70% dioxane-water mixture were studied.[15]

The conditional stability constant of Silymarin–lanthanide metals complexes were determined for all systems by using equation.

K= x / (a_1-x) (b_1-x) = x / (a_2-x) (b_2-x)
K= Conditional stability constant, x = Concentration of complex, a_1 and b_1 were concentration of metal ion and ligand before dilution. The concentration of metal ion and ligand after dilution were a_2 and b_2. The values of 'x' were calculated from graph optical density V^s % composition of metal ions in solution.

From table-3, it was seen that the good agreement among thermodynamic constant obtained from pH metry and spectrophotometrically.

Table-1. Proton-ligand (pK) and metal-ligand stability constant (Log K) values for Yb(III), Dy (III) and Gd(III)with DL-methionine at various ionic strength(μ)

μ	$\sqrt{\mu}$	$\sqrt{\mu}/1+\sqrt{\mu}$	$[\sqrt{\mu}/1+\sqrt{\mu}] -0.3\sqrt{\mu}$	pK	$LogK_1$	$LogK_2$
DL-methionine + Yb(III)						
0.02	0.1414	0.1239	0.0815	7.8074	7.15	4.45
0.04	0.2000	0.1667	0.1067	7.6267	6.65	4.30
0.06	0.2450	0.1968	0.1233	6.8782	6.35	3.60
0.08	0.2828	0.2205	0.1356	5.8940	5.70	3.75
DL-methionine + Dy(III)						
0.02	0.1414	0.1239	0.0815	7.7164	6.90	4.30
0.04	0.2000	0.1667	0.1067	7.6287	6.70	3.65
0.06	0.2450	0.1968	0.1233	6.7752	6.55	3.60
0.08	0.2828	0.2205	0.1356	5.8940	5.40	3.35
DL-methionine + Gd(III)						

0.02	0.1414	0.1239	0.0815	7.6014	7.15	4.35
0.04	0.2000	0.1667	0.1067	7.5237	6.60	4.10
0.06	0.2450	0.1968	0.1233	6.8772	6.15	3.70
0.08	0.2828	0.2205	0.1356	5.6940	6.05	3.15

Table-2. Thermodynamic stability constant (pK^0 and Log K^0) values for Yb(III), Dy (III) and Gd(III) with DL-methionine

System		P^K Vs $\sqrt{\mu}$
DL-methionine + Yb(III)	PK^0	9.9423
	Log K_1^0	8.5829
	Log K_2^0	5.3306
DL-methionine + Dy(III)	PK^0	9.8166
	Log K_1^0	8.4297
	Log K_2^0	5.1004
DL-methionine + Gd(III)	PK^0	9.7318
	Log K_1^0	8.2512
	Log K_2^0	5.6287

Table-3. Metal-ligand stability constants (Log K) values obtained by pH-metry and Spectrophotometry technique (Ionic strength = 0.08m)

System	pH metry	Spectrophotometry
Yb (III)+ DL-methionine	3.75	3.8033
Dy (III)+ DL-methionine	3.35	3.4205
Gd (III)+ DL-methionine	3.15	3.2234

Fig.1 Plot of pK Vs $\sqrt{\mu}$

Fig.3 Plot of logk$_2$ Vs $\sqrt{\mu}$

Fig.3 Plot of logk$_1$ Vs $\sqrt{\mu}$
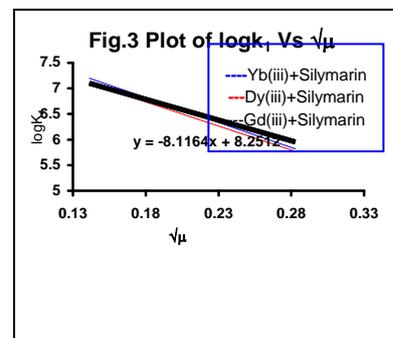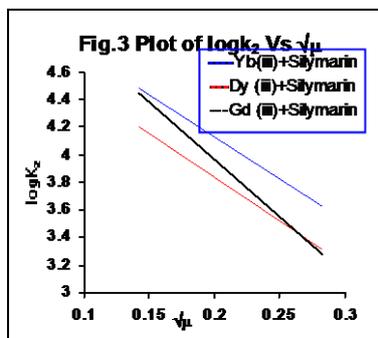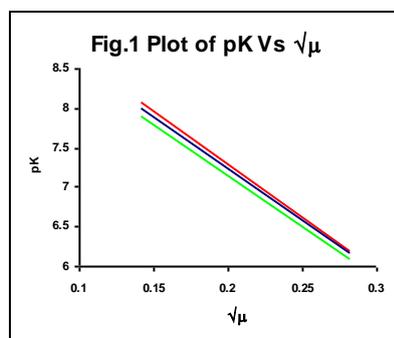
CONCLUSION
The calculated values of stability constant at various ionic strength are high. From data the conclusion is, the complexes of Silymarin with Yb (III), Dy (III), Gd (III) metal ions were quite stable at over all range of ionic strength. The values of thermodynamic parameters are nearly same from all plots was good agreement of results. The values of conditional metal-ligand stability constant shows good agreement with the values determined by pH metrically.

REFERENCES
1. http://www.webmd.com/vitamins-supplements/ingredientmono-42-methionine.aspx?activeingredientid.
2. Dawson, R.M.C.; et al. (1959). Data for Biochemical Research. Oxford: Clarendon Press.
3. Weast, Robert C., ed. (1981). CRC Handbook of Chemistry and Physics (62nd ed.). Boca Raton, FL: CRC Press. p. C-374. ISBN 0-8493-0462-8.
4. Guedes, R. L.; Prosdocimi, F; Fernandes, G. R.; Moura, L. K.; Ribeiro, H. A.; Ortega, J. M. (2011). BMC Genomics. 12 Suppl 4: S2. McCue K. "Chemistry.org: Thanksgiving, Turkey, and Tryptophan". Archived from the original Retrieved 2007-08-17.
5. Deosarkar, S.D., Narwade, M.L., Hiwase, V.V. and Khedkar, K.M., 2009. Ori. J. Chem., 25(1): 233.
6. Saroda devi and Singh, M., 2007. J. Ind. Coun. Chem, 24(2): 32-35.
7. Agrawal ,P.B., Narwade and M.L., 2003. Acta Ciencia Indica, XXIXC(2): 141.
8. Mehram, Y.K., Mandakmare, A.U. and Narwade, M.L., 2000. Orien. J. of Chem., 16(1): 173-176.

9. Khorrami, S.A., Bayat, H., Sharifi, S. and Shafai, M., 1996. *J. Chem. Eng. data*; 41(6): 1322-1324.

10. Majlesi, K., Gharib, F. and Arafati, M., 2006. J. Inorg. Chem; 51(2): 1982-1986.

11. Sharma, S., Shah, M.C., Dalwadi, D., Thakur, F. and Vora, J.J., Research J. of Chem. and Envi., 2008; 12(4): 29-34.

12. Vogel's, G.H., Jaeffery, S., Bassetl, Denney, R.C., "Text book of quantitative chemical analysis". **V^th** Ed., ELBS Longman, 1997; 53.

13. Tekade P. V., Patil K. N. and Narwade M. L., 2006. Asian J. of Chem., 18(4)**:** 2657.

14. Gold K. R. and Vasburgh W. C., *J.* Am. Chem. Soc., 1942; 64: 1630.

15. Rahman, F., Rastogi S.N. and Jettey, U.K., J. Ind. Chem. Soc., 1990; 67: 342.