World Journal of Chemistry 6 (2): 118-121, 2011
ISSN 1817-3128

Spectrophotometric Studies of Dy (III), Nd (III), Sm (III) and Tb (III) Complexes with Substituted Pyrazoles

A.B. Naik

Department of Chemical Technology, SGB Amravati University, Amravati-444602 (M.S.) India

Abstract: The formation of complexes of Dy (III), Nd (III), Sm (III) and Tb (III) with 3-(2-hydroxyphenyl)-5-pyrazole (HPPPZOLE) and 1-phenyl-3-(2-hydroxyphenyl)-5-pyrazole (PHPPPZOLE) was studied spectrophotometerically at (298 ± 0.1) K and ionic strength $\mu = 0.1$ mol.dm^{-3}. The stability constants have been investigated in a 70% dioxane-aqueous mixture by the Job's continuous variation method. The results obtained of stability constants are in good concordance the values obtained by the real stability constant by pH metric technique.

Key words: Metal-ligand complexes · Pyrazole · Stability constant and Spectrophotometer

INTRODUCTION

Heterocyclic compounds provide a great synthetic and structural versatility due to their having a number of potential substitution positions. Furthermore heteroatoms offer the possibility of several modes of coordination. The pyrazoles nucleus received much attention during the last three decades due to their important role in agrochemical and pharmaceutical [1-2]. Many pyrazole derivatives are known to exhibit a wide range of biological and medicinal values [3] such as antifungal [4], antibacterial [5], anti-inflammatory [6] and anti-tumor [7]. The substituted pyrazole [8] has been shown strong anti-invasive activity against human breast carcinoma cells. The different substituted aryl pyrazole used for the protection of plants against fungal diseases [9]. In the literature, the numerous methods have been used to determine the stability, describe in detail the often-intricate calculation and gave a remarkable thorough bibliography of work in this field. It concerns itself with ionic and molecular association in all their forms. The stability constants are neither activity quotients nor thermodynamic constants but rather are concentration constants determined in a constant ionic medium, usually of high strength [10]. A study of the stability of zinc, cobalt, nickel and copper with derivatives of 5-salicylic aldehyde sulfonate[11] has shown that the stability of these chelates increases in the order given and determined entropy. Swami [12] has studied the effect of substitution upon the stability of palladium chelates of substituted hydroxytriazene. It was found that the stability increases when the ethyl or propyl group at N-3 in the order of methyl, ethyl or propyl replaces the methyl group. The Gharib [13] *et al.* have reported the complexation of methyl ion with glutonic acid using spectrophotometeric technique. The study of complexes of Co (II) with HMAPTST[14] has been investigated by using Isobestic method and Job's method, found to be good agreement with real stability constants. The metal-ligand stability constants in some peptides, diketones, pyrazoles and pyrazolines have been studied by many worker [15-17]. Raghuwanshi *et al*. [18] have studied confirmation of complex formation of isobestic and Job's method between Cu (II) and substituted isoxazoline spectrophotometerically. Sondawale and coworker [19] reported the stability constant of Cu (II) with some amino acid peptides. It is shown that Cu (II)-DL-Alanyl-DL-Alanine complex is less stable than the other due to the weaker interaction between metal ion of mixture of *dextro* and *leavo* form.

The extensive literature given above clearly indicates that metal complexes show that thermodynamic study, physical parameter etc. Several complexes especially transition metal ions containing with N-heterocyclic ligands have been reported. However, it is noted that little work has been done on complexes based on substituted pyrazoles. The spectrophotometer methods are in general highly sensitive and no limitation to any pH range or nonaqueous solutions. This is more sensitive for studying chemical equilibria in solution for many decades.

Corresponding Author: A.B. Naik, Department of Chemical Technology, SGB Amravati University, Amravati-444602 (M.S.) India. Tel: +91-721-2553990.

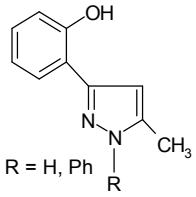

Fig. 1.1:

Experimental: All chemicals used were of analytical grade. The substituted pyrazoles (HPPPZOLE) and (PHPPPZOLE) were prepared by known literature method. The absorbance of the liquid solution and their metal complexes have been measured by UV-VIS spectrophotometer model 1700 (Shimadzu, Japan), accuracy ± 0.005 having spectral range 180 nm to 1100 nm. The quartz cuvettes of 1 cm path length were used for the study of spectra in the 200 nm to 700 nm. The equimolar solution of Dy (III), Nd (III), Sm (III) and Tb (III) with ligand (HPPPZOLE) and (PHPPPZOLE) were mixed in different ratio form 1: 5 to 5:1. The pH in the range 2-3 and ionic strength (μ=0.1) maintained constant throughout by addition of sodium hydroxide and sodium perchlorate respectively.

RESULTS AND DISCUSSION

Job's [20] has described a procedure for determining the formula of an additive complex which is called method of continuous variations. The Job's curve of this system as shown in figure 1.2.

It is observed that from all curves that there is a formation of 1:1 complex in the pH range 2-3. In addition to the wavelength of maximum (λ_{max}) some other wavelengths were selected as proposed by Vosburgh and Gould [21]. The conditional stability constant (Table 1) for all systems was calculated by using following expression;

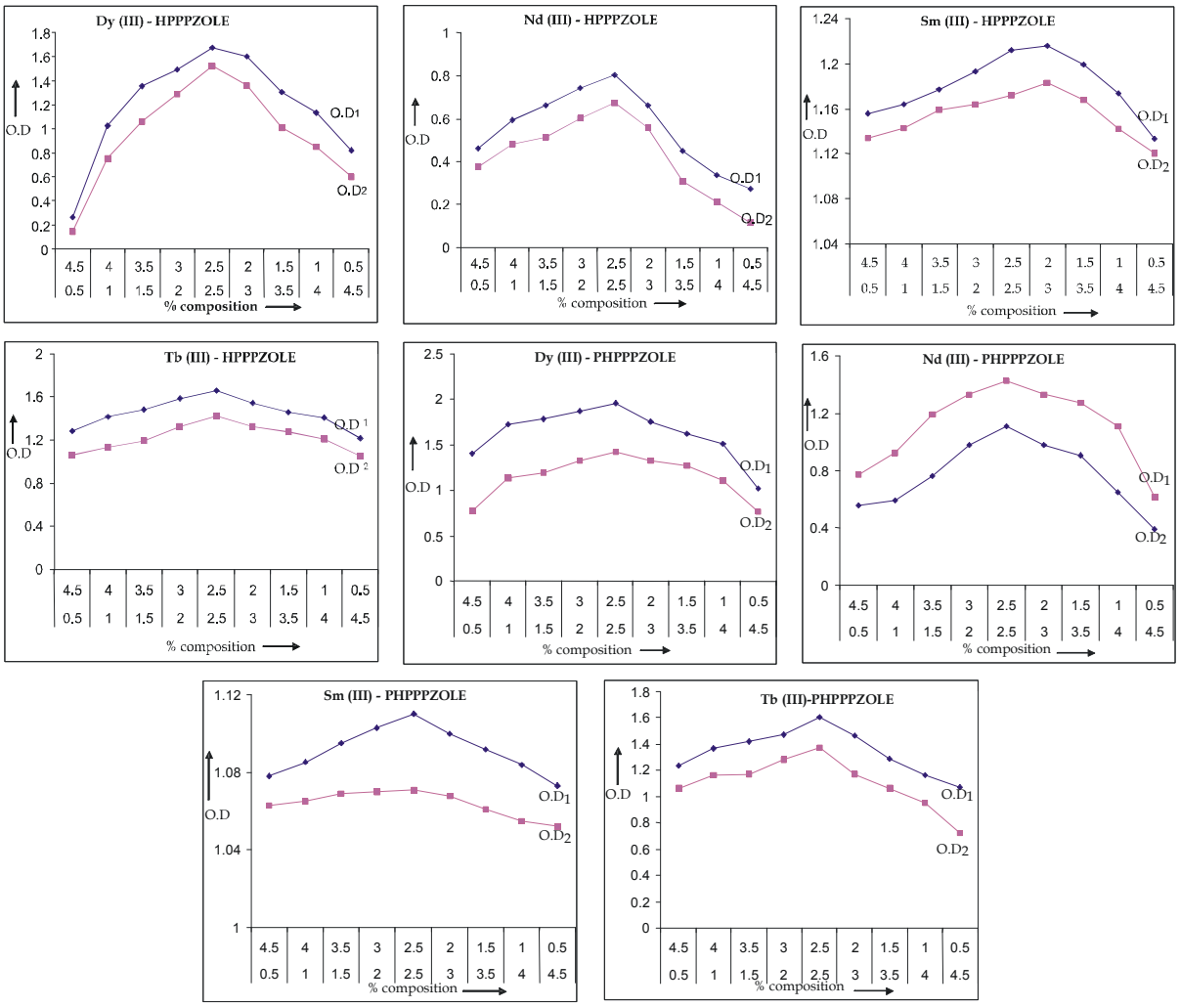

Fig. 1.2:

Table 1:

System	Spectrophotometeric (log K)	pH-metric (log K) [22]
Dy (III)-HPPPZOLE	5.5188	6.2448
Nd (III)-HPPPZOLE	5.5699	6.4449
Sm (III)-HPPPZOLE	4.5190	5.8449
Tb (III)-HPPPZOLE	5.4350	6.3550
Dy (III)-PHPPPZOLE	2.5147	2.650
Nd (III)-PHPPPZOLE	3.3605	3.0440
Sm (III)-PHPPPZOLE	3.7378	3.8437
Tb (III)-PHPPPZOLE	2.5233	3.3477

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

Where a_1 and a_2 = concentration of metal ions from curve
a_1 and a_1 = concentration of ligand from curve
k = conditional metal-ligand stability constant

The values of conditional stability constants are found to be lesser than the real stability constant (Irving Rossotti method). This is because the concentration of free acid at a particular pH was not taken into account as well as the weaker interaction between them.

CONCLUSION

It could be concluded that the agreement between the values obtained by the both techniques is fairly good except the Tb (III)-PHPPPZOLE. There is no appreciable change in the log K values.

ACKNOWLEDGEMENT

The financial support vide project no. F /30-88 /2004 (SR) is sanctioned by the University Grants Commission (UGC), New Delhi for carrying out this research is gratefully acknowledged.

REFERENCES

1. Ancel, J.E., L. Elkam, A. Gadras, L. Grimaud and N.K. Jana, 2002. Studies towards the synthesis of Fipronil analogues improved decarboxylation of α-hydrazonoacid derivates, Tetrahedron Lett., 43(46): 8319-8321.
2. Tang, J., L.M. Shewehuk, H. Sato, M. Haseganis, Y. Washio and N. Nishigaki, 2003. Anilinopyrazole as selective CDK2 inhibitors: design, synthesis, biological evaluation and X-ray crystallographic analysis, Biorg. Med. Chem. Lett., 13: 2985-2988.
3. Majid, T., C.R. Hopkins, B. Pedgrift and N. Collar, 2004. Convenient synthesis of 4-amino-3, 5-disubstituted pyrazoles in one-step from the corresponding diketo oximes, Tetrahedron Lett., 45: 2137-2139.

3a. Dodd, D.S. and R. Martinez, 2004. One-pot synthesis of 5-(substituted-amino) pyrazole, Tetrahedron Lett., 45: 4265-4267.

3b. Sakya, S.M. and B. Rast, 2003. Efficient synthesis of 5-alkyl amino and thioether substituted pyrazoles, Tetrahedron Lett., 44: 7629-7632.

4. Dwivedi, V., A. Jain and G. Sharma, 2008. Synthesis and antifungal activities of some new-1-aroyl-3-methyl-4-substituted phenyl-6-imino1,4,7-trihydro (1, 3)-thiazino(5-4D) pyrazoles, J. of Ind. Council Chem., 25(2): 103-105.
5. Jamode, V.S., P.R. Bhagat and H.S. Chandak, 2004. Synthsis and antimicrobial activity of 1-substituted-3-{3-[(4-chlorophenyl)-sulphonamido]phenyl}-5-aryl-pyrazoles, J. Prad. Nir., 1(4): 14.
6. Bekhit, A.A. and T.A. Aziem, 2004. Design, synthesis and biological evaluation of some pyrazole derivatives as anti-inflammatory-antimicrobial agents, Biorg. Med. Chem., 12(8): 1935-1945.
7. Baraldi, P.G., I. Beria, P. Cozzi, C. Geroni, A. Espinosa, M.A. Gallo, A. Entrena, J.P. Binham, J.A. Hartley and R. Romagnoll, 2004. Cinnamoyl nitrogen mustard derivatives of pyrazoles analogus of tallimustine modified at the amidino moiety: design, synthesis, molecular modeling and antitumor activity studies. Biorg. Med. Chem., 12(14): 3911-3921.
8. Parmar, V.S., N.K. Sharma, M. Husain, A.C. Watterson, J. Kumar, L.A. Samuelson, A.L. Cholli, A.K. Prasad, A. Kumar, S. Malhotra, N. Kumar, A. Jha, A. Singh, I. Singh, Himanshu, A. Vats, Najam A. Shakil, S. Trikha, S. Mukherjee, S.K. Sharma, S.K. Singh, Ajay Kumar, Hriday N. Jha, C.E. Olsen, Christophe P. Stove, M.E. Bracke and M.M. Mareel, 2003. Synthesis, characterization and *In vitro* anti-invasive activity screening of polyphenolic and heterocyclic compounds, Biorg. Med. Chem. Lett., 11: 913-929.
9. Vors, J.P., V. Gerbaud, N. Gabas, J.P. Canselier, N. Jagerovic, M.L. Jimeno and J. Elgnero, 2003. The structure of the agrochemical fungicidal 4-chloro-3-(3,5-dichloro-phenyl)-1*H*-pyrazole (RPA406194) and related compounds, Tetrahedron, 59(4): 555-560.

10. Rossotti, F.J.C. and H. Rossotti, 1961. The determination of stability constants and other equilibrium constants in solution 1961 McGraw Hill Book Co, INC, New York.
11. Calvin, M. and N.C. Malchior, 1948. Stability of chelate compounds. IV effect of the metal ion, J. Am. Chem. Soc., 70(10): 3270-3273.
11a. Calvin, M. and N.C. Malchior, 1948. Stability of chelate compounds. V The *o*-formylnaphthoxide chelates, J. Am. Chem. Soc., 70(10): 3273-3275.
12. Swami, V.K., 2006. Stability constant of palladium chelates of hydroxytriazenes Ultrascience, 18(1): 97-100.
13. Gharib, F., K. Zare and K. Majlesi, 2000. Ionic strength dependence of formation constants, complexation of Molybdenum (VI) with glutamic acid, J. Chem. Engg. Data, 45(5): 833-836.
14. Agrawal, P.B., 2006. Determination of metal-ligand stability constants at 0.1M ionic strength pH meterically. Ultra science, 18(1): 93-96.
15. Meshram, Y.K., A.M. Mandakmare and M.L. Narwade, 2000. Stability constant of Pr (III), Nd(III) and Sm(III) chelates with some substituted pyrazolines, Asian J. Chem., 12(4): 1027-1030.
16. Thakare, V., 2008. PhD Thesis in Chemistry. Amravati University, Amravati, India.
17. Kadu, M.V., V.S. Jamode and M.L. Narwade, 1999. Studies in Co(II) Cu(II) and Ni(II) and complexes with substituted pyrazoline and pyrazole at 0.1 ionic strength pH-metrically, Asian J. Chemistry, 11(2): 420-423.
18. Raghuwanshi, P.B., A. Doshi and M.L. Narwade, 1996. Spectrophotometric investi-gation of conditional stability constants and confirmation of complex formation of Cu(II) complexes with substituted chalcones and isoxazolines, Asian J. Chem., 8(2): 211-15.
18a. Raghuwanshi, P.B., M.L. Narwade and A.G. Doshi, 1997. Spectrophotometric studies of various Fe (III)-1,3-thiazine systems, Asian J. Chem., 9(2): 327-329.
19. Sondawale, P.J. and M.L. Narwade, 1998. Confiramtion of complex formation and determination of conditional stability constants of Cu(II) complexes with some amino acid peptides spectrophotometrically. Samyak J. Chem., 2(3): 30-32.
20. Job's, P., 1928. Anna. Chim., 9(10): 113.
21. Gould, R.K. and W.L. Vosburgh, 1942. Complexions. III. A study of some complex ions in solution by means of the spectrophotometer, J. Am. Chem. Soc., 64(7): 1630-1634.
22. Naik, A.B. and M.L. Narwade, 2009. pH-metric studies on formation constants of the complexes of substituted pyrazoles with some lanthanide metal ions and the influence of ionic strengths on complex equilibria in a 70% dioxane-water mixture Russian J. of Coordination Chemistry, 35(12): 932-937.