

PHYSICAL CHEMISTRY
OF SOLUTIONS

Stability Constants of Complexes of Cr(II) and Sr(II)
with Quinazoline and Dihydropyridine in Dioxane–Water Mixture
on Spectrophotometric Data¹

Pradip V. Tekade^{a,*}, Sonal D. Bajaj^{a,**}, Bhagyashri U. Tale^a, Nandini Authankar^a, and Sonali Sadmake^a

^aDepartment of Chemistry, Jankidevi Bajaj College of Science, Jamnalal Bajaj Marg, Civi Lines, Wardha, India

* e-mail: pradiptekade@gmail.com

** e-mail: sonulstar@gmail.com

Received August 21, 2017

Abstract—The interaction of Cr(II) and Sr(II) with a series of four novel *N*-heterocycles viz. 2-(1,3-dioxoindoline-2-yl)-*N*-(4-oxo-2-phenylquinazolin-3(4H)-yl), 1-(2-((4-oxo-2-phenylquinazolin-3(4H)-yl) carbomoyl), diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)-3-methylbutanoyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate, diethyl 1-(2-(1,3-dioxoisoindolin-2-yl)butanoyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate studied by spectrophotometric technique at 0.01 M ionic strength and 28°C in 70% dioxane–water mixture. The data obtained used to estimate the stability constant of the complexes. Investigation of Cr(II) and Sr(II) complexes with these ligands shows 1 : 1 complex formation. The values of conditional stability constants of Sr(II) complexes are greater than the corresponding Cr(II) complexes. The results obtained of stability constants are in good agreement with the structure of ligand and reactivity pattern of metal ion. These can be of interest for specialists in the field of coordination chemistry.

Keywords: stability constant, chromium complexes, strontium complexes, *N*-heterocyclic ligands, Job's variation method, quinazoline, dihydropyridine

DOI: 10.1134/S0036024418110419

INTRODUCTION

The scientific community is striving to understand the role of heterocycles and fused heterocycles in drug discovery programme due to its impact on multi-drug resistance (MDR) of anticancer drugs. The quinazolines belong to a family of heterocyclic nitrogen compounds that have attracted increasing interest because of their broad spectrum of biological activity [1], including antifungal, anti-tumor, anti-malaria, anti-convulsant, anti-microbial, anti-inflammatory, anti-tumor and antihyperlipidemic activities [2]. Moreover, Pyridine derivatives are very important chemicals with tremendous biological application. The pyridine derivatives have different biological target by interacting with enzymes, proteins and DNA [3]. The stability constants for the metal complex widely used in many fields such as biological processes, analytical processes, pharmaceuticals, etc. Moreover, metal complex play a very important role in nature.

The basic principle of the spectrophotometric technique is the measurement of interaction between energy and electrons of the substance. The spectrophotometric technique is analytical method used for estimating con-

centration of metal ion in liquid solution. One of the most spectacular effects of complex formation is the change of spectral properties. Consequently, spectrophotometry emerged as suitable technique for determination of stability constant of metal complexes with biologically active compounds. Study of stability constant of different complexes reported by many researchers [4–7] in different solvents by spectrophotometric technique. Maurya et al. [8] and Hassan [9] reported the complex formation in benzimidazole derivatives by spectrophotometric study.

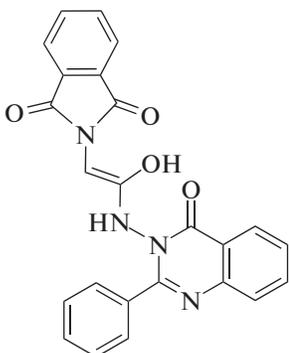
Therefore, we thought to study the chelating properties of some novel *N*-heterocycles viz. dihydropyridine and quinazoline derivatives (ligands 1 to 4) with Cr(II) and Sr(II) metal ions by Job's variation method under suitable conditions spectrophotometrically.

EXPERIMENTAL

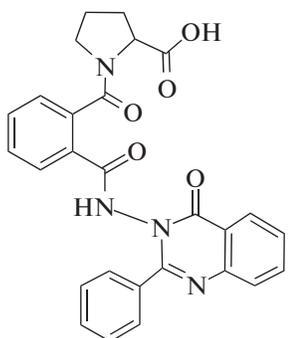
All the chemicals used are of laboratory grade and used without further purification. The ligands prepared by known methods [10, 11]. Compounds recryst-

¹ The article is published in the original.

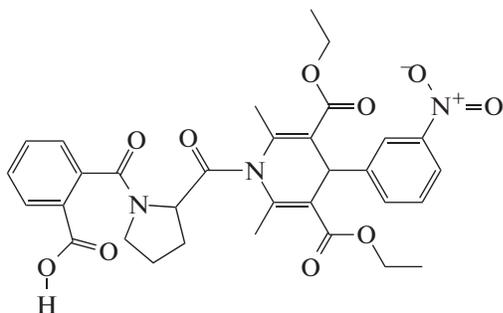
tallized before use. The structures of ligands 1 to 4 are given below:



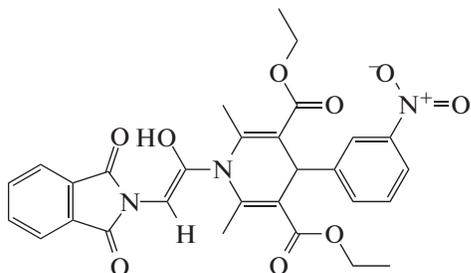
Ligand 1: 2-(1,3-dioxoisindolin-2-yl)-*N*-(4-oxo-2-phenylquinazolin-3(4H)-yl)acetamide;



Ligand 2: 1-(2-((4-oxo-2-phenylquinazolin-3(4H)-yl)carbamoyl)benzoyl)pyrrolidine-2-carboxylic acid;



Ligand 3: diethyl 1-(2-(1,3-dioxoisindolin-2-yl)-3-methylbutanoyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate;



Ligand 4: diethyl 1-(2-(1,3-dioxoisindolin-2-yl)butanoyl)-2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate.

The distilled water used free from carbon dioxide and pH of this water about 6.80. Cr(II) (0.01 M) and Sr(II) (0.01 M) ionic solutions prepared from Chromium chloride and Strontium chloride (AR grade) and standardized by standard methods. 0.01 M KNO_3 used for maintaining ionic strength constants. The ligands are insoluble in water, hence ligand solutions of 0.01 M prepared in 70% dioxane–water (vol/vol) mixture. Contech digital balance (CA 224) having accuracy 0.001 g used for weighing of samples. Bio-Era Elite UV–Vis spectrophotometer with accuracy ± 0.01 units used for absorbance measurements.

Metal–ligand stability constants and confirmation of complex formation studied by and Gürkan [12]. Solutions of metal salt and ligand of equimolar concentration (1.00×10^{-2} M) mixed pairwise in different ratios to prepare Job's solutions. Final volume of each solution made 10 mL after adjusting the appropriate pH and maintaining the constant ionic strength. In addition to the wavelength of maximum (λ_{max}) some other wavelength selected as proposed by Gould and Vosburgh [13].

RESULTS AND DISCUSSION

The concentration of complex (x) in any metal ligand solution is obtained by Job's curve. Initial concentrations of metal and ligand in a particular solution considered a and b and the equilibrium constant determined by the law of mass action.

$$K = \frac{x}{(a-x)(b-x)}$$

or

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

The composition of metal ion solution (1×10^{-2} M) and ligand (1×10^{-2} M) prepared in ten series. Value λ_{max} determined using one of the compositions at conditional stability constants of complexes in which there is maximum absorption. The absorptions for all the compositions recorded at constant wavelength (λ_{max}). Each solution is diluted up to 15 mL and absorptions recorded at same λ_{max} . The data of absorption and percentage composition of metal ion and ligand solutions at constant pH used and the curves constructed. The conditional stability constants obtained by spectrophotometric techniques presented in the Table 1.

It is seen from the above table that, the highest stability constant value obtained for Cr(II)–Ligand 1. This is due to the formation of coordinated bond between –OH group of Ligand 1 (enol form) with the Cr(II) metal ion. Moreover, Ligand 1 contains both –NH and –OH group which are susceptible for the

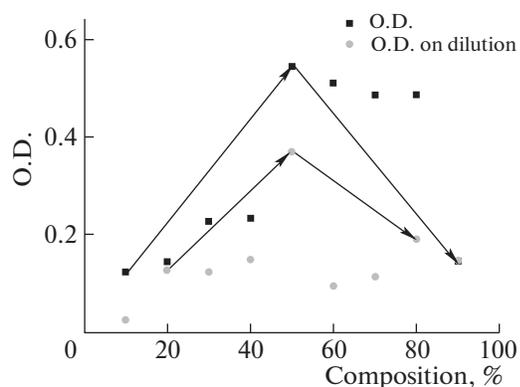


Fig. 1. The variation of O.D. with % composition for system Cr(II)–Ligand 1.

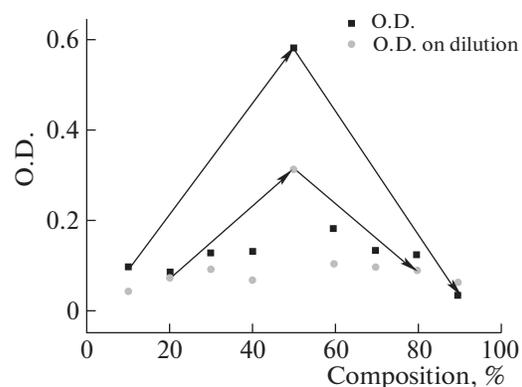


Fig. 2. The variation of O.D. with % composition for system Cr(II)–Ligand 2.

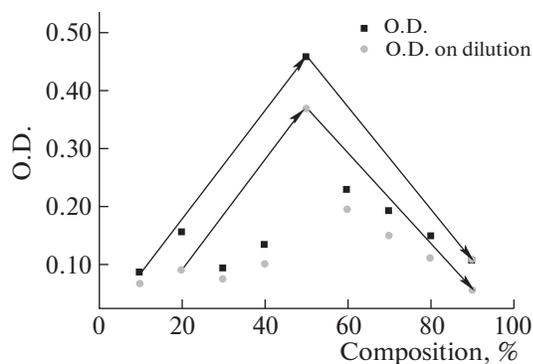


Fig. 3. The variation of O.D. with % composition for system Sr(II)–Ligand 2.

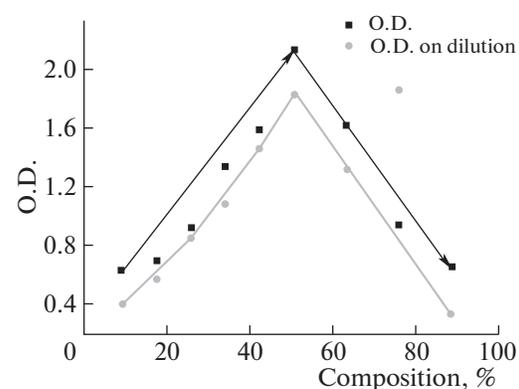


Fig. 4. The variation of O.D. with % composition for system Cr(II)–Ligand 3.

formation of coordinate bond with Cr(II) ion, this is the reason behind its higher stability constant. On the other hand, ligand 2 and 3 both have free $-\text{COOH}$ group which is easily available for formation of coordinate bond with metals. Furthermore, they shows greater stability constant value for Sr(II) complexes

than Cr(II). This may be attributed to the high reactivity of the strontium being alkaline earth metal. Furthermore, for ligand 4, the highest value of stability constant observed for Cr(II) complexes, this is attributed the presence of $-\text{OH}$ group in the structure and small ionic radius of Cr(II) ion than Sr(II) ion.

Table 1. Conditional stability constants of complexes

System	$K \times 10^3$	$\log K$
Cr(II)–Ligand 1	0.933	2.829
Cr(II)–Ligand 2	0.3845	2.584
Sr(II)–Ligand 2	0.6338	2.801
Cr(II)–Ligand 3	0.745	2.872
Sr(II)–Ligand 3	0.838	2.923
Cr(II)–Ligand 4	1.04	3.107
Sr(II)–Ligand 4	0.199	2.298

The curves constructed between the values of optical density and percentage composition of metal ion. The variation of O.D. with % composition for different systems given in Figs. 1–7.

ORDER OF STABILITY CONSTANTS

Cr(II)–Ligand 4 > Cr(II)–Ligand 1 > Sr(II)–Ligand 3 > Cr(II)–Ligand 3 > Sr(II)–Ligand 2 > Cr(II)–Ligand 2 > Sr(II)–Ligand 4.

CONCLUSIONS

In the present study, we have reported spectrophotometric investigation of stability constant of complexes of the novel Quinazoline and Dihydropyridine derivatives with Cr(II) and Sr(II) metal ions. The for-

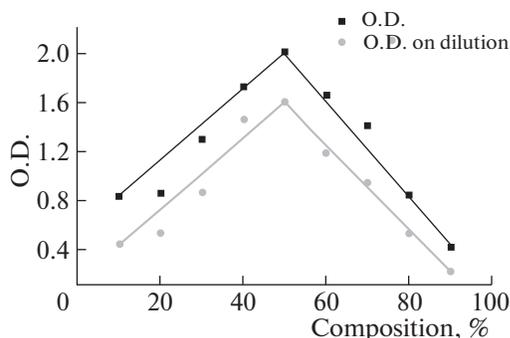


Fig. 5. The variation of O.D. with % composition for systems Sr(II)–Ligand 3.

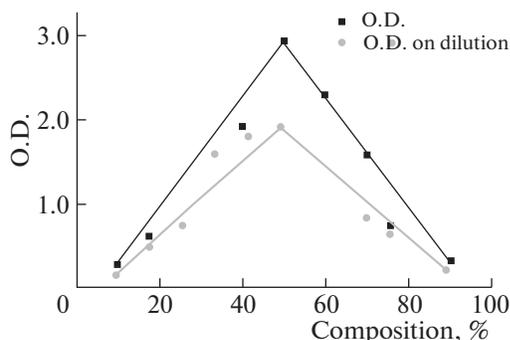


Fig. 6. The variation of O.D. with % composition for systems Cr(II)–Ligand 4.

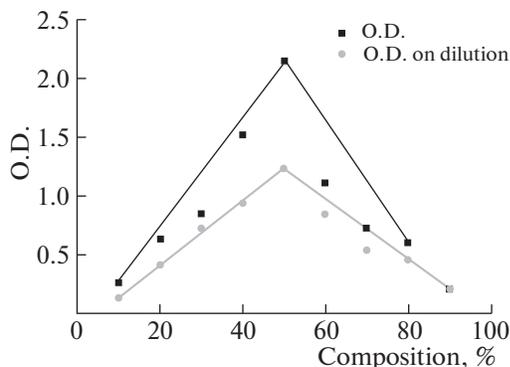


Fig. 7. The variation of O.D. with % composition for systems Sr(II)–Ligand 4.

mation of complexes (1 : 1) studied by Job's variation method. The spectrophotometric study shows the existence of intermolecular interaction between the solute and metal ion solution and the measured condi-

tional stability constant concluded that the complex formation tendency of ligands different with different metal ions. Stability constant of complexes depends upon the structure of ligand and ionic radius of the metal ion. The values of conditional stability constants of Sr(II) complexes are greater than the corresponding Cr(II) complexes. The obtained stability constants are in good agreement with the structure of ligand and reactivity pattern of metal ion.

REFERENCES

1. D. He, M. Wang, S. Zhao, Y. Shu, H. Zeng, C. Xiao, and Y. Liu, *Fitoterapia* (2017). doi 10.1016/j.fitote.2017.05.001
2. D. Kumar and S. Kumar Jain, *Curr. Med. Chem.* **23**, 4338 (2016).
3. A. A. Altaf, A. Shahzad, Z. Gul, N. Rasool, A. Badshah, B. Lal, and E. Khan, *J. Drug. Des. Med. Chem.* **1**, 1 (2015). doi 10.11648/j.jddmc.20150101.11
4. R. Ravichandran, M. Rajendran, and D. Devapiriam, *Food Chem.* **146**, 472 (2014). doi 10.1016/j.foodchem.2013.09.080
5. N. Singh and A. Ahmad, *J. Mol. Struct.* **1074**, 408 (2014). doi 10.1016/j.molstruc.2014.05.076
6. J.-i. Itoh, T. Yotsuyanagi, and K. Aomura, *Anal. Chim. Acta* **76**, 471 (1975). doi 10.1016/S0003-2670(01)85423-4
7. S. A. Tirmizi, F. H. Wattoo, M. H. S. Wattoo, S. Sarwar, A. N. Memon, and A. B. Ghangro, *Arab. J. Chem.* **5**, 309 (2012). doi 10.1016/j.arabjc.2010.09.009
8. M. R. Maurya and N. Bharti, *Trans. Met. Chem.* **24**, 389 (1999). doi 10.1023/A:1006942231677
9. A. Hassan, *Phosphor., Sulfur, Silicon Relat. Elem.* **106**, 55 (1995). doi 10.1080/10426509508027889
10. S. D. Bajaj, O. A. Mahodaya, P. V. Tekade, V. B. Patil, and S. D. Kukade, *Russ. J. Gen. Chem.* **87**, 546 (2017). doi 10.1134/S1070363217030264
11. K. P. Rakesh, H. M. Manukumar, and D. Channe Gowda, *Bioorg., Med. Chem. Lett.* **25**, 1072 (2015). doi 10.1016/j.bmcl.2015.01.010
12. R. Gürkan, N. Altunay, and N. Gürkan, *J. Iran. Chem. Soc.* **1**, 17 (2017). doi 10.1007/s13738-017-1053-9
13. K. R. Gould and C. W. Vosburgh, *J. Am. Chem. Soc.* **64**, 1630 (1942). doi 10.1021/ja01259a044