Effect of 2-Aminopropanoic Acid on The Formation of Polynuclear Heteroligand Cobalt (Ii) And Nickel (Ii) Complexes

Iman Jubeir Obeis[1] and Ghusoon Faidhi Hameed[2]
1, 2Department of Chemistry, Faculty of Education, Al-Qadisiyah University, Al-Qadisiyah, Iraq

Abstract

Spectrophotometric studies of the Co-(II)-Ni (II)-2-aminopropanoic acid (HAla)-DTPA system have been performed at a variety of reagent molar ratios and pH values. It has been found that, when metal ions are in excess with respect to DTPA at pH 5-9, polyheteronuclear complexes [(CoAla)Dtpa(NiAla)]3–, [(CoAla2) Dtpa(NiAla2)]5–, [(NiAla2) Dtpa (CoAla2)2]5–, (CoAla2) Dtpa (NiAla2)2]5– and (NiAla2)2Dtpa(CoAla2) 2]5–. form in a solution. The equilibrium constants of formation of these complexes are their overall stability constants have been calculated. Possible structures of the polynuclear complexes are discussed.

Keywords: cobalt (II), nickel (II), DTPA, alanine, spectrophotometry, polynuclear complexes.

1. Introduction

The conditions for the formation of polynuclear complexes involving complexes are not well understood [1]. High denticity of the structure-forming complex is required for the formation of such complexes, but this is not possible within the inner coordination sphere of a single metal ion. For example, ethylene triamine pentaacetic acid (DTPA) is an eight-dentate ligand that typically forms mononuclear complexes with Co (II) [1, 2], The yield and quality of potato tubers are both improved thanks to the use of metal complexes with DTPA. Chlorosis in plants can be combated with the help of iron complex with DTPA.[3]. Both animal husbandry and the food industry make use of relatively complex biochemical processes [4, 5]. Due to its hexadentate nature, ethylenediaminetetraacetic acid (EDTA) typically forms mononuclear complexes. However, in the presence of excess doubly charged metal ions Ni (II), Co (II) (mix metal), and an additional bidentate ligand (glycine), multi-, binuclear, and tetra-nuclear complexonates can be formed [1]. Stability constants and optimum conditions for formation of heteropolynuclear complexes were previously determined in our studies of Ni (II)-Co (II)-EDTA-Ala [(CoAla)Edta(NiAla)]2–, [(NiAla2)Edta(CoAla2)]4–, [(CoAla2)2Edta(NiAla2)]4–, [(CoAla2)Edta(NiAla2)2]4–, [(CoAla2)2Edta(NiAla2)2]4– [6].

2. Experimental

Spectrophotometric titration was used to examine complex formation in solutions. With an SF-2000 spectrophotometer and its specialized unit, which included a flow type cell made of quartz glasses and a path length of 1cm, we were able to determine the absorbance of the solutions. Thanks to this set-up, we could measure both the pH and absorbance of the solution at the same time. Using an ES-10601/7 working electrode and an ESR 10101 reference electrode, we were able to determine the concentration of hydrogen ions with an I-160MI ionometer. NaOH and HClO4, (pure for analysis) solutions were added to get the desired pH level. A NaClO4 (pure for analysis grade) solution was used to keep the ionic strength at a constant I= 0.2. All experiments were performed at a temperature of 202°C. In order to determine the concentration of metal ions in a solution, complexometric titration was used to dissolve the CoSO4 7H2O and NiSO4 7H2O salts in water. Both DTPA and alanine were dissolved in deionized water to create chemically pure solutions. HypSpec [7] was used to perform the necessary mathematical processing of the results. The ACD/Lab's software enabled the development of intricate models [8].

3. Results and Discussion

The occurrence of speciation in the Co (II)-Ni (II)-HAla-DTPA systems was investigated by monitoring changes in the absorption spectra (in the range 300-1000 nm) induced by a change in solution acidity. The Hyper Spec program allows users to determine the formation constants of complex species and their spectral characteristics for a given complexation model by minimizing (via an iterative process) the spectral absorbance difference between experimental and calculated values [9]. In calculations, a large number of complexation models consisting of different sets of complex species composed of the starting components–M^{2+} (Co^{2+}, Ni^{2+}), DTPA (Dtpa), and alanine (Ala^-)–were considered. The possible formation of mononuclear homoleptic complexes $M[H_iDtpa]^{i-3}$ (i=0-5), $[MH_iAla]$ (i=0, 1), and $[MAla_i]^{2-i}$ (i=0-3); mononuclear heteroligand complexes [MAlaEdta], as well as of hetero polynuclear heteroligand complexes $[M_xM'_yAla_iDtpa]^{2x+2y-i-5}$ (x = 1–3, y = 1–3; i = 2, 4, 6, 8,

doi.org/10.31838/hiv22.02.530 Received: 19.06.22, Revised: 01.08.22, Accepted: 24.08.22

10), was taken into account. In modeling equilibria, we used fixed values of the Co (II) and Ni (II) hydrolysis constants and DTPA and 2-aminopropanoic acid (alanine) dissociation constants taken from [9]. The stability constants of homoleptic complexes and their absorption spectra were calculated during our initial investigation of binary systems (Co (II)-DTPA, Co (II)-HAla, and Ni (II)-DTPA and Ni (II)-HAla) and were subsequently used as constants in calculations of more complex systems involving two metal ions and/or two ligands. The A = *f*(pH) dependences presented below are shown only for the most characteristic wavelengths corresponding to the absorption of Co (II) (λ = 490 nm) or Ni (II) (λ = 985 nm), though the whole spectrum of absorbance was used for the calculations. Figure (1) displays, for one of the systems investigated, a good agreement between the experimental and calculated absorption spectra, as well as the spectral contributions of individual components.

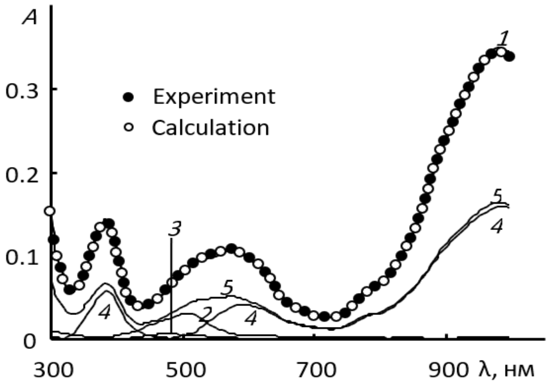


*Fig. 1: the absorption of spectra for (1) the Co (II) – Ni (II) – HAla–DTPA system at the ratio 1:1:2:1, (2) Co2+, (3) [CoDtpa]3–, (4) [NiDtpa]3–, and (5) [(CoAla)Dtpa(NiAla)]3– at pH= 5.22. CCo2+ = CNi2+ = 1.25 *10-2 mol/L*

It is necessary to have knowledge of mononuclear complexes in order to model the equilibria of formation of hetero polynuclear Co (II) and Ni (II) complexes. Stability constants and coordination numbers for these complexes with Ni(II) have been reported in[10, 11], whereas the present study deals with binary and ternary systems for Co(II) Mathematical processing of the A = *f*(pH) the curves for the binary Co(II)-DTPA and Co(II)-HAla systems has demonstrated that completely deprotonated and monoprotonated complexonates are formed in the first system, and deprotonated mono-, bis-, and tris- ligand complexes are produced in the second system (Table 1). Under the same experimental conditions, the stability constants for the Co (II) and Ni (II) complexes show that the Ni (II) complexes are more stable than the Co (II) complexes, which is typical of many other ligands that form complexes with these metals.

At a component ratio of 1:1:1, a precipitate was deposited at pH > 10 in both the Co (II)-HAla-EDTA system and the Co (II)-EDTA system, indicating that hydrolysis of Co (II) had occurred. In contrast, a ternary complex is produced in an alkaline medium by the scheme, so no precipitate is formed even when alanine is present in excess by a factor of ten.

$$[CoDtpa]^{3-} + Ala^{-} \rightleftharpoons [CoAlaDtpa]^{4-}$$

Table 1. Stability constant of Co (II) and Ni (II) complexes with 2-aminopropanoic acid and DTPA (*I* = 0.1 NaClO₄), T = (25 ± 2)C°

Complex	**Co2+**	Ni2+
	lgβ	lgβ
[MDtpa"]3–	18.39±0.06	19.91±0.05
[MHDdta]2–	22.78±0.02	23.60±0.10
[MAla]+	4.38±0.09	6.49±0.02
[MAla2]	8.06±0.06	13.91±0.08
[MAla3]–	9.64±0.06	22.78±0.14
[MAlaDtpa]4–	21.0±0.02	22.5±0.04

In order for the alanine anion to fill the empty coordination sites in the [CoDtpa]$^{3-}$ complex, two glycine rings in the complex must partially open.

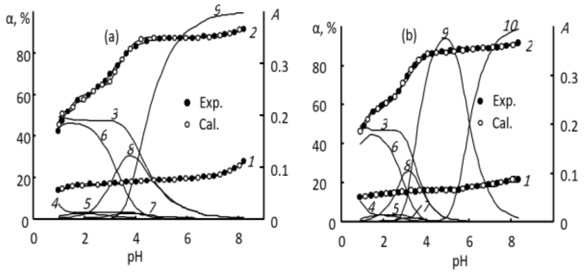


*Fig. 2. Degree accumulation (**α**) and absorbance (A) vs. **pH** in the Co(II)–Ni(II)–HAla–DTPA system at the molar ratio (a) 1:1:2:1 and (b) 1:1:4:1: curve A = f(pH) for **λ** = 490 nm (1) and (2) **λ** = 985 nm , Co2+ (3), Ni2+ (4), [CoHDtpa]2– (5), [NiHDtpa]2– (6), [CoDtpa]3– (7), [NiDtpa]3– (8), [(NiAla)Dtpa(CoAla)]3– (9), [(NiAla)2Dtpa(CoAla)2]5– (10); CCo2+ = CNi2+ = 1.25 *10-2 mol/L*

"At the 1:1:2:1 molar ratio of the components in the Co (II)-Ni (II)-HAla"-DTPA system in an acid medium, uncoordinated Co (II) ions and mononuclear complexes [NiHDtpa]2- and [NiDtpa]3- are dominating (Fig. 2a). In the range 3.0 < pH < 8.0, a binuclear heterometal complex is formed, with the maxi mal degree of accumulation α = 100 % at pH > 8.0. (It should be noted that here and hereinafter α was calculated with respect to the overall concentration of both metals.")". The heterobinuclear complex can form by the following equations (the corresponding equilibrium constants are presented in Table (2):

$$[NiDtpa]^{3-} + [CoAla_2] \overset{K_1}{\rightleftharpoons} [(NiAla)Dtpa(CoAla)]^{3-} \qquad (1)$$

$$[CoDtpa]^{3-} + [NiAla_2] \overset{K_2}{\rightleftharpoons} [(NiAla)Dtpa(CoAla)]^{3-} \qquad (2)$$

$$[NiAla]^{+} + [CoAlaDtpa]^{4-} \overset{K_3}{\rightleftharpoons} [(NiAla)Dtpa(CoAla)]^{3-} \qquad (3)$$

$$[CoAla]^{+} + [NiAlaDtpa]^{4-} \overset{K_4}{\rightleftharpoons} [(NiAla)Dtpa(CoAla)]^{3-} \qquad (4)$$

In the [(NiAla)Dtpa(CoAla)]3- complex, we can assume that the diaminoethane bridge of DTPA is shared by the octahedral coordination polyhedra of

Co (II) and Ni (II) ions; this is because the tridentate imino diacetate moiety of DTPA binds to both metal ions in an equivalent fashion. The alanine residues partially saturate the metal coordination sphere to form five - membered chelate rings.

At the 1:1:4:1 molar ratio in the Co (II)-Ni(II)-HAla-DTPA system (Fig. 2b) in an acid medium (pH<4.0), uncoordinated Co(II) ions as well as protonated and deprotonated mononuclear Ni(II) complexonates are dominating. In the range 3.0 < pH < 8.0, the heterometal complex $[(NiAla)Dtpa(CoAla)]^{3-}$ is formed, with a maximal degree of accumulation of 94 % at pH 5.0. The second complex $[(NiAla_2)Dtpa(CoAla_2)]^{5-}$ is formed at pH > 5.0 , and its 100 % yield is reached at pH > 8.0. The formation of this complex can be described by the following partial equations:

$$[NiAla_3]^- + [CoAlaDtpa]^{4-} \overset{K_5}{\rightleftharpoons} [(NiAla_2)Dtpa(CoAla_2)]^{5-} \qquad (5)$$

$$[(NiAla_2)_2Dtpa]^{5-} + [(CoAla_2)_2Dtpa]^{5-} \overset{K_6}{\rightleftharpoons} 2[(NiAla_2)Dtpa(CoAla_2)]^{5-} \qquad (6)$$

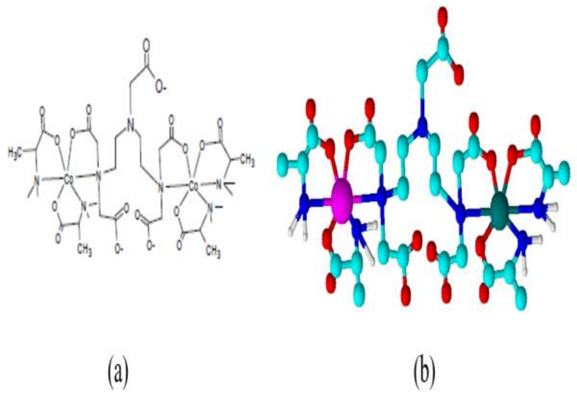
$$[CoAla_3]^- + [NiAlaDtpa]^{4-} \overset{K_7}{\rightleftharpoons} [(NiAla_2)Dtpa(CoAla_2)]^{5-} \qquad (7)$$

The equilibrium constants of these reactions and stability constants of the heterobinuclear complex are presented in Table (2).

Table 2. Equilibrium constants of reactions and stability constants of Co (II) and Ni(II) complexes with 2-aminopropanoic acid and DTPA (I = 0.1 NaClO4), T = (25±2)C°

Complex	№ of reaction	lgKi	lgβ
$[(NiAla)Dtpa (CoAla)]^{3-}$	(1)	5.06	33.06 ± 0.01
$[(NiAla)Dtpa (CoAla)]^{3-}$	(2)	4.38	
$[(NiAla)Dtpa (CoAla)]^{3-}$	(3)	6.78	
$[(NiAla)Dtpa (CoAla)]^{3-}$	(4)	6.18	
$[(NiAla_2) Dtpa (CoAla_2)]^{5-}$	(5)	5.34	39.20 ± 0.05
$[(NiAla_2) Dtpa (CoAla_2)]^{5-}$	(6)	6.38	
$[(NiAla_2) Dtpa (CoAla_2)]^{5-}$	(7)	7.06	
$[(NiAla_2) Dtpa (CoAla_2)_2]^{4-}$	(8)	5.16	53.47 ± 0.01
$[(CoAla_2) Dtpa(NiAla_2)_2]^{4-}$	(9)	4.4	54.01 ± 0.04
$[(NiAla_2)_2Dtpa (CoAla_2)_2]^{4-}$	(10)	7.73	65.40 ± 0.01
$[(CoAla_2)_3Dtpa (NiAla_2)_2]^{5-}$	(11)	9.11	74.84 ± 0.05
$[(CoAla_2)_3Dtpa (NiAla_2)_2]^{5-}$	(12)	6.27	75.02 ± 0.01

In complexes with the components arranged in a 1:1:4:1 molar ratio, the coordination sphere of the metal ions is completely saturated with alanine, and each iminodiacetate moiety of DTPA is connected to the metal ion only through one carboxyl group, leaving the other free. The 3D optimization-derived schematic structure (a) and model (b) of a molecule from this complex, can be visualized as follows:



Mathematical modeling in the Co (II)-Ni (II)-HAla-DTPA system with the 1:2:6:1 and 2:1:6:1 molar ratios of the components has shown that uncoordinated Co (II) and Ni (II) ions as well as mononuclear Ni^{2+} complexes with DTPA are dominating in an acid medium. In weak acid and neutral solutions, homo- and heterobinuclear complexes with DTPA and alanine are formed (Fig. 3).

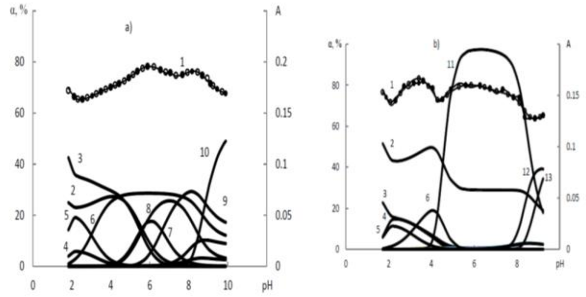


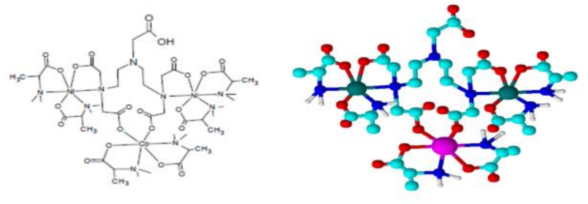
*Fig.3. Accumulation fraction **(α)** and absorbance **(A)** of the complexes in the Co(II)–Ni(II)–HAla–Dtpa system versus pH at a ratio (a) 1:2:6:1 and (b) 2:1:6:1: (1) A = f(pH), (2) Co2+, (3) Ni2+, (4) [CoHDtpa]2–, (5) [NiHDtpa]2–, (6) [NiDtpa]3–, (7) [NiAla]+, (8) [CoAla]+, (9) [CoAla2], (10) [(CoAla)Dtpa(NiAla)2]4–, (11) [(CoAla)Dtpa(NiAla)]4–,(12) [(CoAla)2Dtpa(NiAla)2]4–, (13) [(CoAla)2Dtpa(NiAla)]4–, CCo+2= CNi+2 =1.25·10–2 mol/L, **λ**=985 nm.*

The maximum degree of accumulation 100 % of trinuclear complexes is observed at pH > 8.0. Trinuclear heteroligand complexes are formed at pH > 4.0 by the following equations (the corresponding equilibrium constants are presented in Table (2).

$$[NiAla_2] + [(CoAla_2)_2Dtpa]^{5-} \rightleftharpoons [(CoAla_2)_2Dtpa(NiAla_2)]^{5-} \qquad (8)$$

$$[CoAla_2] + [(NiAla_2)_2Dtpa]^{5-} \rightleftharpoons [(CoAla_2)Dtpa(NiAla_2)_2]^{5-} \qquad (9)$$

DTPA diaminoethane bridge and the bidentate coordination of two imino diacetate groups are thought to connect the coordination spheres of the two metal ions in the trinuclear complex. The two remaining acetate groups from various "halves" of the DTPA molecule serve to bind the third metal ion. Each metal ion also has two alanine residues in its coordination sphere. As an example, the schematic structure (a) and the model of the [(CoAla2) Dtpa (NiAla2)2]4–complex (b) obtained by 3D optimization are shown below:



Co (II)-Ni (II)-HAla-DTPA is a system in which different homo- and heterobinuclear complexes predominate in solution, as predicted by a mathematical model of the speciation equilibrium between the components at a 2:2:8:1 molar ratio in the range 3.0 pH 8.0. At pH = 6.0, the tetranuclear [(NiAla2)2Edta (CoAla2)2]5– complex accumulates in solution (Figure (4)).

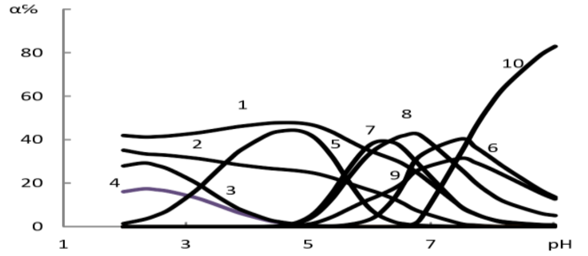
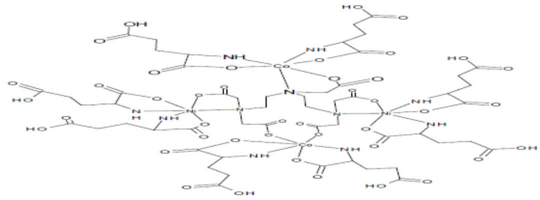


Fig. 4: Degree of accumulation (α) vs. pH in the Co(II)–Ni(II)–HAla–DTPA system at the molar ratio 2:2:8:1 (1) Co2+, (2) Ni2+, (3) [NiHEdta]–, (4) [CoHEdta]–, (5) [NiEdta]3–,(6) [NiAla2], (7) [(NiAla)2Dtpa]3–, (8) [(NiAla)Dtpa(CoAla)]3–, (9) [(CoAla)2Dtpa]3– and (10) [(NiAla2)2Edta(CoAla2)2]5–. CCo+2= CNi+2 =1.25·10–2 mol/L.

The formation of the tetranuclear complex can be represented by one of several possible equations:

2[CoAla2] + [(NiAla2)2Dtpa]5– ⇌ [(CoAla2)2Dtpa (NiAla2)2]5 (10)

The structure of the tetranuclear complex can be schematically presented in the following manner:



The formation pentanuclear complex can be described by the following partial equations:

3[CoAla2] + [(NiAla2)2Dtpa]5– ⇌ [(CoAla2)3Dtpa(NiAla2)2]5– (11)

3[NiAla2] + [(CoAla2)2Dtpa]5– ⇌ [(CoAla2)2Dtpa(NiAla2)3]5– (12)

Thus, “our results are evidence that, when the Co (II) and Ni (II) ions are in excess with respect to DTPA and an additional ligand, alanine, is present in solution, heteropolynuclear heteroligand complexes [CoxNiyAlazEdta]2(x + y) – z – 4 (x = 1–2, y = 1–2, z = 2, 4, 6, 8, 10) are formed. Similar electronic structures and close ionic radii of Co (II) (3d7, r = 72 pm) and Ni (II) (3d8, r = 69 pm) are responsible for their good compatibility in polynuclear ethylene trimine penta-acetates and makes it possible to substitute one cation for the other without noticeable changes in the complex structure. The stability of the heteropoly-nuclear complexes is intermediate between the stabilities of the corresponding homopoly-nuclear complexes and increases in the following series “:

$$[(CoAla)_2Dtpa]^{3-} < [(CoAla)Dtpa(NiAla)]^{3-} < [(NiAla)_2Dtpa]^{3-}$$

lgβ 32.0 33.06 33.64

$$[(CoAla_2)_3Dtpa]^{5-} < [(CoAla_2)_2Dtpa(NiAla_2)]^{5-} < [(NiAla_2)_3Dtpa]^{5-}$$

lgβ 52.95 53.47 54.57

$$[(CoAla_2)_4Dtpa]^{5-} < [(CoAla_2)_2Dtpa(NiAla_2)_2]^{5-} < [(NiAla_2)_4Dtpa]^{5-}$$

lgβ 64.84 65.40 67.10

In all polynuclear complexes, DTPA acts as a structure - forming tri- or bidentate (with respect to each metal cation) ligand; in the tetranuclear complexes, eight of the ten donor atoms of DTPA are involved in coordination, which is possible because of the high flexibility of the DTPA molecule. For stabilization of polynuclear ethylene trimine penta-acetates, a stoichiometric excess of the secondary bidentate ligand is necessary to achieve complete saturation of the coordination spheres of all metal ions.

References

1. V. V. Skopenko, A. Yu. Tsivadze, L. I. Savranskii, and A. D. Garnovskii, Coordination Chemistry: A Textbook (Akademkniga, Moscow, 2007) [in Russian].
2. G. F. Hameed, F. Y. Wadday, N. S. Salman,2021, Modeling and Thermodynamic Values of Complex Equilibrium of Cobalt (II) with Diethylenetriaminepentaacetic Acid in Aqueous Solution, Indones. J. Chem, 21(3), 644-650.

3. El-Sherif, A.A, Shoukry, M.M, Abd Elkarim, A.T, and Barakat, M.H, 2014, Protonation equilibria of biologically active ligands in mixed aqueous organic solvents, Bioinorg. Chem. Appl, 2014, 626719.
4. F. Martak, N.W.D. Cahyani, Z.V. Nugraheni, and W.P. Utomo, 2016, Properties and toxicity of cobalt (II) complex with 2,4,5-triphenyl-1H-imidazole ligand, Indones. J. Chem, 16 (3), 260–267.
5. Rawat, K.S, Kumar, R, and Singh, S.K, 2019, Topographical distribution of cobalt in different agro-climatic zones of Jharkhand state, India. Geol. Ecol. Landscapes 3, 14–21.
6. V. I. Kornev, G. F. Alabdulla, T. N. Kropacheva, and E. V. Batueva, 2017, Formation of Heteropolynuclear Cobalt (II) and Nickel (II) Complexonates with EDTA and 2-Aminopropanoic Acid, J. of In. Chemistry, 62 (5), 659–664.
7. www.hyperquad.co.uk/hyss.htm (HySS2008/Hyperquad Simulation and Speciation).
8. www.acdlabs.com/resources/freeware/chemsketch (ACD/ChemSketch for Academic and Personal Use).
9. www.nist.gov/srd/nist46.cfm (NIST Standard Reference Database 46. Critically Selected Stability Constants of Metal Complexes: Version 8.0).
10. Singh, J, Srivastav, A.N, Singh, N, and Singh, A, 2019, "Stability constants of metal complexes in solution" in Stability and Applications of Coordination Compounds, IntechOpen Limited, London, UK, 90183.
11. Z. Tamiji, A. Yazdanipour, and A. Niazi, 2018, Spectrophotometric and thermodynamic study on the dimerization equilibrium of neutral red in the water and micelle environments by chemometrics methods, Int. J. Exp. Spectrosc. Tech, 3, 15.