

UDC 543.42:546.74:54.412. 2

STUDY INTO COMPLEX FORMATION OF NICKEL (II) WITH 1-PHENYL-2-(2-HYDROXY-4-NITROPHENYLHYDROZO) BUTANEDIONE-1,3 IN THE PRESENCE OF THIRD COMPONENTS

¹V.I. Mardanova, ²Sh.A. Tahirli, ¹A.Q. Babaev, ¹F.M.Chiragov

¹Baku State University

Z. Xalilov str., 23, AZ 1148 Baku Azerbaijan Republic; e-mail:vusala_chem@mail.ru

²Lankaran State University

50, H. Aslanov ave., Lankaran, Azerbaijan Republic

Received 13.02.2019

Abstract: The effect of the third components α, α' -dipyridyl (α, α' -dip), ethylene diamine (Ed) and phenantroline (Phen) on the complexation of nickel (II) with 1-phenyl-2-(2-hydroxy-4-nitrophenylhydrozo)butanedione-1,3 was studied. NiR and mixed ligand (NiR α, α' -dip, NiREd and NiRPhen) complex compounds are formed at pH 6, 5, 4.5 and 5, respectively. The ratio of the reacting components in the composition of homogeneous and mixed ligand complexes was established and the interval of subordination to the Beer's law determined. The developed methodology was applied to specify nickel (II) in the river water.

Keywords: nickel (II), mixed ligand complex, α, α' -dipyridyl, ethylene diamine and phenantroline
DOI: 10.32737/2221-8688-2019-2-316-322

Introduction

Enhanced content of compounds of heavy metals has a negative effect on human health. Note that nickel is pertaining to metals of the above-mentioned sort, so it is essential to monitor the nickel concentration in the samples of natural and waste waters.

There are different reagents for spectrophotometric determination of nickel (II), including β -diketones and oximes [1-11]. Atomic absorption spectrometry of a flame and graphite furnace and spectrophotometric

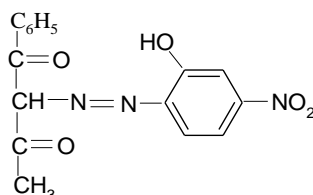
methods provide an accurate and rapid determination of nickel in natural and waste waters.

In the present work, the complexation of nickel (II) with 1-phenyl-2-(2-hydroxy-4-nitrophenylhydrozo) butanedione-1,3(R) in the presence of α, α' -dipyridyl (α, α' -dip), ethylenediamine (Ed.) and phenantroline (Phen) was explored through the use of the photometric method.

Materials and methods

Solutions and reagents: The reagent was synthesized according to the procedure [12, 13], its composition and structure were

determined by the methods of elemental analysis and IR spectroscopy.



Calculated: % C – 58.72; H-3.98; N-12.84, N-8.14, O-24.46

Found: %C – 58.85; H-4.09; N-12.99, N-8.44, O-24.77.

In this work, $1 \cdot 10^{-3}$ M ethanol solution of the reagent and water – ethanol solutions (3:7) of the third components were used and prepared by dissolving their exact weights. A solution of nickel (II) ion was prepared from $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ by dissolving an exact sample in water. To create the required acidity, ammonium acetate buffer solutions were used. All reagents used are qualified not lower than

analytic reagent grade.

Instrumentation: The optical density of the solutions was measured on a Lambda 40 spectrophotometer (Perkin Elmer) and a KFK-2 photocolormeter in a cuvette with a layer 1 cm thick. The acidity of the buffer solutions was measured on a PHS-25 ionomer adjusted with standard buffer solutions.

Results and its discussion

We found that R (in ethyl alcohol) at pH 6 has an absorption band with a maximum ($\lambda = 425$ nm). Under these conditions, it forms a complex with nickel (II) (absorption maximum at 452 nm). The study of the complexes obtained in the presence of α , α' -dipyridyl, ethylenediamine and phenanthroline in a wide pH range showed that under the influence of the third component mixed ligand complexes are formed: Ni (II) -R α , α' -dip ($\lambda =$

482 nm), Ni (II) Red ($\lambda = 478$ nm) and Ni (II) Rphene ($\lambda = 481$ nm). The color of the reagent and complexes depends on pH of the medium, therefore, the absorption spectra during complexation were studied in terms of control experiment R- α , α' -dip, R-Ed and R-Phen. Under the influence of the third components, the bathochromic effect is observed in all the resulting mixed-ligand complexes (Fig. 1).

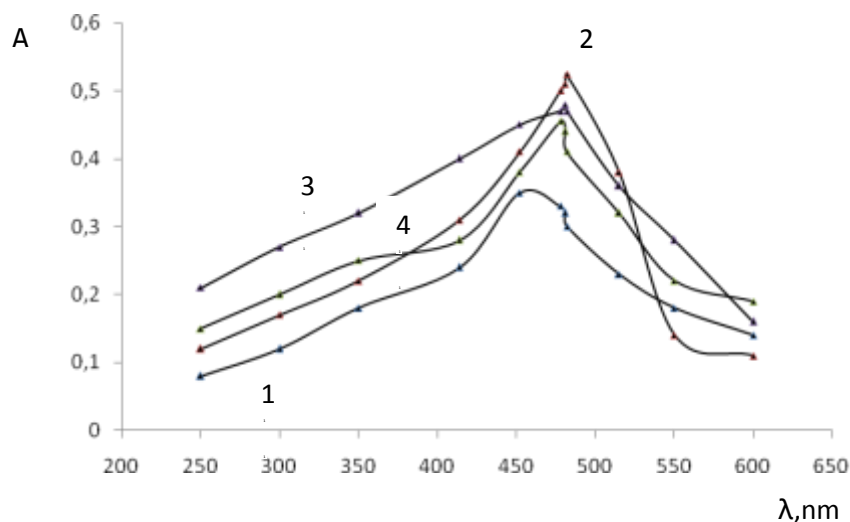


Fig. 1. Absorption spectra of solutions of complexes with nickel (II)
1 – NiR, 2–NiR α , α' -dip. 3- NiRPhen, 4- NiREd $C_{\text{Ni}} = 4 \cdot 10^{-5}$ M ; $C_{\text{R}} = 1 \cdot 10^{-4}$ M

The study into dependence of optical density on the pH of the solution showed that when interacting with α , α' -dipyridyl, ethylene diamine and phenanthroline, the optimal conditions for complexation shift to acidic pH 5, 4.5 and 5, respectively (Fig. 2). To select the optimal conditions, the effect of the concentration of reacting substances, the temperature and the effect of time on the

formation of the binary and mixed-ligand complexes were studied.

The output of the NiR complex is maximum at a concentration of $8 \cdot 10^{-5}$ M R, NiR- α , α' -dip at $8 \cdot 10^{-5}$ M R and $8 \cdot 10^{-4}$ M α , α' -dip, NiRPhen at $8 \cdot 10^{-5}$ M R and $8 \cdot 10^{-4}$ M Phen, NiREd at $8 \cdot 10^{-5}$ M R and $8 \cdot 10^{-4}$ M Ed. All complexes are formed immediately after

mixing the solutions of the components and differ in their stability.

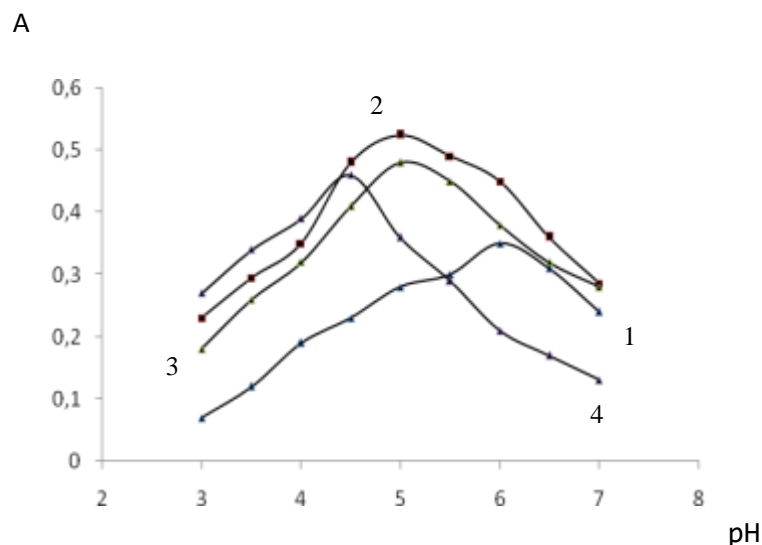


Fig. 2. Dependence of the optical density of nickel solution (II) complexes on pH in the presence/absence of third components at λ_{opt} . in terms of control experience: 1 –NiR, 2- NiR α,α' -dip. 3- NiRPhen, 4- NiREd

The stability constants and the ratios of the components in the composition of the resulting complexes were established through methods of isomolar series, the relative yield of the Starik-Barbanel and the equilibrium shift [14].

The Starik-Barbanel method provides an accurate estimate of the stoichiometric coefficients and can be applied to any

stoichiometric reaction, regardless of the stability of the concentration of interacting substances.

To determine the composition of the complex using this method, prepare a series of solutions: changing the concentration of the reagent $C_{Me} = \text{const}$. Then the dependence is plotted in $A/C_R - A/A_{max}$ coordinates.

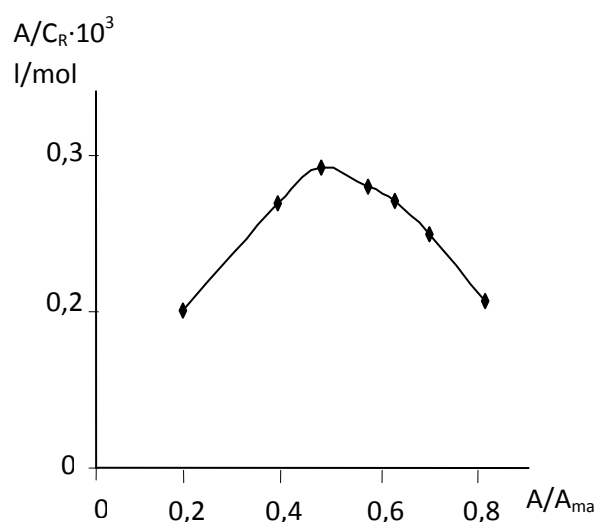


Fig. 3. Determination of the composition of the NiR complex by the method of the StarikBarbanel

$$C_{R_2}$$

If the reaction equation is $Me + nR \Rightarrow MeR_n$, then n is calculated in accordance with the following expression:

$$n = \frac{1}{1 - \frac{A}{A_{\max}}} ; \quad A/C_R = \max$$

Fig. 3 shows the composition of the fraction of NiR complex components revealed by the Starik-Barbanel method.

The ratio of components in the NiR complex is 1: 2.

The study showed that the ratio of components in mixed-ligand complexes is 1: 2: 1 (NiR α , α' -dip, NiREd) and 1: 2: 2 NiRPhen.

The molar absorption coefficients, the linearity range of the calibration curve for the determination of nickel(II), and other analytical characteristics of the reagents are given in Table 1.

Table 1. Spectrophotometric characteristics of the complexes

Complex	pH	λ_{\max} , nm	$\Delta\lambda$, nm	$\varepsilon \cdot 10^{-4}$, l/mol·sm	Me:R	Subordination to the Beer's law, mkg/ml	lgK
NiR	6	452	27	0.875±0.04	1:2	0.46-2.78	8.24±0.04
NiR α , α' -dip	5	482	30	1.31±0.03	1:2:1	0.13 - 2.32	9.19 ±0.06
NiREd	4.5	478	26	1.128±0.02	1:2:1	0.11 - 2.32	9.23±0.06
NiR Φ Phen	5	481	29	1.205±0.03	1:2:2	0.11 - 2.32	9.31±0.04

To establish the influence of the stability of associates and their complexes on the detection limit of nickel (II), the

coefficients of the calibration curve equation were determined by the least squares method [15].

$$\begin{cases} \sum A = a\sum C + nb \\ \sum AC = a\sum C^2 + b\sum C \end{cases}$$

Here A is optical density of complex, C is a concentration of nickel (mkq/ml), n is a number of experiments. Calculation of results show that linear relationship of $A = f(C)$ for the reaction of complex formation. Nickel with reagent can be expressed by the following equations:

$$\begin{aligned} A &= (0.20 \pm 0.02)c + (2.95 \pm 0.12)10^{-2} && \text{NiR} \\ A &= (0.50 \pm 0.01)c + (1.41 \pm 0.10)10^{-2} && \text{NiR}\alpha, \alpha' \text{-dip} \\ A &= (0.45 \pm 0.01)c + (1.32 \pm 0.12)10^{-2} && \text{NiRPhen} \\ A &= (0.35 \pm 0.01)c + (1.74 \pm 0.12)10^{-2} && \text{NiREd} \end{aligned}$$

As can be seen, with an increase in the slope angle (a) of linear equations, the molar

absorption coefficients of the complexes increase.

The effect of foreign ions on the complexation of nickel (II) with R in the absence and in the presence of third components was studied. It found that in the presence of third components the selectivity of complex formation reactions significantly increases (Table 2). These reagents are more selective for the spectrophotometric determination of nickel (II) compared to reagents known from the literature [11]. The developed methodology has been applied to determine nickel (II) from the water of the rivers.

Table 2. Admissible ratios of foreign ions to nickel (II) when it is determined in the form of homogeneous and mixed ligand complexes (5% error)

Foreign ions	R	R- α,α' -dip	R-ЕД	R-Phen	2 - [(2-mercaptophenyl imino) methyl] phenol [11]
Na(I)	*	*	*	*	300
K(I)	*	*	*	*	300
Mg(II)	166	248	496	579	250
Ca(II)	413	689	827	965	250
Ba(II)	236	236	472	944	
Zn(II)	112	224	448	672	300
Cd(II)	113	270	215	386	50
Co(II)	20	30	61	81	20
Cu(II)	**	22	44	110	20
Mn(II)	94	189	293	569	200
Al(III)	93	279	456	665	250
Fe(III)	2	19	96	135	20
Cr(III)	179	258	358	537	20
Pb(II)	21	35	71	142	
V(V)	87	123	175	263	
W(VI)	197	952	1268	1903	
Mo(VI)	248	248	372	620	
F ⁻	319	6379	1276	6379	
C ₂ O ₄ ²⁻	22	43	217	434	
HPO ₄ ²⁻	123	617	1234	2468	300
Citric acid	116	231	462	462	
Tartaric acid	517	1551	1551	2586	
Thiourea	26	131	262	786	

Note: * does not interfere, ** interferes

Determination of nickel in rivers water.

For the analysis, 1 liter of water from a river bank was taken provided that non-boiling evaporated water obtains a precipitate. The resulting precipitate was dissolved in 5 ml of HNO₃ and transferred to a 50 ml flask and

diluted to the mark with distilled water. When determining nickel (II) by the photometric method, an aliquot part of the obtained solution is placed in a 25 ml flask, 2 ml of 1·10⁻³M R and 2 ml of 1·10⁻²M α,α' -dipyridyl are diluted to the mark with pH 5.

Table 3. Results of nickel determination (II) in river waters (n=5, P=0,95)

Water sample	Revealed by photometric method, Ni, mg/l	Revealed Ni, mg/l (ICP-OES thermo ICAP 7400 Duo)
I sample river water	0.160±0.005	0.170±0.004
II sample river water	0.175±0.004	0.190±0.003

The optical density of the solutions is measured at $\lambda = 490$ nm in a cuvette with $l = 1$ cm on KFK-2 relative to the test solution.

The correctness of the procedure was checked using the "ICP-OES thermoICAP 7400 Duo" instrument. The results are

presented in table. 3

These methods can be applied for determination of nickel (II) in different natural and artificial objects. Elaborated methods can be used for nickel determination (II) in various natural and artificial water facilities.

REFERENCES

1. Xiao-Dong Li and Qing-Zhou Zhai. Spectrophotometric determination of arsenic nickel with chlorophosphonazo-III. *Chemical Science Transactions*. 2014, vol. 3, no. 3, pp.1023-1026.
2. Sarma L.S, Kumar J.R, Reddy K.J, Thriveni T., Reddy A.V. Development of highly sensitive extractive spectrophotometric determination of nickel(II) in medicinal leaves, soil, industrial effluents and standard alloy samples using pyridoxal-4-phenyl-3-thiosemicarbazone. *Trace Elem Med Biol*. Sep 19. 2008, vol. 22, no. 4, pp.285-295.
3. Zaijun Li, Jiaomai Pan, Jan Tang. Determination of nickel in food by spectrophotometry with o-Carboxyl benzene diazoaminoazobenzene. *Analytical Letters*, 2002, vol. 35, no. 1, pp.167-183.
4. Qiufen H., Guangyu Y., Zhangjie H. and Jiayuan Y. Determination of nickel with 2-(2-quinolylazo)-5-diethylaminoaniline as a chromogenic reagent. *Analytical Sciences*. 2003, vol. 19, no. 10, pp.1449-1458.
5. Banjit Barman, Sudarsan Barua. Spectrophotometric determination of nickel(II) by using bis-[2,6-(2'-hydroxy-4'-sulpho-1'-naphthylazo)]pyridine disodium salt. *Asian Journal of Chemistry*. 2009, vol. 21, no.7, pp. 5469-5474.
6. Jagasia Pooja V., Dave D.P. Sequential separation and spectrophotometric determination of cobalt and nickel using α -oximinoacetoacetanilide-benzoylhydrazone *Journal of the Indian Chemical Society*. 2003, vol. 80, no. 2, pp. 145-146.
7. Haji Shabani A.M., Dadfarnia S., Shahbaazi Z. and Jafari A.A. Extraction-spectrophotometric determination of nickel at microgram level in water and wastewater using 2-[(2-mercaptophenylimino)methyl]phenol. *Chemical Society of Ethiopia*. 2008, vol. 22, no. 3, pp. 323-329.
8. Prashant A. Borade; Anandkumar S. Gupta; Barhate V.D. Development of extractive spectrophotometric determination of nickel(II) with isatin-3-semicarbazone (hisc) as an analytical reagent. *Asian Journal of Research in Chemistry*. 2011, vol. 4I, no. 12, pp. 1905-1913.
9. Shar G.A. and Soomro G.A. Derivative spectrophotometric determination of nickel(II) with 1 nitroso-2-naphthol in aqueous phase. *Jour.Chem.SocPak*. 2006, vol. 28, no. 4, pp. 331-336.
10. Prasad N. B. L., Hussain Reddy K. Spectrophotometric determination of nickel(II) in aqueous medium using 1-phenyl-1,2-propanedione-2-oxime. *Talanta*. 2004, vol. 62, no. 5, pp. 971-976.
11. Haji Shabani A.M., Dadfarnia S., Shahbaazi Z. and Jafari A.A. Extraction-spectrophotometric determination of nickel at microgram level in water and wastewater using 2-[(2-mercaptophenylimino)methyl]phenol. *Chemical Society of Ethiopia*. 2008, vol. 22, no. 3, pp. 323-329.
12. Problems of chemistry and use of β -diketonates of metals. Under ed. Spitsyna V.I. Moscow: Nauka Publ., 1982, 264 p.
13. Busev A.I. Synthesis of new organic reagents for inorganic analysis. Moscow: MGU Publ., 1972. 245 p.
14. Bulatov M.I., Kalinkin I.P. A practical guide to photometric and

- spectrophotometric method of analysis. Leningrad: Himiya Publ., 1972, 407 p.
15. Khudyakova T.A., Kreshkov A.P. Theory and practice of conductometric and chronoconductometric analysis. Moscow: Himiya Publ., 1976, 304 p.

NİKELİN(II) 1-FENİL-2-(2-HİDROKSİNİTROFENİLHİDRAZO) BUTADİON-1,3 –REAGENTİ İLƏ ÜÇÜNCÜ KOMPONENTLƏR İŞTİRAKINDA KOMPLEKSƏMƏLƏGƏTİRMƏSİNİN TƏDQIQI

¹V.İ. Mərdanova, ²Ş.A. Tahirli, ¹Ə.Q. Babayev, ¹F.M. Çıraçov

¹Bakı Dövlət Universiteti

AZ 1148 Bakı, Z.Xəlilov küç., 23; e-mail: vusala_chem@mail.ru

²Lənkəran Dövlət Universiteti

Nikelin(II) 1-fenil-2-(2-hidroksinitrofenilhidrazo)butadion-1,3 reagenti ilə üçüncü komponentlər α,α' -dipiridil (α,α' -dip), etilendiamin (Ed) və fenontrolin (Fen) iştirakında kompleksəmələgətirməsi öyrənilmişdir. Birli (NiR) və qarışıqlıqandlı (Ni(II)-Ra, α' -dip, Ni(II)-REd və Ni(II)-RFen) komplekslər uyğun olaraq pH 6, 5, 4.5 və 5 əmələ gəlir. Qarşılıqlı təsirdə olan komponentlərin tərkibi binar və qarışıqlıqandlı komplekslərdə təyin edilmişdir. Ber qanununa tabeçilik intervalı təyin edilmişdir. Nikelin çay sularında təyin edilməsi üçün metodika işlənib hazırlanmışdır.

Açar sözlər: nikel(II), qarışıqlıqandlı komplekslər, α,α' -dipiridil, etilendiamin, fenontrolin.

ИЗУЧЕНИЕ КОМПЛЕКСООБРАЗОВАНИЯ НИКЕЛЯ(II) С 1-ФЕНИЛ-2-(2-ГИДРОКСИ-4-НИТРОФЕНИЛГИДРОЗО)БУТАДИОНОМ-1,3 В ПРИСУТСТВИИ ТРЕТЬИХ КОМПОНЕНТОВ

¹V.И. Марданова, ²Ш.А. Тахирли, ¹А.Г. Бабаев, ¹Ф.М. Чырагов

¹Бакинский Государственный Университет

AZ 1148 Баку, ул. З.Халилова, 23; e-mail: vusala_chem@mail.ru

²Ленкоранский Государственный Университет
Азербайджан, г. Ленкорань, пр.А.Асланова,50

Изучено влияние третьих компонентов α,α' -дипиридила (α,α' -дип), этилендиамина (Ed) и фенантролина (Фен) на комплексообразование никеля(II) с 1-фенил-2-(2-гидрокси-4-нитрофенилгидрозо)бутадиионом-1,3. Однородно- (NiR) и смешанолигандные (Ni(II)-Ra, α' -дип, Ni(II)-Red, Ni(II)-RФен) комплексные соединения образуются при pH 6, 5, 4.5 и 5, соответственно. Установлено соотношение реагирующих компонентов в составе однородно- и смешанолигандных комплексов. Определен интервал подчинения закону Бера. Разработанная методика применена для определения никеля(II) в речной воде.

Ключевые слова: никель(II), разнолигандный комплекс, α,α' -дипиридил, этилендиамин и фенантролин