COMPLEX FORMATION IN A LIQUID-LIQUID EXTRACTION SYSTEM CONTAINING NICKEL (II), 2,6-DITIOL-4-ETYLPHENOL AND BATHOPHENANTROLINE

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ABSTRACT

Complex formation and liquid-liquid extraction were studied in a system containing nikel(II), 2,6-ditiol-4-etylphenol (DTEP), bathophenantroline (BPhen), water, and chloroform. The effect of some experimental parameters (pH, shaking time, concentration of DTEP, and concentration of BPhen was systematically investigated, and the optimum conditions for nickel extraction as an ion-association complex, Ni(DTEP) (BPhen)$_2$, were found. The following key equilibrium constants were calculated: constant of stability ($\lg\beta$ = 19.08), constant of distribution ($\log K_D = 2.09 \pm 0.01$), and constant of extraction ($\lg K_{ex} = 18.67$). Beer's law was obeyed for Ni concentrations up to 16 μg $\times$ mL^{-1} with a molar absorptivity of 2.83 x 10^4 L mol^{-1} cm^{-1} at λ_{max} = 475 nm. Some additional characteristics, such as limit of detection, limit of quantification, and Sandell's sensitivity, were estimated as well.

KEYWORDS: Spectrophotometry; nickel(II), 2,6-ditiol-4-etylphenol, water, chloroform.

1. INTRODUCTION

Nickel is widely used in electroplating, the manufacture of Ni-Cd batteries, rods for arc welding, pigments of paints, ceramic, surgical and dental prostheses, magnetic tapes and computer components and nickel catalysts. Nickel enters waters from dissolution of industrial processes and waste disposal. Nickel is essential constituent in plant urease. Jack beans and soybeans generally contain high concentration of nickel.[1]

Nickel-containing sewage is harmful after ingress into water. This fact explained the importance of the monitoring of nickel concentration in natural and waste water samples. Flame and graphite furnace atomic absorption spectrometry and spectrophotometric methods provides accurate and rapid determination of nickel in natural and waste waters.[2] However, very frequently a direct determination cannot be applied due to low concentration of analyte or matrix interferences.

Several analytical methods have been used for nickel determination, including flame atomic absorption spectrophotometry[3], graphite furnace atomic absorption spectrometry[4], electrothermal atomic absorption spectrometry[5], atomic fluorescence spectrometry[6], inductively coupled plasma-optical emission spectrometry[7], and spectrophotometry.[8, 9, 10, 11, 12]

The methods involving spectrophotometry are rather poplar due to their simplicity, inexpensive instrumentation and easy automation. Nickel(II) chelates of several ligands like diphenylcarbazone, diphenylthiocarbazone, 8-quinolinol and its substituted analogues produce intense absorption in the optical spectra, in the visible range, which is characteristic of the ligand itself. Structural changes occurred in the nickel(II) chelates on addition of nitrogen bases forms adduct which gives rise to profound spectral changes. Such bathochromic and hypsochromic shifts observed in the visible region of the spectra of nickel(II) chelates of dithizone, dipheylcarbazone, 8-quinolinol, methylsubstituted 8-quinolinols, substituted diphenylcarbazones and dithizones on addition of nitrogen bases. These were employed for the determination of adduct formation constants.[13, 14, 15]

Oxyphenolate and dithiophenolate complexes of nickel insoluble in chloroform, while mixed - ligand complexes with hydrophobic amines and aminophenols easily dissolve in various organic solvents.[16- 23]

In the present paper we study the complex formation in a liquid-liquid extraction system containing Ni(II), 2.6-dithiol-4-ethylphenol (DTEP) and bathophenantroline (BPhen), and show the potential of this system for Ni(II) determination in real samples.

2. Experimental

2.1. Reagents and Apparatus

The standard solution (1mg / ml) Ni (II) was prepared by dissolving in water an exact linkage $(NH_4)_2Ni(SO_4)_2 \times 6H_2O$ in water containing 2 ml conc. H_2SO_4.[15]

Solutions of DTEP and BPhen in chloroform (0.01M) were used. DTEP were synthesized according to the procedure.[24] Their purity was verified by melting point determination and pa-per chromatography. To create the optimal acidity, 0.1M solutions of KOH and HCl or ammonium acetate buffers were applied. Acetate buffer solution, prepared by mixing of 2 $mol \times L^{-1}$ aqueous solutions of CH_3COOH and NH_4OH.

The extractant was purified chloroform

The absorbance of the extracts was measured using a SF 26 spectrophotometer (USSR) and KFK 2 photocolorimeter (USSR). Glass cells with optical path of 5 or 10 mm were used. pH of aqueous phase was measured using an I-120.2 potentiometer with a glass electrode. Muffle furnace was used for dissolution of the samples.

2.2. General Procedure

2.2.1. General procedure for the determination of nikel (II)

Portions of stock solutions of nikel(II) varying from 0.1 to 1.0 mL with a 0.1-mL step, a 2.4 mL portion of a 0.01 M solution of DTEP, and a 2.2 mL portion of a 0.01M solution of BPhen were placed in to calibrated test tubes with ground-glass stoppers (the volume of the organic phase was 5 mL). The required value of pH was adjusted by adding 1M HCl. The volume of the aqueous phase was increased to 20 mL using distilled water. In 15 minnute after the complete separation of the phases, the organic phase was separated from the aqueous phase and the absorbance of the extracts was measured on KFK-2 at room temperature and 440 nm (l=0.5cm).

2.2.2. Determination of Nickel (II) in steel

A weighed sample of 0.2 g was dissolved in 20 ml of H_2SO_4 (1: 1) was oxidized with a few drops of concentrated nitric acid and evaporated twice lo vapor SO_3. The precipitated salt was dissolved in 20 ml of 15% tartaric acid under heating, the solution was cooled, adjusted with water to 100 ml in a volumetric flask, stirred and filtered. An aliquot of 5 ml was put into a separatory funnel, was added 1 ml of 10% hydroxylamine solution, 1 ml of 3% ascorbic acid and was determined cobaltusing the proposed procedures.

2.3.3. Determination of Ni (II) in sewage water and Bottom sediments

1l taken for analysis of waste water is evaporated to obtain a precipitate, do not boil. The precipitate was dissolved in 5 ml of HNO_3, was transferred to a 50 ml flask and diluted to the mark with water.

3. RESULTS AND DISCUSSION

Ni(II) reacts with 2.6-dithiol-4-methylphenols (DTEP) and gives a yellow colored complexes. These complexes are insoluble in non-polar solvents. Experiments on electromigration in a U-shaped tube and on sorption on EDE-10P (EDE- ethylenediamine, epichlorohydrin; 10- serial number of the brand: P- means that the matrix has a macroporous structure) anion exchangers have demonstratedthe anionic nature of single-ligand complexes, in the electromigration study of the complexes, it was found that the yellow dithiophenolate complexes of Nikel (II) moved to the cathode. When the sign of the charge of the single-ligand complexes was determined by ion chromatography, the EDE-10P anion exchanger completely absorbed the colored component of the solution. When hidrophob amins (BPhen) were introduced into the system, the extraction of these compounds into the organic phase as a mixed-ligand complex (MLC) was observed.

3.1. The choice of the extractant

Different organic solvents like chloroform, 1, 2-dichloroethane, tetrachloromethane, dichloromethane, benzene, chlorobenzene, toluene, xylol, isobutanol, isoamyl alcohol, cyclohexane, ethyl acetate, 1-butanol, isoamylacetate and their mixes were tried for extraction. Extractibility of complexes was estimated in coefficient of distribution and extent of extraction. Thus basicity of amines has no noticeable impact on conditions and extraction of complexes. Fast division of layers and the maximum value of molar coefficient of absorption were received at extraction of complexes by chloroform. After a single extraction with chloroform, 99.2% of copper was extracted as an MLC (in a case the dichloroethane and carbontetrachloride was removed 96.6% of nickel). Further researches were conducted with chloroform. The concentration of nickel in the organic phase was determined with dimethylglyoxime[15] by photometric measurements after back extraction, while in the aqueous phase it was determined by the difference.

3.2. Absorption spectra

Spectra of the extracted ternary Ni-DTEP-BPhen complex and the blank are shown in Figure 1. A maximum is recorded at 475 nm, where the blank absorbs insignificantly. It is shifted to 10 nm as compared to the maximum of the binary Ni-DTEP chelate existing in aqueous medium (in the pH interval from 4 .0 to 9.2) 440 nm. The observed bathochromic effect is small and gives us grounds to suggest the formation of a ternary compound of the ion-association type.
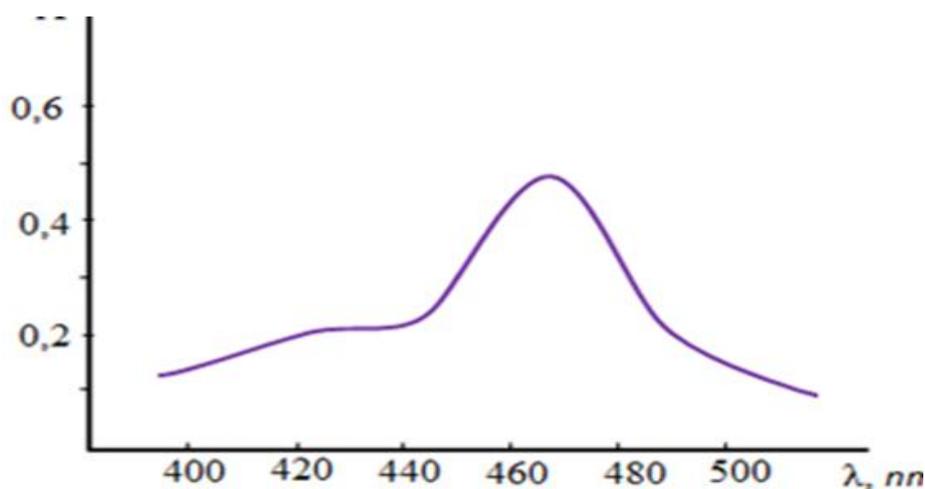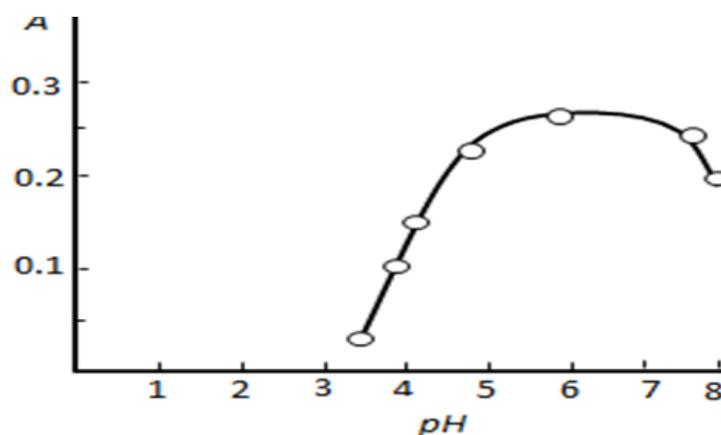
Fig. 1: Absorption of mixed-ligand complexes.

$C_{Ni}=2.035\times10^{-5}$ M. $C_{DTEP}=1.0\times10^{-3}$, $C_{BPhen}=0.92\times10^{-3}$ M, SF-26, l=1.0 cm.

3.2. Effect of pH

Results showed that the optimal pH for the extraction of Ni(II) with DTEP and BPhen is 5.6–6.5 (Figure 2). A buffer solution with a concentration of 2 mol L^{-1} was applied to control pH. The use of 0.25–5 mL of the buffer solution per 10 mL (final aqueous solution) was found to give a constant absorbance. All further experiments were carried out with 5 mL buffer solution with pH = 7.0.

Fig. 2: Absorbance of mixed-ligand complexes as a function of the pH of the aqueous phase. $C_{Ni}=2.035\cdot10^{-5}$ M. $C_{DTEP} = C_{BPhen}=1.0\times10^{-3}$ M, 440 nm, l=0.5 cm.

3.3. Effect of Reagents' Concentrations

For the formation and extraction of MLC, a 10-15-fold excess of complexing reagents is required; for example, the optimal conditions for formation and extraction of these compounds are provided by 1.0×10^{-3} M DTEP and 0.92) $\times10^{-3}$ M BPhen. A large excess of

hydrophob amin interferers with the determination. However it was found that the presence of excess of the reagent solution does not alter the absorbance of the color reaction.

3.4. Effect of shaking time

The extraction equilibrium is reached for a short shaking time (about 5 seconds). It was found that a shaking time longer than 1min can bring about to a slight decrease (5-6%) of the absorbance values. To avoid this disadvantage and to guarantee complete transfer of the complex into organic phase, even under nonoptimum conditions, the authors extracted in their experiments for 15–20 seconds. Unlike single-ligand complexes, mixed-ligand complexes of Ni(II) with DTEP and BPhen were stable in aqueous and organic solvents and did not decompose for two days, or over a month after extraction. The required duration of the phase contact was 10 min.

3.5. Stoichiometry of the complexes and the mechanism of complexation

The molar DTEP-to-Ni(II) and BPhen-to-Ni(II) ratios were determined by the mobile equilibrium method[25], molar ratio method[25], and the method of Asmus.[25] The results showed that the ternary complex has a composition of Ni: DTEP: BPhen = 1:1 : 2. The mentioned formula and the known properties of DTEP and BPhen fit well to the observed pH curve of the ternary complex presented in Figure 3.
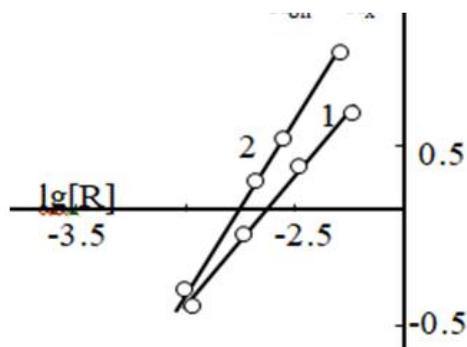
Fig. 3: Determination of the ratio of components by method of Asmus for.

1. Ni(II):DTEP; 2. Ni(II) : BPhen

$C_{Ni(II)}=2.035 \cdot 10^{-5}$ mol L^{-1}, $C_{BPhen}=.0.92 \times 10^{-3}$ mol· L^{-1}; C $_{DTEP} = 1.0 \times 10^{-3}$ mol· L^{-1}, pH = 6, 440 nm, l=0.5 cm.

The disappearance of the pronounced absorption bands in the 3200-3600 cm^{-1} with a maximum at 3420 sm^{-1} observed in the spectrum of DTEP, says that the -OH group is involved in the formation of the complex. The observed decrease in the intensity, absorption

bands in the area 2570 sm^{-1} shows that one of the -SH groups involved in the formation of coordination bond in the ionized state. Detection of the absorption bands at 1480 cm^{-1} indicates the presence of a coordinated phenantroline.[26,27]

Calculation of extent of polymerization of complexes was carried out on the equation.[28] The made calculations showed that MLC in an organic phase won't be polymerized and are in a monomeric form (γ=1.1). It was found using the Nazarenko method that Ni(II) in the complexes was present in the form of Ni^{2+}. The number of protons replaced by cobalt in one DTEP molecule appeared to be one.[29,30]

The stability constant of Ni(II)-DTEP-BPhen complexes was calculated and found to be lgβ = 18.54 at room temperature.

3.6. Influence of interfering ions

The effect of various ions and reagents on the extraction-spectrophotometric determination of 5 mg nikel (II) is summarised in Table 1. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, NH_4^+, Cl^-, $S_2O_3^{2-}$, F^-, NO_3^-, SO_4^{2-}, ClO_4^-, PO_4^{3-}, tartrate, citrate, oxalate and tiron; moderate amounts of Cr(VI), Cr(III), Zn(II) and Cd(II); and small amounts of Mn(II), Sn(II), Cu(II), Al(III), ascorbic acid and SCN$^-$ are tolerable. Co (II), Fe(II,III), V(IV,V), W(VI), Mo(VI), Ti(IV) and Nb(V) interfere determination of Ni(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA (see Table 3).

Table 1: Influence of interfering ions on the determination of nikel(II) as MLC with DTMP and BPhen (30,0 μg Ni added).

Ion	Molar excess of the ion	Masking agent	Found Ni, μg	S_r
Co(II)	30		30.2	5
Fe(II)	90		29.6	3
Cd(II)	100		30.4	4
Al(III)	180		30.5	4
Fe(III)	60		30,2	5
Zr(IV)	50		29.5	4
Cu(II)	25	Thiourea	30,1	5
Hg(II)	40		30.1	5
Ag(I)	25		29.3	
Ti(IV)	30	Ascorbic acid	29.9	4
V(IV)	20		30,6	5
Mo(VI)	15	EDTA	30.4	4

W(VI)	18		29,8	4
Cr(III)	120		29.8	4
Nb(V)	50	$C_2O_4^{2-}$	30.7	4
Ta(V)	50	$C_2O_4^{2-}$	29.7	5
UO_2^{2+}	50		30.2	4
Salicylic acid	25		30.5	4
Sulphosalicylic acid	30		29.5	6
Ascorbic acid	120		30.0	3
Tartaric acid	120		30.2	5
Oxalate	30		29.8	4
Fluoride	15		29.3	5
Phosphoric acid	30		30.2	4
Thiourea	20		29.5	3

3.7. Beer's law, molar absorptivity, and other analytical characteristics

The range of adherence to Beer's law was studied at the optimum conditions (Table 1). The linearity is observed up to 16 μg ml^{-1} of Ni with a correlation coefficient of 0.9973. The obtained straight line equation is $Y = 0.037+0.0252x$. The molar absorptivity was calculated to be 2.15×10^4 L mol^{-1} cm^{-1}. This value could compete successfully with the ones obtained for similar DTEP-containing complexes (Table 3). The limit of detection (LOD) and limit of quantification (LOQ) were estimated at 3 times and 10 times standard deviation of the intercept divided by the slope. Sandell's sensitivity was calculated as well. The values of the above-mentioned characteristics are included in Table 2. Sandell's sensitivity (μg· cm^{-2}) 2.05.[31]

Table 2: Optical characteristics, precision and accuracy of the spectrophotometric determination of Ni(V) with DTEP and BPhen.

Parameter	Value
Color	red
The pH range of education and extraction	4,0-9,2
The pH range of maximum extraction	5,6-6,5
Concentration of DTMP: mol· L^{-1}	1.0×10^{-3}
Concentration of DPG: mol· L^{-1}	0.92×10^{-4}
Organic solvent	Chloroform
Extraction time	3 min
λmax (nm)	475
Molar absorptivity (L· mol^{-1} cm^{-1})	$2.83\cdot10^4$
Sandell's sensitivity (μg· cm^{-2})	0.00205
R,%	99.2
The equation of calibration curves	0.037+0.0252x
lgK$_e$	5.23
lgK$_{Ex}$	18.67± 0.07
Stability constant (β)	19.08 ± 0.06

Beer's law range (μg· ml^{-1})	0.5-18
Correlation coefficient	0.9973
Limit of detection (LOD): ng ·mL^{-1}	11
Limit of quantification (LOQ): ng ·mL^{-1}	35

The proposed method compares favourably with the existing ones (Table **3**) and offers the advantages of better simplicity, rapidity, sensitivity and selectivity.

Table 3: *Comparative characteristics of the procedures for determining nikel.*

Reagent	pH (solvent)	λ, nm	$\varepsilon \cdot 10^{-4}$	Beer's law range (μg· ml^{-1})
Dimethylglyoxime[32]	12	470		0.26-2.1
N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone.[33]	6.0	400	1.114	
7-Methl-2-chloroquinoline-3-carbaldehyde thiosemicarbazone[34]	6.0	410	1.67	
Thiazole-2-carbaldehyde 2-Quinolylhydrazone[35]	8.7 -9.5	522	7.17	0-0.7
pyridoxal-4-phenyl-3-thiosemicarbazone[36]	4-6	430	1.92	0.5-5
4-gidroksibenzal'degid-4-brom fenilgidrazin[37]	4	497	12.85	0.01-0.1
DTEP+BPhen	5.6-6.5	475	2.83	0.5-18

3.8. Analytical Applications

The proposed method under the already established optimum conditions was applied for the determination of Ni(II) in various objects. The results presented in Table 4 and Table 5 indicate the successful applicability of the proposed method to real sample analysis.

Table 4: Determination of nikel in steel (n=5, P=0.95).

Reagent.	$\bar{X}$, %	S_x	ε	S_r	μ
8ХФ (С16^6)					
Dimethylglyoxime	0.259	0.00725	0.0083	0.028	0.259±0.0083
Ni - DTEP -BPhen	0.258	0.00645	0.0074	0.025	0.258±0.0074

Table 5: Determination results of nikel (II) in the sewage water and bottom sediments ($n = 6, P = 0.95$).

Analysis object	Added, μg	Found, μg	Found in the sample, μg / kg $\overline{X} \pm \dfrac{t_s \, S}{\sqrt{n}}$	S_r
Sewage water				
Sample 1	2.0	2.55	0.55±0.044	0.08

Sample 2	5.0	6.64	1.64±0.098	0.06
Bottom sediments				
Sample 1	2.0	3.46	1.46±0.102	0.07
Sample 2	5.0	5.25	2.25±0.0625	0.05

4. CONCLUSIONS

1. The results obtained show that the newly developed method in which the reagent DTEP was used, can be effectively used for quantitative extraction and estimation of Ni (II) from aqueous media.

2. Mixed-ligand complexes of nickel (II) with 2, 6-dithiol-4-ethylphenol (DTEP) in the presence of bathophenantroline (BPhen) have been investigated by spectrophotometric method.

3. Extraction of mixed ligand complexes is maximal at pH 5.6-6.5. The proposed method is quick and requires less volume of organic solvent.

4. The optimal conditions for the formation and extraction of mixed-ligand compounds have been found and the ratios of components I the complexes have been determined.

5. The Beer's law was applicable in the range of 0.5-16 μg/ml.

6. A simple, rapid and sensitive methods proposed for the determination of trace amounts of nickel. The developed techniques are used to determine nickel in sewage water and bottom sediments and in steel.

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