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NEW ORGANIC REAGENTS FOR THE EXTRACTION OF NICKEL (II) PICRATE FROM THE SOLID PHASE

Abstract: The article presents the results of a study of an important area of analytical chemistry - extraction-photometric determination of nickel ions from the solid phase. We have studied the extraction of nickel picrate ($NiPik_2$) from the solid phase using organic reagents of the acetylene series (L_1, L_2, L_3, L_4) in a chloroform solution. A new technique for the extraction-photometric determination of the nickel ion from the solid phase is proposed. It has been established that organic reagents (L_1-L_4) exhibit a high extraction ability (0.11-0.64 mg/l) of Ni picrate from the solid phase, and the extraction activity of organic ligands changes in the series as follows $L_4> L_3> L_1> L_2$. The impact of a magnetic field has a positive effect on the extraction of nickel picrate from the solid phase, increasing it by 3-4%.

Key words: extraction ability, nickel (II) picrate, organic reagents, solid phase, equilibrium, magnetic field.
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Introduction

The extraction of transition metal ions from the solid phase by the extraction-photometric method has not yet been studied in detail, and information in the world scientific literature is limited. In this regard, studies on the extraction of ions from the solid phase with the help of organic ligands are very topical. From the analytical point of view, the separation of ions from the solid phase is of particular importance in the development of technology for obtaining pure, chemically pure, pure for analysis, and ultrapure metal salts [1–5].

There is also extraction, which is not accompanied by chemical interaction and can be

considered as a case of simple physical distribution. This is how symmetrical covalent molecules are extracted, for example, I_2, $GeCl_4$, the solubility of which in an organic solvent is usually an order of magnitude higher than in water. The same type includes the extraction of weak acids if their dissociation is completely suppressed in the presence of a strong acid [6-12].

For many years, liquid extraction, precipitation, centrifugation, column and thin layer chromatography have been the main methods for isolating, purifying, and concentrating analytes. Such preparation of samples is a lengthy and multi-stage process that requires the consumption of a large amount of extra

pure (does not introduce impurities!) Solvents and reagents, additional equipment and labor costs.

Experimental part

For the extraction of Ni (II) ions from the solid phase, we used chloroform solutions of new organic reagents synthesized by us (L₁, L₂, L₃, L₄). These are tetrahalogen-containing hydrophobic organic compounds of the bicycloquinone type with an acetylene moiety.

To determine the degree of extraction - Nickel A-ion from the solid phase with organic ligands L1-L₄, solutions of organic ligands shown in Table 1 were prepared with a content of L_1 = 71.2 mg; L_2=59.6 mg; L_3=106.2 mg; L_4=109.6 mg, which were dissolved in 200 ml of chloroform ($CHCl_3$) and a 10^{-3} molar solution was prepared. Chemically pure nickel picrate ($NiPik_2$) was used for extraction.

To determine the optical density of organic ligands L_1-L_4, dried at 110-1150C salt of picrate and nickel in the form of a powder weighing 200 mg was poured into a conical flask and 30 ml of a chloroform solution of organic ligands -L_1-L_4 with a concentration of 1.10^{-3} - 2.10^{-3} M was added. Solution mixed with a magnetic stirrer for 3 hours at a temperature of 18 - 20^0C. Every 10 min. a sample was taken from the organic phase in a volume of 2 ml. On the device Spekol (l=1.0 cm, λ=375 nm) was determined by the optical density - A, and the content of nickel ions in the solid phase.

To determine the time of establishing the chemical equilibrium of the nickel ion extraction process, 200 mg of nickel (II) picrate salt powder was poured into a conical flask with a capacity of 100 ml and 30.0 ml of a 10^{-3} M chloroform solution of organic ligands L_1-L_4- was added to it. After inserting a magnetic stirrer into the flask, the neck of the flask was closed with a polished stopper. Stirring was carried out for 5 hours. Every 20 min. the concentration of the organic phase (A) was measured on a Spekol-10 spectrophotometer (l=5.0 cm. λ=375 nm) and the time of chemical equilibrium (τ) between the phases was examined.

Results and discussions

We synthesized organic ligands with a quantitative yield of up to 86%.

- **$C_{13}H_{10}Cl_4O_2$-**1,2,3,4-tetrachloro-7,8-quinone-5-(3-methyl-oxy-1-butyl)bicyclo[2,2,2]octene-2 - (L_1);

$C_{13}H_{10}Cl_4O_2$-1,2,3,4-tetrachloro-7,8-quinone-5-ethynyl-bicyclo [2,2,2]octene-2 - (L_2);

$C_{13}H_{10}Br_4O_3$-1,2,3,4-tetrabromo-7,8-quinone-5-(4-methyl-4-oxy-2-pentenyl) bicycle [2,2,2]octene-2 - (L_3);

$C_{14}H_{12}Br_4O_3$-1,2,3,4-tetrabromo-7,8-quinone-5-(4-methyl-oxy-2-pentenyl)bicyclo[2,2,2] octene-2- (L_4)

Their structure was studied by the IR spectroscopic method, and the melting points and molecular weights were determined.

As a result of the experiments on the extraction of nickel picrate from the solid phase, the extraction activity of organic ligands was established - R: L_1 - R=75%, L_2- up to 69.60%, L_3- up to 88.05%, L_4 up to 95.25%. The amount of Ni ion from 0.49 mg to 0.64 mg was determined by the extraction-photometric method. It was found that the ability to extract organic ligands (L_1-L_4) is arranged in a row as follows L_4> L_3> L_1> L_2 (Table 1).

Table 1. Maximum extraction of nickel picrate by chloroform solutions L_1 -L_4 from the solid phase, τ=2.5 h, λmax=375 nm, l=5.0 cm

Organic ligands	Optical density, A	Quantity, Ni^{2+}, мg/l	Extraction, R, %
L_1	0,28	0,49	75,0
L_2	0,26	0,45	69,6
L_3	0,33	0,56	88,05
L_4	0,33	0,64	95,25

As a result of studying the chemical equilibrium of the nickel ion extraction process with organic ligands, it was determined that in the case of the L_1, L_2 ligand, complete chemical equilibrium between the phases is established after 3 hours, and in the case of L_3, L_4 - after 2.5 hours. Magnetic stirring for 5 hours does not disturb the chemical equilibrium (Figure 1).
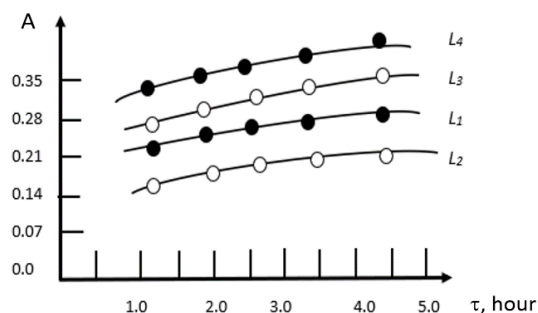
Figure 1. Change in optical density (A) over time for organic ligands - L_1, L_2, L_3, L_4

We also studied the effect of a magnetic field on the extraction of a nickel ion by the photometric method with chloroform solutions of organic ligands - L_1-L_4 with a concentration of $0.25 \cdot 10^{-3}$ - $2 \cdot 10^{-3}$ M. The equilibrium between the phases is established after 80 minutes, and the extraction of nickel into the organic phase increases by 4 %. The results obtained are presented in table 2.

As can be seen, nickel picrate salts are extracted from the solid phase into the organic phase in an amount of 0.12-0.65 mg/l, and the extraction increases to 99%.

The process of extraction of metal ions from the solid phase to complex formation with ligands forming an internal complex is mainly controlled by the following factors: the structure of organic ligands containing halogen atoms, acetylene fragments (-C≡C-), functional groups ≡ N, =NH, - NH₂, -OH, =C=O, -S-, =NOH, etc. As a result, internal complex compounds are formed due to the coordination bond

with the transition metal ion. Thus, these organic ligands diffuse into the pores of the metal salt in the solid phase. After a certain time between the phases, a chemical equilibrium occurs between the liquid organic ligand and the solid phase, which depends on factors such as temperature, pressure, metal salt surface, particle size, phase structure of the crystal, ionic radius of the metal. In addition, it also depends on the contact time of the phases, the amount of acetylene fragment (-C≡C-) and functional groups in tetrahaloorganic ligands.

Ultimately, there is a transition from the solid phase to the liquid (anhydrous) phase with tetrahalogenbenzoquinone organic ligands (L_1, L_2 L_3 L_4), i.e., macromolecular ions are formed - associates, which are extracted into the liquid organic phase due to diffusion.

The proposed scheme for the formation of such an associate is shown in Figure. 2.

Table 2. Physical and chemical characteristics of organic ligands and the degree of nickel ion extraction in a magnetic field
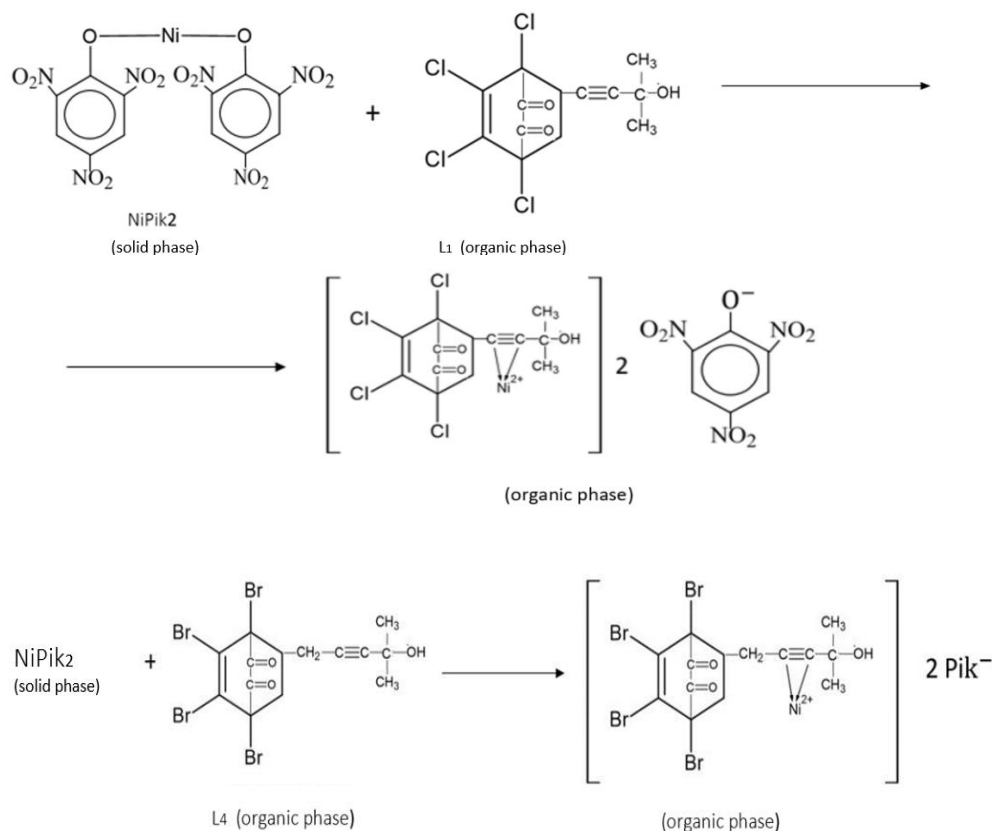
Organic ligands L_n	Concentration, $C \cdot 10^{-3}$ M	Optical density, A	Quantity Ni^{2+}, мg/l	Extraction, R, %
$C_{13}H_{10}Cl_4O_2$-	0,25	0,074	0,12	18,75
	0,50	0,152	0,235	36,72
	0,75	0,223	0,356	55,62
L_1	1,00	0,29	0,48	75,00
	1,25	0,29	0,48	75,00
	1,50	0,28	0,48	75,00
$C_{13}H_{10}Cl_4O_2$-	0,25	0,106	0,113	17,4
	0,50	0,136	0,224	34,8
	0,75	0,201	0,34	52,2
L_2	1,00	0,261	0,45	69,6
	1,25	0,261	0,45	69,6
	1,50	0,262	0,45	69,6
$C_{13}H_{10}Br_4O_3$-	0,25	0,084	0,14	22,01
	0,50	0,171	0,28	44,02
	0,75	0,202	0,43	66,03

L_3	1,00	0,331	0,56	88,05
	1,25	0,331	0,56	88,05
	1,50	0,332	0,56	88,05
$C_{14}H_{12}Br_4O_3-$	0,25	0,091	0,16	23,81
	0,50	0,185	0,32	48,62
	0,75	0,281	0,48	92,43
L_4	1,00	0,361	0,65	98,25
	1,25	0,361	0,65	98,55
	1,50	0,362	0,65	98,55

Figure 2. Scheme of nickel ion extraction from the solid phase by organic ligands

Conclusion: Thus, as a result of our study, we have developed a new method for the extraction of transition metal salts with organic ligands of tetrahalobicyclic reagents L_1, L_2, L_3, L_4 into the organic phase.

Synthesized and determined the physicochemical properties of organic ligands L_1, L_2, L_3, L_4. The Spekol device (l=1.0 cm, λ=375 nm) measured the optical density of organic ligands and the degree of extraction of nickel ions from the solid phase, which was more than 95%. It has been established that the magnetic field has a positive effect on the degree of nickel ion extraction.

The proposed method can be used to obtain ultrachemically pure salts of nickel and other metals, as well as the synthesis of some organic substances by interfacial catalysis. In addition, it opens up opportunities for studying the mechanism of the extraction process from the solid phase.

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