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# STUDY OF INTERACTION IN HEXACIANOFERRATE (III) -, VANADYL - AND NICKEL (II) - CONTAINING SYSTEMS

## Post 2.

## Study of the system $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$

**Abstract.** In this paper considered study of interaction process in the system $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$, using the pH metric titration method in the pH range 2-12. It was established that the nature of the titration curves of an aliquot of the studied system with sodium hydroxide solution depends on its concentration. The most complex character is the titration curve of 0.1 mol/L sodium hydroxide, on which mild leaps are recorded at pH 3.4 and 4.0 and intense leaps at pH 5.6 and 7.7. Conditions for the formation of complex compounds of vanadium and nickel ferrocyanides in acidic medium are created. In this system as well as vanadium and nickel hydroxides were formed in alkaline medium. Precipitates of various shapes and colors, the color characteristic of which corresponds to the above-mentioned compounds, are separated from the studied system.

**Key words:** potassium hexacyanoferrate (III), titration, vanadyl sulfate, nickel (II) sulfate, complexation, pH.

**Introduction.** Large amounts of waste are formed at the present stage of development of oil production technology in the exploitation of oil fields. Thus there is environmental pollution with hydrocarbons. This occurs at all stages of working with them, starting with the development of the field and ending with the storage of finished petroleum products. In addition, not only oil and gas but also by-products get into the natural environment. Thus, along with emissions of associated gases, drilling muds are poured during drilling of oil wells, and, formation water comes out during production along with oil, which is poured. When oil is transported through the pipeline, gaseous products are leaking due to the leakiness of the locking fittings and valves. Sources of environmental pollution during the development of fields are exploratory drilling, well operation, oil and gas spills in the container, their transportation and emergency situations. Poisoning of wastewater from boreholes and drill cuttings contributes to soil and water poisoning. A significant part of oil waste predominantly accumulates in sludge collectors and sludge pits.

The problem of neutralization and utilization of industrial waste is important and relevant for most oil and gas companies in developed countries. This is mainly due to the fact that waste-free technologies, as we know, do not exist, and with almost complete elimination of harmful emissions into the atmosphere or water, the bulk of toxic components are concentrated in the form of solid or pasty (semi-liquid) waste [1]. According to the data of American specialists, about 40 thousand tons of solid or pasty oily wastes accumulate at large oil refineries (15–16 thousand tons per day) per year. It should be noted that there is no unified method for processing oil sludge and barn oil for the purpose of neutralization and disposal. Their disposal and neutralization solves two important tasks: protecting the environment from hazardous pollution and using secondary raw materials contained in them. Despite the enormous costs of solving this global problem in many highly developed countries, such as the USA, Japan, Germany, etc., there are still no optimal ways to recycle the oil industry.

Search for solutions to this problem and various methods of innovative technologies by large oil and gas companies of the country are continuing. However, the existing methods of utilization of oil waste or their use as a secondary raw material in Kazakhstan so far only remains at the level of scientific research and do not find wide industrial use. The complexity of the problem of disposal of oil waste is not only in its scale, but also in the development of criteria and methods of processing. This is associated with complex and non-permanent waste, which makes it difficult to choose a unified approach to solving the problem [2, 3].

The process of processing oil sludge is a complex scientific and technical challenge and is carried out by various technological methods. Especially important is oil sludge from various components, including from a number of heavy metals, especially nickel and vanadium present in it [4]. Vanadium-, nickel-containing compounds in oil sludge and barn oil pollute the environment, but both components are valuable metals that are necessary for the economy of Kazakhstan [5].

Vanadium and its compounds have unique physicochemical properties, which leads to their use in many areas - ferrous and nonferrous metallurgy, aircraft manufacturing, space technology, marine shipbuilding, nuclear energy, chemical industry. In the world, the volume of vanadium production is growing, making 76 thousand tons in 2013 [6]. Over 85% of vanadium is used in ferrous metallurgy as an effective alloying additive in the production of various steel grades. Approximately 8% of vanadium is used in non-ferrous metallurgy, mainly in the form of aluminum-vanadium alloys used in aircraft manufacturing, space technology and in marine shipbuilding [7]. The rest of the consumed vanadium (5%) accounts for the chemical industry, in particular, the production of batteries and catalysts for the production of sulfuric acid, the processes of oil cracking, the production of acetic acid, and many other products.

Vanadium is predominantly in the dispersed state and is found in iron ores, oils, asphalt, bitumen, oil shale, coal, etc. The total reserves of vanadium are at least 60 million tons and concentrated in 19 countries. Moreover, 90% are in South Africa, Russia, Venezuela, USA, and China. Production in these countries amounts to 50-60 thousand tons (in the United States, 2/3 of the oil comes from the source) [7-9].

In Kazakhstan, vanadium ores were found in the Cambrian shales in the north-east of Karatau, in the Talas Alatau and Terskey-Alatau ridges. The largest deposits are Balasauskandyk, Kurumsak, Zhabagly (about 3 million tons of vanadium pentoxide). Vanadium accompanies the Mangistau oil fields. Karazhanbas and Talgyztyuban oil fields (Mangyshlak, Kazakhstan) are unique; in one tonne it contains more than 250 g of vanadium [10]. In addition, it is possible to produce vanadium from vanadium-containing bauxite, coal-uranium, phosphate and titanium-zirconium deposits. Reserves of vanadium ores in Kazakhstan are significant, but a significant part of them are not yet involved in the operation [11, 12].

Vanadium refers to the group V of the periodic system. It exhibits variable valence from +2 to +5 in compounds. The transition of vanadium from the highest oxidation state +5 to the lowest +2, through all intermediate oxidation states, can be observed when the sodium metavanadate solution in an acidic medium interacts with zinc:

$$VO_3^{\,-} \rightarrow VO_2^{\,+} \rightarrow VO^{2+} \rightarrow V^{3+} \rightarrow V^{2+} \qquad (1)$$

Compounds of divalent and trivalent vanadium are unstable and are strong reducing agents. The greatest practical importance are the derivatives of pentavalent vanadium. However, it is characterized by a fairly easy transition from the valence of $V^{5+}$ to the valence of $V^{4+}$ and back. Moreover, in oxygen compounds, the most stable oxidation state is +4 (in an acidic medium) and +5 (in neutral and alkaline environments). Compounds of tetravalent vanadium are still relatively stable [13].

Vanadium (IV) salts (vanadyls) are oxo salts (oxovanadium (IV) ions, or vanadyl $VO^{2+}$). Hydrated vanadyl salts isolated from the solution are blue, anhydrous salts are green or brown. The vanadyl ion ($VO^{2+}$) resulting from this reaction is very stable and retained not only in aqueous solutions of salts, but also in the composition of vanadium hydroxide (+4) $VO(OH)_2$ [14]. The color of aqueous solutions of vanadium (IV) compounds is blue, which gives them hydrated ion $[VO(H_2O)_5]^{2+}$ (vanadyl ion or oxovanadium (IV)) [15]. Vanadium exists in aqueous solution in the oxidation state (IV) at certain pH values (0.1–4), usually in the form of a $VO^{2+}$ vanadyl ion [16]. Light blue acid hydrates of vanadyl sulfate $2VOSO_4{\cdot}H_2SO_4$ crystallize from solutions with an excess of sulfuric acid during evaporation; it is also called dioxotrisulfate divanadic (IV) acid $H_2[V_2O_2(SO_4)_3]$.

The alkali metal salts of tetravalent vanadium crystallize from solutions in the form of hydrates of the composition $M_2V_3O_7 \cdot nH_2O$. Vanadates (IV) of other compositions were obtained in the anhydrous state. They hydrolyze with water and decompose with mineral acids [17].

When alkalies act on vanadyl solutions, a dirty gray hydrate $V_2O_4{\cdot}7H_2O$ drops out:

$$2VOSO + 4NaOH + 5H_2O = V_2O_4{\cdot}7H_2O + 2Na_2SO \qquad (2)$$

When alkali is added to solutions of vanadium (IV) salts, a pink-brown precipitate of vanadium hydroxide (oxohydroxide) $VO(OH)_2$ is formed:

$$VOSO + 2NaOH = VO(OH)_2\downarrow + Na_2SO \qquad (3)$$

Crystalline $VO(OH)_2$ consists of octahedra $[VO_6]$, interconnected in a chain. Vanadium (IV) hydroxide, like oxide, has amphoteric properties, i.e., it is soluble in acids and alkalis [18].

When dissolved in acids, derivatives of vanadyl-ion ($VO^{2+}$) are formed:

$$VO(OH)_2+H_2SO_4=VOSO_4+2H_2O, \qquad (4)$$

and when dissolved in alkali, vanadates (IV) (vanadites) of different composition are formed:

$$4VO(OH)_2 + 2KOH = K_2[V_4O_9] + 5H_2O \qquad (5)$$

$$18VO(OH)_2 + 12KOH = K_{12}V_{18}O_{42} + 24H_2O \qquad (6)$$

Vanadates (IV) are substances of brown color, stable in alkaline medium and easily oxidized in air. In a strongly alkaline medium at pH>13, monomeric orthovanadate ions $VO_4^{3-}$, which are regular tetrahedra, predominate [19]. They correspond to solid orthovanadates, for example, $Na_3VO_4$, $Cu_3VO_4$, which are isostructural with similar orthophosphates. At lower pH orthovanadate is protonated:

$$VO_4^{3-} + H_2O = HVO_4^{2-} + OH^-; K=10^{-1} \qquad (7)$$

then the individual tetrahedra are merged first into dimers:

$$4HVO_4^{2-} = V_2O_7^{4-} + H_2O; K=47.8, \qquad (8)$$

then into cyclic or linear oxo anions:

$$2V_2O_7^{4-} + 2H_2O = V_4O_{12}^{4-} + 4OH^- \qquad (9)$$

Since vanadium (IV) easily transforms into vanadium (V), and the transition is reversible, it is necessary to describe pentavalent vanadium. Vanadates (V) - salts color of which from light yellow (lemon) to orange. The oxidation state +5 for vanadium is realized in oxocations $VO^{2+}$, $VO^{3+}$ (vanadyl ions) and oxoanions $VO_4^{3-}$, $V_2O_7^{4-}$, $V_3O_9^{3-}$, etc. (vanadate (V) -ions). Vanadium (V) is in solution in the form of the cation $VO^{2+}$, neutral compounds $VO(OH)_3$, anions: decavanadate ($V_{10}O_{26}(OH)_2^{4-}$, $V_{10}O_{27}(OH)^{5-}$ and $V_{10}O_{28}^{6-}$), monovanadate - $VO_2(OH)^{2-}$, $VO_3(OH)^{2-}$ and $VO_4^{3-}$ and polyvanadate - $V_2O_6(OH)^{3-}$, $V_2O_7^{4-}$, $V_3O_9^{3-}$ and $V_4O_{12}^{4-}$ [19,20]. Metavanadate and decavanadate ions exist at concentrations of vanadium lower than 0.1 mol/l.

Vanadium exists mainly in the form of $VO^{2+}$ cations and the decavanadate anion $H_2V_{10}O_{28}^{4-}$ at pH<2.40, when the content of $V_2O_5$ is 2-3 g/l.

In acidic solutions, V (V) forms an aqua complex $[VO_2(H_2O)^{4+}]$. Therefore, in many cases, the complexation of V (V) in aqueous solutions of acids is advisable to consider as the process of replacing water molecules with ligands located in the inner sphere of the aqua complex [16]:

$$[VO_2(H_2O)^{+}{}_4]_nA \leftrightarrow [VO_2(H_2O)^{+}{}_{4-n}A^{1-n}] + H_2O \qquad (10)$$

In strongly alkaline solutions, it is part of the mononuclear particle - orthovanadate ion. With decreasing alkali concentration, polynuclear anionic particles appear, the maximum degree of condensation, equal to 10, is characteristic of weakly acid solutions [21, 22].

According to the proposed model of polycondensation in an acidified solution containing $VO_4^{3-}$ [23, 24], the distribution of vanadium (V) polyanions in the range of pH 1-13 at different ratios of the total concentration of hydrogen in solution to the total concentration of vanadium Z is in the range of 0-3, 00 on the background of nitrate ions proceeds as follows. There are metapolyvanadate anions $V_3O_9^{3-}$, $HV_3O_9^{2-}$, $V_4O_{12}^{4-}$ and $HV_4O_{12}^{3-}$ at $1.75 < Z < 2.40$, and decavanadate anion $V_{10}O_{28}^{6-}$ at $Z > 2.40 – 3.00$. The existence of tetravanadate and hydrometavanadate anions was confirmed by chemical and IR spectroscopic methods of the synthesized salts $Na_6V_4O_{13}\cdot 2H_2O$ and $Na_3HV_4O_{12} \cdot 5H_2O$.

There is an extensive class of vanadium complex compounds [25, 26]. During their formation, vanadium participates in any of the known oxidation states. The charge of its cations in solutions does not exceed three. Vanadium in oxidation states +4 and +5 forms stable oxocations $VO^{2+}$ and $VO_2^{3+}$, as well as $VO^{3+}$. According to their ability to co-ordinate predominantly in complex compounds with donor atoms of the N, O and S ligands, vanadium (IV) and (V) cations form a stronger bond with oxygen than with nitrogen, in contrast to vanadium (III) cations. Heterocycles arise in the formation of complex compounds, in which vanadium cations are acceptors of electronic pairs of oxygen and nitrogen.

Vanadium forms a series of complex salts, the so-called heterocomplexes: vanadium molybdates, vanadium phosphates, uranium vanadates, vanadium volphramates. A series of hetero compounds of vanadium and molybdenum can be expressed by the formula: $mMeO\cdot nV_2O_5\cdot pMoO_3\cdot gH_2O$ (Me – $NH_4^+$, $Na^+$, $K^+$, $Ba^{2+}$; m = 2-3; n = 1-2; p = 4-5; g=4-48); vanadium hetero compound series with tungsten − $mMe_2O\cdot nV_2O_5\cdot pWO_3\cdot gH_2O$ (Me – $NH_4^+$ , $Na^+$ , $K^+$ , $Ba^{2+}$ , $Ag^+$ , $Cu^{2+}$; m = 2-3; n = 1-3; p = 4-6; g = 6-24) [18].

In all oxidation states, vanadium, as a rule, has a coordination number of 6. In the degrees of oxidation (IV) and (V), compounds with a coordination number of 4 are also formed (for example, in meta-, di-, and orthovanadates), as well as 5 and 8 [20, 27].

Many studies have been devoted to elucidating the forms of the state of vanadium in aqueous solutions, but so far this issue is far from complete resolution. The variety of ionic forms of vanadium in solutions leads to the formation of a large number of compounds with different ratios of metals and vanadium, as well as complex compounds with inorganic and organic ligands.

As far as ferrocyanides are concerned, the tri- and tetra valence of the $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ anions allows for a huge variety of variations in the production of mixed ferrocyanides, in combination with vanadium, of different composition with a change in wide the limits of both the number of outer-sphere cations and the ratio between them, as well as the possibility of introducing the anion into the inner sphere.

However, ferrocyanides of tetravalent vanadium (formal ferrocyanide $V^{4+}$) are not sufficiently described in the scientific literature. It is known that when vanadyl salts are exposed to solutions of ferrocyanide salts, a slightly soluble yellow-green precipitate $(VO)_2[Fe(CN)_6]$-$xH_20$ is deposited. The possibility of excess absorption of the salt of $Na_4[Fe(CN)_6]$ by precipitate formed in the system $VOSO_4$ – $Na_4[Fe(CN)_6]$ [28]. The precipitate begins to coagulate with the formation of phases of variable composition $x(VO)_2[Fe(CN)_6]\cdot y\ Na_4[Fe(CN)_6]$ at $n > 1$. A mixed vanadyl and potassium ferrocyanide $K_2(VO)_3[Fe(CN)_6]_2\cdot xH_2O$ was obtained in the $VOSO_4$ - $K_4[Fe(CN)_6]$ - $H_2O$ system, which in its composition is of the type of mixed ferrocyanides of divalent cations.

If vanadyl sulfate $VOSO_4$ containing the anion $VO^{2+}$ ($V^{4+}$) is used as the vanadium salt, and salt with the anion $[Fe(CN)_6]^{3-}$ as the ferrocyanide-containing component then it can be expected that redox accompanied by a change in the valence of vanadium and the reorganization of the ferricyanide anion into a ferrocyanide anion in a system under certain conditions [29, 30].

Summarizing the above and considering the joint presence of nickel and vanadium in the oil-containing raw material and wastes, it can be noted that the selected objects for the study and $K_3[Fe(CN)_6]$ – $VOSO_4$ – $NiSO_4$ — $H_2O$ system based on them are very interesting in terms of chemistry complex compounds. Although full charge compensation of the $[Fe(CN)_6]^{4-}$ anion is achieved only on tetravalent elements, but considering that the tetravalent vanadium salt exhibits redox properties, i.e., reversible transition $V^{4+} \leftrightarrow V^{5+}$ is characteristic for vanadium, then we can expect the formation of mixed salts in the studied system. It is possible the occurrence of various combinations of cations present in the solution.

The purpose of the study is to determine the effect of pH on the method of titration with sodium hydroxide solution on the interaction process in the ternary system $K_3[Fe(CN)_6]$–$VOSO_4\cdot 3H_2O$– $NiSO_4\cdot 7H_2O$– $H_2O$.

## EXPERIMENTAL PART

The method of titration of the $K_3[Fe(CN)_6]$–$VOSO_4\cdot 3H_2O$– $NiSO_4\cdot 7H_2O$ water-salt three-component system was used with sodium hydroxide solution (NaOH). Using the method of pH metrics in the study of complexation in complex systems enables to determine not only the formation of complexes, but also their stability.

The salts of vanadyl sulfate $VOSO_4\cdot 3H_2O$, nickel sulfate $NiSO_4\cdot 7H_2O$, potassium (III) hexacyanoferrate (ferrocyanide) $K_3[Fe(CN)_6]$ were used.

For the study, mixtures of $K_3[Fe(CN)_6]$ and $VOSO_4\cdot 3H_2O$ solutions with a concentration of $2\cdot 10^{-3}$ mol/l, as well as $NiSO_4\cdot 7H_2O$ with a concentration of $2\cdot 10^{-2}$ mol/l, taken in a ratio of 1:1:1, were used.

Titration of an aliquot of the studied system was carried out with a solution of sodium hydroxide NaOH with a concentration of 0.01 mol/l, 0.1 mol/l and 0.2 mol/l at room temperature. The pH value was measured on a universal pH meter 150 MI at room temperature. Glass electrode ELS 6307 used as the indicator electrode. The reference electrode was a saturated silver chloride EVL-1M3 electrode.

## RESULTS AND DISCUSSION

It was previously established that an aqueous solution of $K_3[Fe(CN)_6]$ has a neutral medium (pH 6.7). A solution of $VOSO_4{\cdot}3H_2O$ has an acidic medium and its pH is 3.1, and a solution of $NiSO_4{\cdot}7H_2O$ - weakly acidic medium (pH 5.03). When merging the above solutions in a 1: 1: 1 ratio, the $K_3[Fe(CN)_6]$–$VOSO_4{\cdot}3H_2O$–$NiSO_4{\cdot}7H_2O$–$H_2O$ ternary system becomes an acidic medium with a pH value of 4.1.

The figure shows the pH – metric titration curves of an aqueous solution of the ternary system $K_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O$ – $NiSO_4{\cdot}7H_2O$ with a total concentration of components $6{\cdot}10^{-8}$ mol/L by sodium hydroxide solution of different concentrations. It ensues from the obtained results that as the concentration of sodium hydroxide solution increases, the consumption of alkali for titration is noticeably reduced, and the nature of the titration curves changes slightly.

Two leaps are recorded on the curve of the aliquot titration with a NaOH solution of weak concentration (0.01 mol/l) (figure a). The first intense leap is observed in the pH range 3.7–7.8 and the second less intense leap in the pH range 8.6–10.5. Considering the wide range of pH values of the first leap, it can be attributed to the formation of complex compounds of vanadium and nickel with hesacyanoferrate (III) potassium of the type $(VO)K[Fe(CN)_6]$, $(VO)_3\,[Fe(CN)_6]$ and $Ni_3[Fe(CN)_6]_2$ [28,31-33]. The second leap relates to the alkaline medium and, apparently, due to the formation of nickel ($Ni(OH)_2$) and vanadium ($VO(OH)_2$) hydroxides:

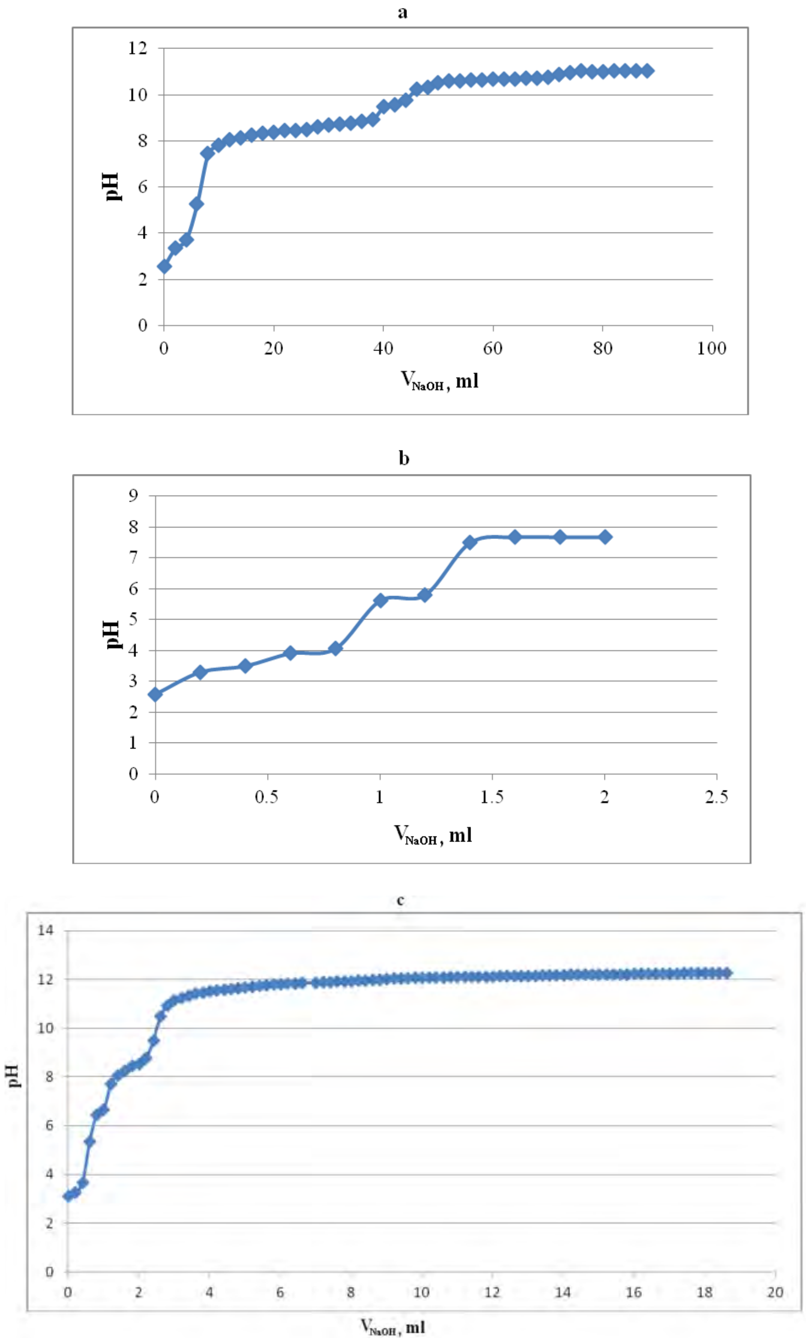
$$VOSO_4 + 2NaOH = VO(OH)_2\downarrow + Na_2SO_4 \quad (11)$$

$$NiSO_4 + 2NaOH = Ni(OH)_2\downarrow + Na_2SO_4 \quad (12)$$

At higher pH, i.e. yellow-brown-green solutions are formed in the conditions of excess alkali. In this case, the dissolution of vanadium hydroxide is possible with the formation of various vanadates (IV) - ions [34].

Increasing the concentration of sodium hydroxide solution to 0.1 mol/L leads to the appearance of two additional leaps on the titration curve (figure b). The acidic medium is characterized by two weakly leaps at pH 3.4 and 4.0 and an intensive leap at pH 5.6. The first two leap apparently relate to the formation of two different types of complex compounds - vanadium hexacyanoferrates.

The leap on the titration curve in a very weakly acidic medium at pH 5.6 correspond to the formation of nickel hexacyanoferrate $Ni_3[Fe(CN)_6]_2$. Increasing the pH of the solutions to 7.7 leads to an intense leap in the curve and corresponds to the appearance of vanadium and nickel hydroxides and vanadates in the system.



**C** $_{K3[Fe(CN)6]}$ = C $_{VOSO4\cdot3H2O}$ = $2\cdot10^{-3}$ mol/L; **C**$_{NiSO4\cdot7H2O}$ – $2\cdot10^{-2}$ mol/L
C$_{NaOH}$: a – 0,01 mol/L, b – 0,1 mol/L, c – 0,2 mol/L
Titration curves of solutions in the triple system
$K_3[Fe(CN)_6]–VOSO_4\cdot3H_2O–NiSO_4\cdot7H_2O–H_2O$

The leaps in the acidic medium disappear on the titration curve in the conditions of titration of an aliquot of the ternary system with a concentrated solution of NaOH (0.2 mol/L), (figure c). That is, during the titration of an aliquot of the ternary system with a concentrated solution of NaOH, the formation of complex compounds is accelerated and overlapped by the formation of metal hydroxide.

The separated precipitate from the triple system $K_3[Fe(CN)_6]$–$VOSO_4{\cdot}3H_2O$–$NiSO_4{\cdot}7H_2O$–$H_2O$ contained differently colored crystals of various shapes. It was possible to select needle-shaped crystals that had a light yellow color, corresponding to the complexes of vanadium hexacyanoferrate, fine-crystalline brownish-yellow crystals, indicating the presence of $VO(OH)_2$, bluish-greenish crystals in the form of fluffy twigs, which characterize the presence of $Ni(OH)_2$, and gray-green crystals related to nickel hexacyanoferrate.

Thus, the obtained data indicate a complex process of complexation in the triple system $K_3[Fe(CN)_6]$–$VOSO_4{\cdot}3H_2O$–$NiSO_4{\cdot}7H_2O$–$H_2O$. At the same time, complexes of different composition are formed depending on the pH of the solution, and vanadium and nickel hydroxides are present in the alkaline medium.

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## Резюме

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### ГЕКСАЦИАНОФЕРРАТ (III) –, ВАНАДИЛ – ЖӘНЕ НИКЕЛЬ (II) – ҚҰРАМДЫ ЖҮЙЕЛЕРДЕГІ ӨЗАРА ӘРЕКЕТТЕСУ ПРОЦЕСІН ЗЕРТТЕУ

2-хабарлама.

$K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$ жүйесін зерттеу

Компоненттері 1:1:1 қатынасында алынған $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$ жүйесіндегі өзара әрекеттесу процесін pH 2-12 аралығында pH метрлік титрлеу әдісі арқылы зерттеу нәтижелері келтірілген. Зерттеліп отырған жүйені натрий гидроксиді ерітіндісімен титрлеу қисықтарының сипаты оның концентрациясына тәуелді болатыны анықталды. Ең күрделі сипатқа 0,1 моль/л натрий гидроксидімен титрлеу қисығы ие болып табылады, онда pH 3.4 және 4.0 болған кезде әлсіз байқалатын тербелістер мен pH 5.6 және 7,7 болғанда қарқынды тербелістер пайда болады. Зерттелетін жүйеде қышқыл ортада кешенді қосылыстар, яғни ванадий және никель ферроцианидтері, сондай-ақ сілтілік ортада ванадий және никель гидроксидтері түзілу жағдайлары беріледі. Зерттеліп отырған жүйеден пішіндері мен түстері әртүрлі тұнбалар бөлініп алынды, олардың түс сипаттары жоғарыда аталған қосылыстарға сай келеді.

## Резюме

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### ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ В ГЕКСАЦИАНОФЕРРАТ (III)-, ВАНАДИЛ- И НИКЕЛЬ (II) - СОДЕРЖАЩИХ СИСТЕМАХ

Сообщение 2.

Исследование системы $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$

Представлены результаты исследования процесса взаимодействия в системе $K_3[Fe(CN)_6]$–$VOSO_4 \cdot 3H_2O$ – $NiSO_4 \cdot 7H_2O$ – $H_2O$, компоненты которой взяты в соотношении 1:1:1, с помощью метода pH метрического титрования в интервале pH 2-12. Установлено, что характер кривых титрования аликвоты исследуемой системы раствором гидрокисида натрия зависит от его концентрации. Наиболее сложный характер имеет кривая титрования 0,1 моль/л гидроксидом натрия, на которой прописываются слабо выраженные скачки при pH 3.4 и 4.0 и интенсивные скачки при pH 5.6 и 7,7. В исследуемой системе создаются условия образования комплексных соединений – ферроцианидов ванадия и никеля в кислой среде. а также гидроксидов ванадия и никеля в щелочной среде. Из исследуемой системы выделены осадки различной формы и окраски, цветовая характеристика которых соответствует выше указанным соединениям.