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U. ZH. JUSSIPBEKOV, R. M. CHERNYAKOVA, A. A. AGATAYEVA,
K. Y. YERMEKOVA, R. A. KAIYNBAYEVA

JCS «A.B. Bekturov Institute of Chemical Sciences», Almaty, Republic of Kazakhstan

STUDYING THE INFLUENCE OF A NUMBER OF FACTORS ON THE PROCESS OF INTERACTION IN SYSTEMS $К_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O/NiSO_4{\cdot}7H_2O$ – H_2O and $К_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O$– $NiSO_4{\cdot}7H_2O$ – H_2O

Message 3. Study of the effect of the concentration of $VOSO_4{\cdot}3H_2O$ on the composition of the interaction products in the $К_3[Fe(CN)_6]$ – $VOSO_4{\cdot}3H_2O$ – H_2O system using IR spectroscopy

Abstract. The effect of vanadyl sulfate concentration $VOSO_4{\cdot}3H_2O$ on the composition of interaction products in the system $К_3[Fe(CN)_6]$–$VOSO_4{\cdot}3H_2O$–H_2O was studied by IR spectroscopy. The analysis of the IR spectra of samples isolated from the studied equimolecular system indicates the complex nature of the processes occurring in it. It was revealed that in the system under study, mixed ligand complexes of varying composition with the content of H_2O and sulfate groups in the internal sphere are formed. In products with a molar ratio $К_3[Fe(CN)_6]/VOSO_4{\cdot}3H_2O$ equal to 0.22-10, adsorbed and hydrolyzed water is also present. It is established that in the obtained compounds there is a bond V=O and V-O. It is shown that the outer and inner sphere undergo changes due to the transition of the valence of the Fe (III) ↔Fe (II) complexing agent and vanadium, with the formation of complexes of the vanadium aquatic cyanosulfate type.

Keywords: potassium hexacyanoferrate (III), vanadyl sulfate, hexacyanoferrate (II) ion, hexacyanoferrate (III) ion, complexation, IR spectroscopy.

Introduction. In recent years, considerable attention has been paid to the study of complex compounds of vanadium (IV, V) with various bioactive organic and inorganic compounds [1-3]. However, the study of the complexation processes of inorganic salts with vanadium (IV) is limited. It is known that the formation of complex compounds with oxygen-donor and nitrogen-donor ligands is characteristic of vanadium (IV) [4,5]. In the majority of known complex cyan-, vanadium-containing compounds, for example, in cyanide $K_2[VO(CN)_4]$, oxalate $K_2[VO(C_2O_4)_4]$ and acetylacetonate VO_2, there is a bond V = O, similar to that found in vanadyl salts. Moreover, the number of vanadium (IV) complexes that do not contain the V = O bond is extremely limited [6].

A characteristic feature of vanadyl ion is its tendency to various complexation reactions. Therefore, the interaction of vanadyl sulfate $VOSO_4{\cdot}3H_2O$ with potassium hexacyanoferrate (III) in an aqueous medium does not exclude the formation of complex compounds of different composition, including crystalline hydrates. Crystal hydrates are the most difficult objects to study. In works related to this direction, the influence of a number of factors, such as donor-acceptor interaction between anions and water molecules, the crystal structure and location of water in the crystal lattice, the nature and properties of the cation, etc., on the state of water in the crystal is shown [7]. Despite the fact that at the present time numerous studies of crystalline hydrates have been carried out, the results obtained in most cases are not straightforward, especially if we are talking about studying the state of water in them.

In the study of complex compounds of complicated composition to the effective methods include infrared spectroscopy (IR). The method of infrared spectroscopy is a universal physico-chemical method, which is used in the study of the structural features of various inorganic and organic compounds. Differences in chemical structure change the nature of the IR spectrum. The number of characteristic absorption bands of atomic groups, their intensity and the position of the maxima observed in the infrared spectra give an idea of the composition of complex substances. In this connection, the most commonly used method for studying complex compounds of various derivatives with transition metals is IR spectroscopy as a mobile and highly sensitive method for obtaining information [8].

The method of infrared spectroscopy is based on the registration and analysis of infrared absorption spectra or incomplete internal reflection of a substance. Most vibrational transitions in molecules and crystal structures of various compounds are realized in the wavelength range 400-4000 sm^{-1}. The wavelength for each vibration depends on which atoms are involved in it, and it also depends little on their medium. That is, for each functional group (CN, Fe-C, O-H, V-O, etc.), a series of oscillations are characteristic (respectively, of the bands in the IR spectrum). It is on these properties of the IR spectra that the identification of compounds from spectral data is based [9]. From the IR spectra in complex compounds, by comparing them with tabular data and starting compounds, the functional groups and skeleton of the obtained compound can be determined. Indicators of complexation are displacement, splitting, the appearance of new bands, as well as the disappearance of any frequencies from the spectrum serve.

EXPERIMENTAL PART

The study of the effect of the concentration of vanadyl sulfate $VOSO_4{\cdot}3H_2O$ on the interaction process in the equimolar system $K_3[Fe(CN)_6]$–$VOSO_4{\cdot}3H_2O$–H_2O was carried out at room temperature (25°C) in an acidic medium under mixing conditions. The concentration of vanadyl sulfate $VOSO_4{\cdot}3H_2O$ was changed from $3{\cdot}10^{-3}$ to $2{\cdot}10^{-4}$ mol/l. The initial acidity of the medium (pH 3.0) was created with 0.1 N sulfuric acid. After pouring solutions of potassium hexacyanoferrate (III) ($CK_3[Fe(CN)_6] = 2{\cdot}10^{-3}$ mol/l) and vanadyl sulfate with a given concentration and subsequent exposure of the mixture at a certain time (15 min), the precipitates were filtered. The separated precipitates were dried at 30 °C and the IR spectra were taken.

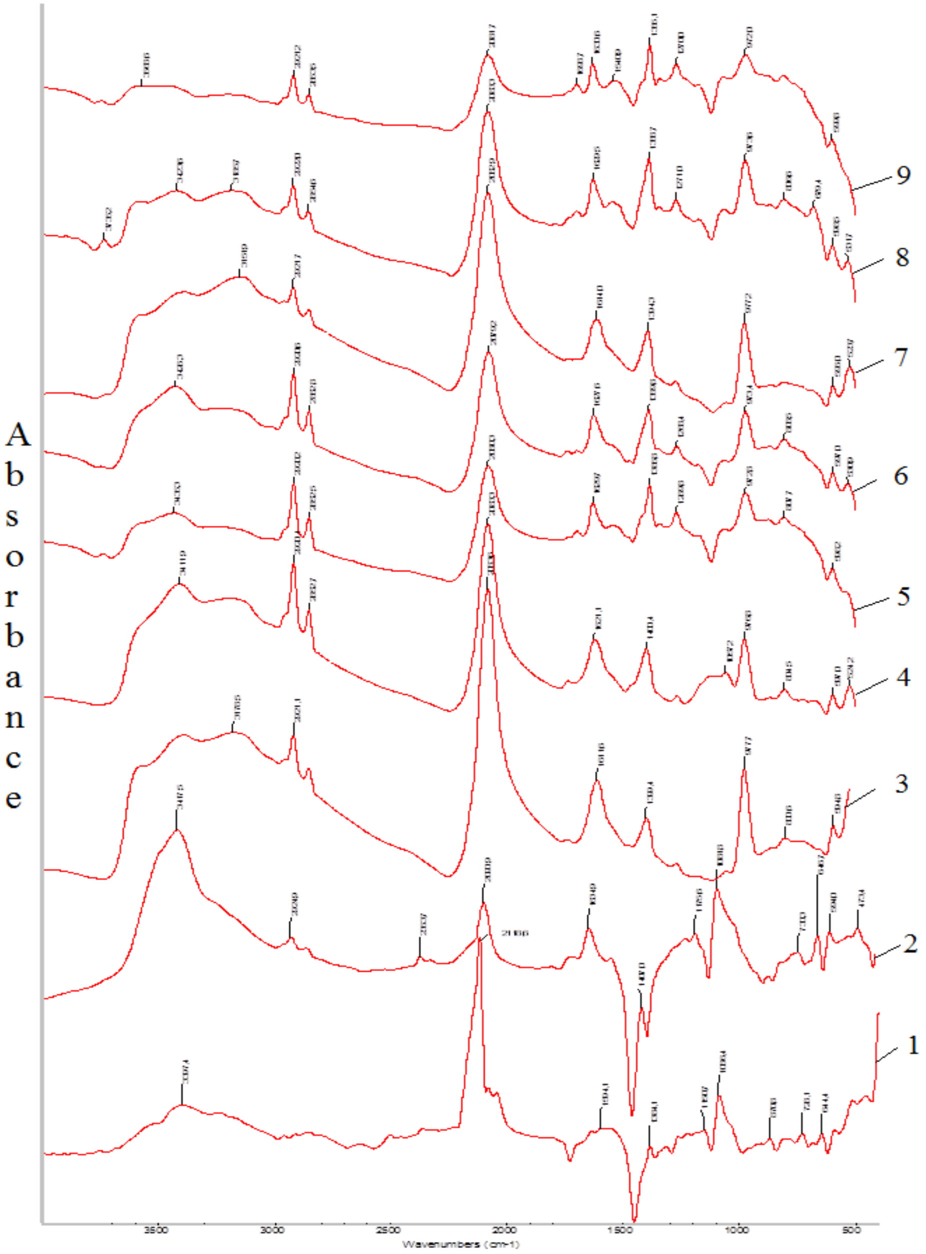
IR spectra were recorded on a «Specord M-80» infrared spectrophotometer in the spectral range of 400-4000 $см^{-1}$. Samples for the study were prepared by the standard method of fitting with KBr.

RESULTS AND DISCUSSION

IR spectroscopic analysis showed that the spectra of the samples under study (curves 3–9) undergo noticeable changes in comparison with the spectra of the initial salts (curves 1, 2). The area of stretching vibrations of water in products isolated from the equimolecular system $K_3[Fe(CN)_6]$–$VOSO_4{\cdot}3H_2O$–H_2O is described by a wider intense range than in the spectrum of vanadyl sulfate (curve 2). The broadening of the absorption band of ν OH oscillations and the appearance of additional peaks on it from the high-frequency side in the area of 3748.9-3722.2 cm^{-1} and low frequencies in the area of 3151.9-3200 cm^{-1}, 2955.6-2921.2 cm^{-1} and 2844.4-2882.8 cm^{-1} due to the presence of a large number of water molecules located in different ways relative to the cation and anion and corresponds to at least two types of hydrogen bonding [4, 10, 11]. The first type reflects a strong bond between the interaction of water molecules with each other and a less strong bond between the interaction of water molecules with an ion, and the second type reflects a stronger H-bond with an anion, and a less strong bond between water molecules.

In all the spectra of the samples under study, a wide band of ν O oscillations has two allowed maxima, the position and intensity of which is determined by the concentration of $VOSO_4{\cdot}3H_2O$ in solution (curves 3–9). According to [12, 13], the high-frequency absorption band in the low-wavelength area of 3388.9-3568.6 cm^{-1} can be attributed to stretching asymmetrical (ν_{as}) oscillations, and the frequency in the longer-wavelength area of 3151.9-3200.0 cm^{-1} to symmetric (ν_s) oscillations of OH groups of water molecules. As the concentration of $VOSO_4$ decreases, their maxima shift to high or low frequencies, and their intensity redistributes. Thus, in the IR spectra of samples obtained from a system with a salt concentration of $VOSO_4{\cdot}3H_2O$ equal to 0.03-0.009 mol/l, where the initial molar ratio of potassium ferricyanide $K_3[Fe(CN)_6]$ to the salt of vanadyl sulfate $VOSO_4{\cdot}3H_2O$ (n) equal to 0.07-0.22, the maxima of low-wave ν_{as} and high-wave ν_s of OH band oscillations are shifted towards high frequencies, respectively, from 3400 to 3435.3 cm^{-1} and 3178.5 to 3200 cm^{-1} (curves 3-5). Moreover, the frequency intensity ν_{as} > frequency intensity ν_s. The decrease in the concentration of $VOSO_4{\cdot}3H_2O$ to 0.007-0.004 mol/l (n = 0.29-0.5) shifts these ranges to low frequencies, respectively, from 3426.3 to 3388.8 cm^{-1} and from 3195 to 3151.9 cm^{-1}, and the intensity of the frequency ν_{as} becomes < intensity of the frequency ν_s (curves 6, 7).

A further decrease in the $VOSO_4{\cdot}3H_2O$ concentration from 0.0004 to 0.0002 mol/l (curves 8.9, n = 5-10) is reflected in the enhancement of the low-wave frequency ν_{as} (3423.6 ← 3568.6 cm^{-1}) and the decrease in high-wave strips ν_s (3185.7 → 3177.8 cm^{-1}). Thus, in the IR spectrum of a sample obtained with C_{VOSO4} = 0.0002 mol/l (n = 10), the low-wave frequency ν_{as} shifts towards higher frequencies by 145 cm^{-1}, and the frequency ν_s of OH vibrations is represented by a diffuse range shifted by 8 cm^{-1} to the long-wave area (in the direction of lower



IR spectra of the initial salts and products obtained in the $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – H_2O system.

The initial salt: **1** – $K_3[Fe(CN)_6]$, **2** – $VOSO_4 \cdot 3H_2O$. Interaction products in the system $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – H_2O: curves **3-9**: **C_{VOSO_4},** mol/l**:** **3** – $3 \cdot 10^{-2}$ (n=0,07); **4** – $1 \cdot 10^{-2}$ (n=0,2); **5** – $9 \cdot 10^{-3}$ (n=0,22); **6** – $7 \cdot 10^{-3}$ (n=0,29); **7** – $4 \cdot 10^{-3}$ (n=0,5); **8** – $4 \cdot 10^{-4}$ (n=5); **9** – $2 \cdot 10^{-4}$ (n=10) frequencies) with a simultaneous decrease in its intensity (curve 9). This is due to the strengthening of the H-bond in the sample structure [14].

The revealed changes in the water oscillations in the ν_{as} and ν_s area indicate that the H-bond with the anion increases with decreasing $CVOSO_4$ in the product [14]. Such an enhancement is possible due to the transformation of the structure to oxonium, when particles appear more prone to intermolecular type of interaction. The presence of the oxonium ion H_3O^+ can be judged by the frequencies in the spectrum of the studied samples in the area of 2955.6-2920.4 cm^{-1} and 2844.4-2882.8 cm^{-1}, the intensity of which increases with decreasing $CVOSO_4$ from 0.03 to 0.007 mol/l (n = 0.07-0.29) (curves 3-6), as well as the presence of weak absorption in the area of 1699-1748.8 cm^{-1}, corresponding to the vibration of the H_3O^+ ion (curves 3-9). Oxonium ion is located inside a three-dimensional ferrocyanide lattice, when water molecules, both coordination and zeolite, are linked into chains of H-bonds with H_3O^+ ions. This leads to the effect of tunneling or proton transfer along the axis of H-bonds: H_2O ... H_3O^+ ... H_2O. Moreover, such processes are usually facilitated in hydrates [15].

This assumption is confirmed by the fact that on the IR spectra of the studied samples, the δ_{FeCN} bond oscillations (495 and 418 cm^{-1}) overlap with a stronger vibration of the Me-O bond and are not register in the spectra [16]. The found changes in the described spectra of the studied products are explained by the introduction of water molecules directly into the ferrocyanide lattice by equilibrium:

$$[Fe(CN)_6]^{3-} + H^+ + H_2O \leftrightarrow [Fe(CN)_5OH_2]^{3-} + HCN.$$

In this case, the replacement of CN^- by H_2O reduces the manifestation of oscillations of the ν_{FeCN} band in the long-wavelength area, which is reflected in the simplification of the spectra of the samples in the low-frequency area: the frequencies 728.1 and 870 cm^{-1} disappear, as well as the bands 1300 and 1384.1 cm^{-1}. Apparently, a high content of vanadium in solutions initiates the formation of H-bonds, since with the increase in $CK_3[Fe(CN)_6]$, the intensity of the frequencies in the indicated areas somewhat decreases (curves 7-9).

The deformation oscillations of water in the IR spectra of the studied products are recorded in two ranges in the area of 1630-1611 cm^{-1} (δ_1 OH) and 1400.4-1385.1 cm^{-1} (δ_2 OH). Moreover, the latter frequency overlaps the absorption of ν_{CN} (1384.1 cm^{-1}), which is characteristic of the initial $K_3[FeCN)_6]$. Comparison of the indicated absorption ranges of the studied samples with similar frequencies in the spectrum of the initial vanadyl sulfate revealed their shift to the long-wavelength area (towards lower frequencies), broadening and increased intensity due to the presence of water of different nature. Although the ranges of deformation oscillations of water are less sensitive to the formation of water by hydrogen bonds of different strength than the frequencies of its valence oscillations [11, 12], however, δ OH fluctuations in the samples under study change (curves 3-9). So, as $CVOSO_4$ decreases in the IR spectrum of samples, the low-wave frequency δ OH (at high frequencies) shifts towards higher frequencies (1611.6…1630 cm^{-1}), and the high-wave frequency δ OH (at low frequencies) shifts to lower frequencies (1399...1385 cm^{-1}). This indicates first the enhancement of the H-bond, then the H-anion bond, and the presence of a frequency of 1630 cm^{-1} in samples with a concentration of 0.0004–0,0002 mol/l (*n* = 0.5–10) is already due to the presence of molecular adsorbed water [12]. It should be noted that with decreasing $CVOSO_4$ (respectively, in samples $CK_3[FeCN)_6]$ increases, the nature of the deformation oscillations of water changes. If in samples obtained from solutions with $CVOSO_4$ = 0.03-0.01 mol/l (*n* = 0.07-0.2), the intensity δ_1 OH > δ_2 OH (curves 3,4), then in the sample with $CVOSO_4$ = 0.009-0.007 mol/l (*n* = 0.22-0.29), intensity δ_1 OH < δ_2 OH, and the bands become narrower (curve 5) with subsequent broadening (curve 6). In the sample separated from the solution with $CVOSO_4$ = 0.004 mol/l (*n* = 0.5), the δ_1 OH > δ_2 OH (curve 7), and in the samples obtained from the solution with $CVOSO_4$ = 0.0004-0,0002 mol/l (*n* = 5-10), there is a redistribution of the intensity of these frequencies (δ_1 OH < < δ_2 OH) and they become narrower (curves 8.9). Significant changes in the δ OH oscillations bands reflect the above described frequency variations in the area of stretching oscillations of the OH group and are associated with the same processes.

Analysis of IR spectra in the area of valence and deformation oscillations of water showed that there is coordination-related water in all selected products, when a stronger bond corresponds to the interaction of water molecules between a hydrogen bond, where the H-bond is stronger with the anion, and less strong between water molecules and also hydrolyzed H_2O. Moreover, the use in our case of the salt of vanadium, containing the sulfate ion $VOSO_4 \cdot 3H_2O$, strengthens the H-bond in the crystal hydra.

As shown in [12, 14, 16], water molecules that are part of inorganic crystalline hydrates are not neutral structural elements in the hydrate lattice, but participate in various interactions with the cationic and anionic salt sublattice. Therefore, the fact of the presence of H_2O in the studied samples, which is confirmed by the presence of the absorption region of 1590-1650 cm^{-1}, can serve as evidence of the existence of a water molecule as a whole in the studied compounds. In addition, a weak absorption is recorded in the spectra of all products in the area of 3748.9-3722.2 cm^{-1}, which characterizes the oscillations of free hydroxyl acids resulting from hydrolysis [17, 18].

Thus, crystallization water is present in the obtained samples – this is the H_2O molecule trapped in the crystal lattice by forming hydrogen bonds with the anion or by forming weak ionic bonds with the metal, adsorbed water and non-hydrogen bonds (free) hydroxyl groups, the appearance of which can be explained as the result of a possible hydrolysis process.

There is an intense absorption peak in the IR spectra of all studied samples in the area of 2079.2-2083.6 cm^{-1} and a weak band in the area of 1268.4-1288.8 cm^{-1}, corresponding to the vibrational frequencies of the ferrocyanide ion ν (CN) and confirming the presence of the ferrocyanide phase. Comparison of the IR spectra of the studied samples with the spectra of the initial $K_3[FeCN)_6]$ revealed a significant difference in this area.

The main frequency ν (CN) active in IR absorption shifts the side of lower frequencies by (34.9-39.3) cm^{-1} (curves 3-9) on all IR spectra of the samples under study, compared to the spectrum of the initial salt $K_3[FeCN)_6]$ (curve 1). Moreover, with a decrease in $CVOSO_4 \cdot 3H_2O$ in solution from 0.03 to 0.007 mol/L (n = 0.07-0.29), an increase in the shift of the intense ν (CN) oscillation band towards lower frequencies is observed in the spectra of the obtained products, 2083,6→2083,3→2080,3→2079,2 cm^{-1} (curves 3-6). A further decrease in the concentration of $VOSO_4 \cdot 3H_2O$ in the solution from 0.004 to 0.0002 mol/l (n = 0.5-10) increases this frequency to 2082.9 ... 2083.3 cm^{-1} (curves 7-9), i.e. shifts it toward higher frequencies already (2.6-4.1) cm^{-1} compared to the frequency of the previous sample (2079.2 cm^{-1}) (curve 6). In addition, clear broad absorption bands of 1526.6 and 1540.9 cm^{-1} are recorded on the IR spectra of samples isolated from the system with $VOSO_4$ = (0.0004-0,0002) mol/l (n = 5-10), which refer to the ν CN oscillations, and with a decrease in the concentration of $VOSO_4 \cdot 3H_2O$ shift towards higher frequencies (curves 8, 9).

The less intense frequency of valence oscillations of CN bonds in the long-wavelength area of 1268.4-1288.8 cm^{-1} is also shifted toward lower frequencies compared to the similar band in the initial salt $K_3[Fe(CN)_6]$ (1300 cm^{-1}). Howe-ver, in contrast to the main ν (CN) band, which lies in the high-frequency area, the described frequency shifts to 0.01 mol/l in the solution towards higher frequencies (1271.1→1288.8 cm^{-1}), and as further decreases, $CVOSO_4$ shifts towards lower frequencies, but with a tendency to a slight increase in samples isolated from a solution with a low content of vanadium salts: 1269.8→1268.4 (for n = 0.22-0.29) and 1268.8→1271→1270 cm^{-1} (for n = 0.5-10).

It should be noted that the change in the intensity of the absorption band ν (CN), depending on $CVOSO_4$, is undulating. So the intensity of the frequency in the area of 1268.4-1288.8 cm^{-1} with decreasing $CVOSO_4$ from 0.03 to 0.009 mol/l (n = 0.07-0.22) decreases (curves 3-5), from 0.007 to 0.004 mol/l (n = 0.29-0.5) increases (curves 6.7), and from 0.0004 to 0.0002 mol/l (n = 5-10) decreases again (curves 8.9). While the main frequency ν CN, lying in the area of 2079.2-2083.6 cm^{-1}, with the same concentrations of $VOSO_4 \cdot 3H_2O$ first increases, then decreases and then increases again.

A low-intensity band is recorded in the low-frequency area of 800-810 cm^{-1} in the IR spectra of all samples, which also characterizes the oscillations ν CN and is shifted relative to the analogous frequency in the spectrum of the initial salt $K_3[Fe(CN)_6]$ (870.8 cm^{-1}) by 70,8-60.8 cm^{-1} towards low frequencies. At the same time, with decreasing $CVOSO_4$, the nature of this frequency changes noticeably. It is prescribed by a narrow absorption band in samples with n = 0.07-0.29 (curves 3-6), then it is noticeably broadened in the sample with n=0.5 (curve 7), and with a subsequent decrease in the concentration of vanadyl sulfate again narrows (n=5 and 10, curves 8.9) with a simultaneous decrease in intensity in the last sample (n=10).

Since the frequencies ν CN undergo changes in all the studied samples, this means that the relative increase or decrease in the values of frequencies and their intensity is due to changes in the force coefficients. It is known that for Fe (II) and Fe (III) hexacyanocomplexes, a decrease in the oxidation state of iron from 3 to 2 reduces the basic frequency ν (CN) [4,19], and an increase in the oxidation state of Fe from 2 to 3 increases its frequency [4]. Perhaps the change in the valence of the Me-complexing agent (Fe) explains the fact that with decreasing $CVOSO_4$ there is a tendency first to decrease in the frequencies ν CN, then to increase them and then again to decrease. The wavy frequency change is accompanied by restructuring of the hexacyanoferrate anion: hexacyanoferrate (III) $[Fe(CN)_6]^{3-} \rightarrow$ $\rightarrow$ hexacyanoferrate (II) $[Fe(CN)_6]^{4-}$ and hexacyanoferrate (II) $[Fe(CN)_6]^{4-} \rightarrow$ $\rightarrow$ hexacyanoferrate (III), that is, the transition of $Fe^{III} \leftrightarrow Fe^{II}$ occurs [4, 19]. Moreover, the presence in the system of hexacyanoferrate (III) ion $[Fe(CN)_6]^{3-}$ is possible both due to the formation of $[Fe(CN)_6]^{3-}$ ($Fe^{III} \rightarrow Fe^{II}$ transition), and due to its excess, when $CVOSO_4 \cdot 3H_2O < CK_3[Fe(CN)_6]$ conditions are created in the system under study.

According to [4], characteristic frequencies v(CN) and v FeC are sensitive to the nature of the outer-sphere ion in the IR spectra of ferri- and ferrocyanide compounds. So, the frequencies v(CN) hexacyanoferrate (III) ion $[Fe^{III}(CN)_6]^{3-}$ are higher than the frequencies v(CN) $[Fe^{II}(CN)_6]^{4-}$, the frequencies vFeC of ferricyanide are less than vFeC of ferrocyanides, which is associated with the greater role of π- dative components in bonds of ferrocyanide groups. In this case, the kinematic interaction coefficients are practically independent of the type of hexacyanoferrate ion. The change in the intensity and position of frequencies is explained by a decrease in the contribution of the π-dative component to the $Fe^{I}CN$ bonds (iron-cyano groups), which leads to stabilization of the CN bonds and a decrease in the order of the FeC bonds. With an increase in the polarizing effect of the outer-sphere cation, the bonds of the NM are strengthened due to the displacement of electrons from the loosening orbitals of the CN groups, as a result the CN bond is strengthened. This effect is transmitted through the CN groups to strengthen the FeC bond and causes electrons to be pulled away from the iron atom towards the CN groups. As a result of the described processes, there is a change in the valence of iron in hexacanoferrate-ion and its restructuring and, as a consequence, a change in the intensity of the frequencies. Since, with decreasing $CVOSO_4$, the main frequencies of ν CN bonds oscillations undergo changes of a wave-like nature, it is possible to form hexacyanoferrate complexes with both ferrocyanide and ferricyanide anions. A change in the ferrocyanide lattice in the obtained products is also indicated by the absence in the spectra of all samples of the frequency of 1150.7 cm^{-1} and the absorption bands of 728.1; 644.4 and 418 cm^{-1}, characteristic for the oscillations of the ν and δ CN bonds, recorded in the IR spectrum of the individual salt $K_3[Fe(CN)_6]$ (curve 1).

In the IR spectra of the samples under study, the area of oscillations of VO bonds undergoes significant changes as compared with the spectrum of the initial salt $VOSO_4·3H_2O$. Thus, the frequencies of 730.3 and 473.4 cm^{-1} disappear from the spectra of the studied products, which correspond to oscillations of VO bonds in $VOSO_4·3H_2O$. The frequency is fixed in the area of 972.0-977.7 cm^{-1} in all IR spectra, the position of which allows to refer it to the oscillations of the double V = O bond [5,20,21]. Moreover, the maximum of this frequency relative to the peaks of the initial salt of $VOSO_4·3H_2O$ (1081.8 cm^{-1}) shifts toward lower frequencies by 109.8–104.1^{-1}. A comparative analysis of the IR spectra of the obtained samples showed that with a decrease in the concentration of $VOSO_4·3H_2O$ from 0.03 to 0.009 mol/l (n = 0.07-0.22), the absorption intensity of the indicated frequency decreases with a simultaneous shift of maximum to the lower frequency area 977, 7 cm^{-1} ← 976.8 cm^{-1} ← 972.8 cm^{-1} (curves 3-5). The intensity of the band increases slightly with its simultaneous shift towards high frequencies 973.4 cm^{-1} → 977, 2 cm^{-1} (curves 6,7) in samples isolated from the system with $CVOSO_4·3H_2O$ = 0.007- 0.004 mol/l (n = 0.29-0.5), and with $CVOSO_4$ = 0.0004-0,0002 mol/l (n = 5-10), the frequency intensity decreases again with its maximum shifted towards low frequencies 973.6 cm^{-1} ← 972 cm^{-1} (curves 8, 9).

A new frequency is recorded in the low-frequency area 522.2-531.7 cm^{-1} (curves 3-4 , 6-8) in the IR spectra of samples obtained from a system with *n* = 0.07-0.2 and *n* = 0.29-5.0, which is absent in the spectra of samples isolated from the system with *n* = 0.22 and 10 (curves 5 and 9). A comparison of the IR spectra of the studied samples showed that in samples with *n* = 0.07–0.2 and *n* = 0.29, the described absorption band shifts towards high frequencies 522.2 → → 524.2…. → 530 cm^{-1}, in for a sample with *n* = 0.5, it decreases by 6.3 cm^{-1} (523.7 cm^{-1}), and with n = 5 it increases again with respect to the previous frequency by 8 cm^{-1} (531.7 cm^{-1}). According to [20,21], the described frequency by its position in the IR spectrum can be attributed to the vibrations of ordinary V–O bonds. The appearance of such a connection in the obtained products is probably due to the formation of new coordination compounds. According to [23-26], in the IR spectra of products isolated from water-salt vanadium-containing systems, the V = O and V–O bonds were found. Moreover, vibrations of V-O bonds are most sensitive to the structure of the complex due to the stretching of O-O bonds in the complexes [23, 24]. In this case, the valence vibrations of the V = O bond in the tetravalent vanadium oxo complexes are usually found in the higher frequency range compared to the pentavalent vanadium oxo complexes [26, 27]. Infrared spectroscopy is used by us to prove the presence of functional groups in the molecule. Therefore, we believe that the identified shift of the vibrational frequencies of the VO bonds in the IR spectra of the samples under study indirectly indicates the formation in them of an ordinary V-O and double bond. This is confirmed by the appearance of a weakly pronounced band in the area of 800–810 cm^{-1} in the spectra of the studied samples. This frequency characterizes the stretching of O-O bonds [22-24, 25]. Therefore, its wave-like character of displacement depending on $CVOSO_4$: 800.6 (n = 0.07) ← 800.4 (n = 0.2) ← 807.7 (n = 0.22) → 806.5 (n = 0 , 29) → 800 (n = 0.5) → 806.6 (n = 5) → 810 cm^{-1} (n = 10) is due to the formation of both V = O and V-O bonds in products.

According to [20, 28], in a complex ion with the same coordination number of the central atom, an increase in the valence of the cation by one shifts the absorption bands to higher frequencies. The detected change in the IR spectra of the samples under study, as well as the values of the frequencies of valence oscillations of the V = O bonds, are explained by redox processes occurring in the $K_3[Fe(CN)_6]–VOSO_4·3H_2O–H_2O$ system. It is known that vanadium in oxidation states (IV) and (V) and iron in oxidation states (II) and (III) are a very complex redox system [6]. In this case, vanadium (IV) easily transforms from the tetravalent state (+4) to the pentavalent (+5) and back [29], and Fe (III), Me-complexing agent in potassium ferricyanide, to Fe (II) and back [4, 19]. Given the properties of vanadium (IV, V) and hexacyanoferrate (III, II), it can be said that under certain conditions in the system under study changes in the valence of the $V^{4+}↔V^{5+}$ and Fe (II)↔Fe cations, which leads to the above-described shift of the vibration absorption bands VO and CN links in the high-frequency or low-frequency area. In addition, the average intensity frequencies of 1081.8 and 1086.4 cm^{-1}, corresponding respectively to the vibrations of the V = O and CN bond groups in the initial salts of $VOSO_4 \cdot 3H_2O$ and $K_3[Fe(CN)_6]$ (curves 1, 2), disappear in obtained samples, instead of the expected amplification of the peak intensity due to the superposition of close signals of the specified frequencies. In this case, in the IR spectrum of the selected samples, starting from n = 0.2 (curve 4-9), there is a weakly pronounced band of 1057.2 cm^{-1}. With decreasing $CVOSO_4$ in a solution, the intensity of the frequency in the IR spectra of the selected samples decreases, and its *maximum* wave-like shifts to the low- or high-wave area. So in the spectra of samples with n = 0.22 (curve 5) *maximum* is shifted towards high frequencies (1066.6 cm^{-1}), with n = 0.29-0.5 (curves 6.7) - into the low frequency area (1064.8 and 1055.5 cm^{-1}), and at higher values of n = 5-10 (curves 8.9) - again to the side from high frequencies (1066.7 cm^{-1}). The revealed changes in the nature and position of this frequency in the spectrum are apparently due to the above-described processes, accompanied by a change in the valence of the Me complexing agent and the vanadium (IV) cation.

The range of oscillations of the SO_4^{2-} ion is noteworthy. On the IR spectra of all samples, there is a clearly pronounced absorption band in the area of 594.0-599.8 cm^{-1}, which belongs to the δ SO_4^{2-} ion oscillations, which indicates the presence of a sulfo group in the obtained compounds. Moreover, the maximum shift of the signal of this band to the high frequency area 594.0.....599.8 cm^{-1} as $CVOSO_4·3H_2O$ decreases in solution (n increases) indicates the in-sphere state of SO_4^{2-} in the complex [20]. Probably in this case the SO_4^{2-} ion is coordinated with the metal, its symmetry is reduced from Td (SO_4^{2-} ion) to C_{2V} with the formation of a bidentate complex [20]. This assumption is confirmed by the presence of weak peaks at 1100 and 1166 cm^{-1} (curve 4) in samples with n = 0.2, and 679.4 cm^{-1} (curve 6) in the sample with n = 5, as well as the absence in all spectra frequencies of 646.7 cm^{-1}, corresponding to the deformation vibrations (δ) of the SO_4^{2-} ion. The formation of complex compounds containing a sulfo group is reflected not above the described displacement and redistribution of the intensities of the characteristic absorption frequencies of the ferrocyanide anion, as well as the VO bonds. The presence of the SO_4^{2-}-anion in the samples under study is also indicated by the pattern of changes in the spectrum in the area of the deformation and stretching vibrations of water compared with the IR spectrum of the initial vanadium ferricyanide salt (curve 2). However, given the nature of the change in ν OH vibrations and the previously described introduction of H_2O molecules into the ferrocyanide lattice, we can assume the formation of complex compounds with ligands, including both the sulfo group and the water molecule. The formation of different-ligand compounds in the system under study, depending on the concentration of vanadium salt, is also indicated by the wave-like nature of the change in the value of frequencies corresponding to fluctuations in the SO_4 group. So, in the IR spectra of samples with n=0.07–0.22, the δ SO_4^{2-} band with decreasing $CVOSO_4$ is shifted to the long-wavelength area (594 ← 597 ← 598.2 cm^{-1}), in samples with n = 0.29-0.5 fixed in the low-wave area (597 and 596 cm^{-1}), as compared with the previous one (598.2 cm^{-1}), and in samples with n = 5.0-10.0 it moves back to the long-wave area 598.5 cm^{-1} → 599.8 cm^{-1}. The introduction of the sulfo group into the complex is confirmed by the appearance in the spectrum of the sample with n = 5 an additional signal of 679.4 cm^{-1}, which refers to the stretching vibrations of the S-O bonds and the SO_4^{2-} groups [20, 30]. The presence of sulfate-ligand in the spectrum of the samples under study indicates the complex nature of the vanadium ion [4, 20-23].

Thus, on the basis of the conducted studies, it was revealed that the concentration of vanadyl sulfate has a significant effect on the composition of complex compounds obtained in the equimolecular system $K_3[Fe(CN)_6]–VOSO_4·3H_2O–H_2O$. In the system under study, mixed ligand (mixed) complexes of variable composition are formed. In the inner sphere of such complexes are water and the sulfate group, i.e. aquatic sulfate complexes are formed. Moreover, in complex compounds with *n* = 0.22–10 (curves 5–9) there is also adsorbed and hydrolytic water, which is located in the external sphere. Judging by the nature of the IR spectra, the external and internal spheres undergo changes due to the transition of the Fe (III) ↔ Fe (II) complexing agent and the change in Me valence in the external sphere, i.e. replacing K^+ with V^{4+} or VO^{2+} to form compounds - vanadium aquatic sulphates (vanadyl). It is possible that under certain conditions (a change in $VOSO_4$) the transition V(IV)↔ V(V) takes place, and, starting with *n*=0.29 to *n*=5, aquatic sulfate vanadates are also formed. It should be noted that it is quite difficult to fully identify the vibrations of hexacyanoferrate complexes with vanadium (vanadyl), since the IR spectra represent a complex system of absorption bands of hexacyanoferrate ligands, bonds of the mixed ligand Me (VO), as well as distorted crystal lattice [31]. The analysis of the IR spectra of samples isolated from an equimolecular system at different concentrations of the salt $VOSO_4 \cdot 3H_2O$ indicates the complex nature of the processes occurring in it.

REFERENCES

[1] Lapochkin O.V. Preparation and study of complex compounds with amino acids: glycine, [A]-alanine, [B]-alanine: Abstract – 15.00.02. Pyatigorsk, 2008. 22 p.

[2] Kornev V.I., Kropacheva T.N., Sorokina U.V. Coordination compounds of oxovanadium (IV) with organophosphorus complexes in aqueous solutions // Journal of Inorganic Chemistry. 2015. Vol. 60, N 3. P. 458-464.

[3] Popova T.V., Scheglova N.V., Petrova I.V. Complexation of vanadium (III) with pyro-phosphate - anions // Her. higher studies institutions. Chemistry and Chemical technology Series. 2009. Vol. 52, N 3. P. 11-15.

[4] Tananaev I.V., Seifer G.B., Kharitonov Yu.Y., Kuznetsov V.G., Korolkov A.P. Chemistry of Ferrocyanides. M.: Science, 1971. 320 p.

[5] Kolosov N.A. Coordination compounds of vanadium (+3, +4, +5) with ligands of OO-, ONO- and OON-types as catalysts for the reaction of polymerization and oligomerization of α-olefins: Abstract … 02.00.01; 02.00.06. M., 2017. 24 p.

[6] Based on site materials: helpiks.org›6-37234.html (date of the application 20.02.2019).

[7] Based on site materials: msd.com.ua›sostoyanie-vody-v…i…
kristallogidratax(date of the application 20.02.2019).

[8] Degtyarik M.M., Gaponik P.N., Ivashkevich O.A. Investigation of complex compounds of copper (II) by N-monosubstituted tetrazoles by the method of IR - spectroscopy // Bulletin of BSU. 2009. Series 2, N 2. P. 3-6.

[9] Panikorovsky T.L., Britvin S.N. The use of infrared spectroscopy to study the structural features of organic and inorganic compounds // St. Petersburg state university, 2013. P. 1-5: based on site materials: xrd.spbu.ru›netcat_files/userfiles/
About use…(date of the application 20.02.2019).

[10] Yukhnevich G.V. Infrared Water Spectroscopy. M.: Science, 1973. P. 1762-1766.

[11] Karyakin A.V., Kriventsova G.A. State of water in organic and inorganic compounds. M.: Science, 1973. 123 p.

[12] Based on site materials: msd.com.ua›sostoyanie-vody-v-organicheskix …voda-v… (date of the application: 22.01.2019).

[13] Ordinartsev D.P., Sviridov A.V., Naboichenko S.S., Yurchenko V.V. Sorption extraction of vanadium compounds from acid solutions by highly dispersed modified aluminosilicate // SUSU Journal. Metallurgy Series. 2017. Vol. 17, N 10. P. 79-82.

[14] Stenkin Yu.A. Spectroscopic manifestations of the hydrogen bond in dielectric crystals and amorphous systems during radiation and thermal effects: abstract.…02.00.04.: Omsk, 2000. 16 p.: based on site materials: dissercat.com›…proyavleniya…v-dielektricheskikh…i…(date of the application: 22.01.2019).

[15] Timokhin V.M., Garmash V.M., Tedzhetov V.A. Infrared spectra of wide-gap crystals with proton conductivity // Electron. scientific Journal: Current problems of science and education. Section: Physics and Mathematics. 2013. N 3: based on site materials: science-education.ru›ru/article/view…(date of the application: 22.01.2019).

[16] Makatun V.N., Shchegrov L.N. The state of water in inorganic crystalline hydrates and the peculiarities of the reaction of their dehydration // Advances in Chemistry. 1972. Vol. 41. P. 1937-1950.

[17] Vorobeva N.M., Fedorova E.V., Baranova N.I. Vanadium: biological role, toxicology and formacological use // Medits. scientific and applied journals "Biosphere". 2013. Vol. 5, N 1. P. 77- 82.

[18] Anisimov A.V., Lesnugin A.Z., Senayvin V.M., Vedorova E.V. Vanadium peroxo complexes with pyridine ligandes as sulfide oxidation catalysts // Petroleum Chemistru. 2002. Vol. 42. P. 121-123.

[19] Chernyakova R.M., Jussipbekov U.Zh. IR spectroscopic and X-ray diffraction studies of ferrocyanide compounds obtained in systems «$K_3[Fe(CN)_6]$- $FeSO_4 \cdot 7H_2O$-H_2O» and $K_4[Fe(CN)_6]$-$FeSO_4 \cdot 7H_2O$-H_2O» // Chemical Journal of Kazakhstan. 2013. N 4. P. 98-107.

[20] Based on site materials: vuzlit.ru›321639/ionnoe…vanadiya… produktivnogo…

[21] Itkis D.M. Superfine materials based on vanadium and manganese oxides for lithium-ion and lithium-air chemical current sources: Abstract ... 02.00.21; 02.00.05. M.: 2-nd format, 2010. 24 p.

[22] Wu J.-Q., Li Y.-S. Well-defined vanadium complexes as the catalysts for olefin polymerization // Coord. Chem. Rev. 2011. Vol. 255. P. 2303-2314.

[23] Fedorova E.V., Rybakov V.B., Senyavi V.M., et al. Synthesis and crystal structure of sodium (2,2-bipyridyl)oxodiperoxovanadate(V) octahy-drate // Russ. J. Coord. Chem. 2002. Vol. 28. P. 483-486.

[24] Anisimov A.V., Fedorova E.V., Nesterenko P.N., Senyavin V.M., Tarakanova A.V. Stereoselective Oxidation of Sulfides in the Presence of Chiral Peroxovanadium Complexes // Bulletin of Moscow State University. Series 2: Chemistry. 2007. N 3. P. 201-206.

[25] Podvalnaya N.V., Volkov V.L. Hydrolytic precipitation of calcium polyvanadates in solutions of vanadium (IV), (V) // Journal of Inorganic Chemistry. Series: Physico-chemistry solutions. 2007. Vol. 52, N 9. P. 1566-1571.

[26] Fedorova E.V. Oxidation of organic sulfides with hydrogen peroxide in the presence of vanadium peroxocomplexes: Abstract ... 02.00.13: petrochemistry. M.: MSU, 2003. 34 p.

[27] Vorobeva N.M., Fedorova E.V., Baranova N.I. Vanadium: biological role, toxicology and formacological application // Interdisciplinary scientific journal "Biosphere". 2013. Vol. 5, N 1. P. 77-96.

[28] Based on site materials: cryst.geol.msu.ru›literature/kurs/2008_03_…(date of the application: 22.01.2019).

[29] Sukhanov A.A., Yakutseni, Petrova Yu.E. Evaluation of the prospects for the industrial development of the metal-bearing potential of oil and possible ways of its implementation // Oil and Gas Geology. Theory and practice. 2012. Vol. 7, N 4. P. 1-23.

[30] Nwe Schwan U. Sorption extraction of vanadium (V) from dilute solutions: Dis. ... Candidate of Technical Sciences: 05.17.02 / Mendeleev RCTU. - M., 2014. 150 p. Inv. No. 005550507.

[31] Nakamoto K. IR spectra and Raman spectra of inorganic and coordination compounds. M.: Mir, 1991. 536 p.

Резюме

Ө. Ж. Жүсіпбеков, Р. М.Чернякова,
А. А. Ағатаева, Қ. Е. Ермекова, Р. А. Қайыңбаева

$K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$/$NiSO_4 \cdot 7H_2O$ – H_2O және $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$– $NiSO_4 \cdot 7H_2O$ – H_2O ЖҮЙЕЛЕРІНДЕГІ ӨЗАРА ӘРЕКЕТТЕСУ ПРОЦЕСІНЕ КЕЙБІР ФАКТОРЛАРДЫҢ ӘСЕРІН ЗЕРТТЕУ

3-хабарлама. $K_3[Fe(CN)_6]$ – $VOSO_4 \cdot 3H_2O$ – H_2O жүйесіндегі өзара әрекеттесу өнімдерінің құрамына $VOSO_4 \cdot 3H_2O$ концентрациясының әсерін ИҚ-спектроскопия әдісі арқылы зерттеу

ИҚ-спектроскопия әдісімен $K_3[Fe(CN)_6]$–$VOSO_4 \cdot 3H_2O$–H_2O жүйесіндегі өзара әрекеттесу өнімдерінің құрамына ванадил сульфаты $VOSO_4 \cdot 3H_2O$ концентрациясының әсері зерттелді. Зерттеліп отырған эквимолярлы жүйеден бөліп алынған үлгілердің ИҚ-спектрлеріне талдау жасау нәтижесі ондағы жүретін процестердің өте күрделі екенін көрсетті. Зерттеліп отырған жүйеде ішкі сферасында H_2O мен сульфат топтары бар ауыспалы құрамды әртүрлі лигандалы (аралас) кешендер түзілетіні анықталды. $K_3[Fe(CN)_6]$/ $VOSO_4\cdot 3H_2O$ мольдік қатынасы 0,22-10 тең өнімдерде, сондай-ақ, абсорбцияланған және гидролизді су бар. Алынған қосылыстарда V=O және V-O байланысы болатыны анықталды. Сыртқы және ішкі сфералары ванадий аквацианосульфаты секілді кешенді түзе отырып, кешен түзушінің Fe(III)↔Fe(II) және ванадийдің валенттілігі ауысуына негізделген өзгерістерге ұшырайтыны көрсетілді.

Түйінді сөздер: калий (III) гексацианоферраты, ванадил сульфаты, гексацианоферрат (II) ионы, гексацианоферрат (III) ионы, кешен түзілу, ИҚ-спектроскопия.

Резюме

У. Ж. Джусипбеков, Р. М. Чернякова,
А. А. Агатаева, К. Е. Ермекова, Р. А. Кайынбаева

ИЗУЧЕНИЕ ВЛИЯНИЯ РЯДА ФАКТОРОВ НА ПРОЦЕСС ВЗАИМОДЕЙСТВИЯ В СИСТЕМАХ $K_3[Fe(CN)_6]$ – $VOSO_4\cdot 3H_2O/NiSO_4\cdot 7H_2O$ – H_2O и $K_3[Fe(CN)_6]$ – $VOSO_4\cdot 3H_2O$– $NiSO_4\cdot 7H_2O$ – H_2O

Сообщение 3. Изучение влияние концентрации $VOSO_4\cdot 3H_2O$ на состав продуктов взаимодействия в системе $K_3[Fe(CN)_6]$ – $VOSO_4\cdot 3H_2O$ – H_2O методом ИК-спектроскопии

Методом ИК-спектроскопии исследовано влияние концентрации сульфата ванадила$VOSO_4\cdot 3H_2O$ на состав продуктов взаимодействия в системе $K_3[Fe(CN)_6]$–$VOSO_4\cdot 3H_2O$–H_2O. Проведенный анализ ИК-спектров образцов, выделенных из исследуемой эквимолекулярной системы, указывает на сложный характер протекающих в ней процессов. Выявлено, что в исследуемой системе образуются разнолигандные (смешанные) комплексы переменного состава с содержанием H_2O и сульфатогруппы во внутренней сфере. В продуктах с мольным соотношение $K_3[Fe(CN)_6]/VOSO_4\cdot 3H_2O$, равным 0,22-10 присутствует также адсорбированная и гидролизная вода. Установлено, что в полученных соединениях присутствует связь V=O и V-O. Показано, что внешняя и внутренняя сфера претерпевает изменения, обусловленные переходом валентности комплексообразователя Fe (III)↔Fe (II) и ванадия, с образованием комплексов типа аквацианосульфатов ванадия.

Ключевые слова: гексацианоферрат (III) калия, сульфат ванадила, гексацианоферрат (II) ион, гексацианоферрат (III) ион, комплексообразование, ИК-спектроскопия.