Phase Ratios in the K_2O–V_2O_4–SO_3 System at High Sulfur Trioxide Concentrations

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Abstract—-Phase ratios in the three-component oxide system K_2O–V_2O_4–SO_3 in the region of the sulfur trioxide concentrations corresponding to its concentrations in the active component of vanadium catalysts for SO_2 to SO_3 conversion have been studied using powder X-ray diffraction, IR spectroscopy, microscopy, and chemical analysis. Four individual compounds ($K_2VO(SO_4)_2$, $K_2(VO)_2(SO_4)_3$, $K_2VO(SO_4)_2S_2O_7$, and $K_2(VO)_2(SO_4)_2S_2O_7$) and $K_2(VO)_2(SO_4)_2S_2O_7$ and $VOSO_4$-base solid solutions of composition $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ ($0 \le x \le 1.5$) were found in the system. $K_2VO(SO_4)S_2O_7$ and $K_2(VO)_2(SO_4)_2S_2O_7$ lose their sulfur trioxide when heated above 350°C under an inert atmosphere, and convert to $K_2VO(SO_4)_2$ and $K_2(VO)_2(SO_4)_3$, respectively. This implies that $K_2VO(SO_4)_2S_2O_7$ and $K_2(VO)_2(SO_4)_2S_2O_7$, as well as $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ solid solution, cannot exist in the active component of real industrial catalysts.

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The M_2O–V_2O_5–V_2O_4–SO_3 systems (where M stands for an alkali metal) model the active component of vanadium sulfate catalysts in sulfur dioxide conversion [1, 2]. Three-component systems M_2O–V_2O_5–SO_3 may serve to model the essential processes that occur at the high-temperature stage of formation of vanadium-containing contact masses during the sulfuric acid process and their saturation with sulfur trioxide in the absence of SO_2 or at high SO_2 conversions, when the reducing activity of sulfur dioxide is low and when the decrease in the vanadium oxidation number in the active component can be ignored. To elucidate the character of chemical transformations of the active component of vanadium catalysts under the effect of a gas reaction mixture (SO_2, SO_3, O_2, N_2), one should first of all study the phase composition of M_2O–V_2O_4–SO_3 three-component oxide systems of which the K_2O–V_2O_4–SO_3 system has the highest applied significance. For this reason, here we will focus on phase ratios in the region of high SO_3 concentrations that correspond to the composition of the active component of real catalysts and on the properties of the compounds formed in the title system.
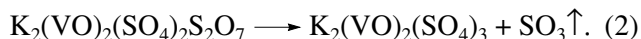
Test samples were synthesized by solid-phase anneals of mixtures based on K_2SO_4 (high purity grade), $K_2S_2O_7$, V_2O_4, and $VOSO_4$ under an inert atmosphere and in the presence of SO_3 vapor. Original procedures were developed for preparing individual compounds. Potassium disulfate was prepared through the thermolysis of $K_2S_2O_8$ (pure for analysis) at 350°C; $VOSO_4$, through the dehydration of $VOSO_4 \cdot 3H_2O$

(pure for analysis) in vacuo at 375°C; and V_2O_4, through reacting SO_2 with KVO_3 at 500°C: $2KVO_3 + SO_2 = V_2O_4 + K_2SO_4$ [3]. To keep the reagents and products from contact with atmospheric moisture, they were stored in sealed vessels. A possible effect of water vapor was taken into account in all experiments. Phase control was performed by means of a DRON-2 diffractometer using CuK_α radiation and a POLAM C112 polarized-light microscope in transmitted light. The refractive indices of individual compounds were evaluated using an IZh standard kit of immersion liquids at room temperature. IR spectra were recorded on a Specord 75 IR spectrophotometer in the range of 4000–400 cm^{-1}. Thermal curves were recorded on a Q-1500D derivatograph in the heating mode at 10 K/min. Equilibrated samples were analyzed for potassium, sulfur, vanadium(V), vanadium(IV), and vanadium(III) using routine procedures.

We showed in [4] that the system K_2O–V_2O_4–SO_3 at 410°C forms two compounds that are stable in an inert medium: $K_2VO(SO_4)_2$ and $K_2(VO)_2(SO_4)_3$. The existence of SO_4 groups coordinated to vanadium atoms and multiple V–O bonds in the structure of these compounds was confirmed by IR spectroscopic data; this means that these compounds may be treated as vanadium(IV) complexes, i.e., potassium oxosulfatovanadates(IV) [3, 4]. From an analysis of the phase ratios in the system K_2O–V_2O_4–SO_3 carried out in this work over a wide temperature range from 150 to 550°C, we recognized four individual compounds ($K_2VO(SO_4)_2$, $K_2(VO)_2(SO_4)_3$, $K_2VO_2(SO_4)S_2O_7$, and $K_2(VO)_2(SO_4)_2S_2O_7$) and $K_2(VO)_2(SO_4)_2S_2O_7$ and

$VOSO_4$-base solid solutions of composition $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ with $0 \leq x \leq 1.5$ in this system (Fig. 1). We have not confirmed the existence of $2K_2SO_4 \cdot VOSO_4$ [5] and $K_2SO_4 \cdot 3VOSO_4$ [6], nor the existence of $2K_2SO_4 \cdot 3VOSO_4$ or $K_4(VO)_3(SO_4)_5$, which was crystallized from the melt of the $K_2S_2O_7$–V_2O_5 system under an $SO_2 + O_2 + N_2$ (10 : 11 : 79 vol/vol) gas mixture [7]. With the synthesis parameters chosen, two product phases ($K_2VO(SO_4)_2$ and $K_2(VO)_2(SO_4)_3$) corresponded to the ratio $K_2SO_4 \cdot VOSO_4 = 2 : 3$. Dashed lines in Fig. 1 indicate suggested sections, which were drawn in view of the existence of a phase of variable composition $V_2O_4 \cdot nSO_3$ [8] (we have not synthesized this phase).

The system K_2O–V_2O_4–SO_3 is stable in an inert atmosphere. The secondary ternary system K_2O–V_2O_4–$K_2S_2O_7$ is equilibrated in the subsolidus region (at $410 \pm 5°C$). The thermal stability of the secondary ternary system $K_2S_2O_7$–V_2O_4–$K_2S_3O_{10}$ is limited to $150°C$ because of the low thermal stability of $K_2S_3O_{10}$ [9]. In the secondary ternary system K_2SO_4–$VOSO_4$–$K_2S_2O_7$, there are $K_2VO(SO_4)S_2O_7$ and $K_2(VO)_2(SO_4)_2S_2O_7$, which decompose in air or under an inert gas atmosphere at 310 and $350°C$, respectively:

$$K_2VO(SO_4)S_2O_7 \longrightarrow K_2VO(SO_4)_2 + SO_3\uparrow, \quad (1)$$

$$K_2(VO)_2(SO_4)_2S_2O_7 \longrightarrow K_2(VO)_2(SO_4)_3 + SO_3\uparrow. \quad (2)$$

The $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ solid solution decomposes to $K_2(VO)_2(SO_4)_3$ and β-$VOSO_4$. For this reason, these compounds and $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ ($0 \leq x \leq 1.5$) solid solution were synthesized by the solid-phase annealing of $K_2S_2O_7$ and $VOSO_4$ mixtures in sealed quartz ampoules filled with argon. The inert gas pressure generated by temperature elevation was sufficient to avoid gas evolution and suppress reactions (1) and (2), which in turn allowed for a 100–150°C increase in the synthesis temperature. The interplanar spacings and line intensities in the X-ray diffraction spectra of the compounds formed in the $K_2S_2O_7$–$VOSO_4$ system are listed in Table 1.

The existence of intermediate compounds in the quasibinary system $K_2S_2O_7$–$VOSO_4$ has been reported several times, but the compositions reported vary greatly, e.g., $0.433K_2S_2O_7 \cdot 0.567VOSO_4$ and $0.14K_2S_2O_7 \cdot 0.86VOSO_4$ [10] or $0.6K_2S_2O_7 \cdot 0.4VOSO_4$ and $0.3K_2S_2O_7 \cdot 0.7VOSO_4$ [11]. This variance is due to the synthesis schedule: the synthesis was carried out in air, and the possibility was ignored for vanadium(IV) oxidation, the decomposition of reaction products with sulfur trioxide evolution, and their hydration by water vapor at room temperature.

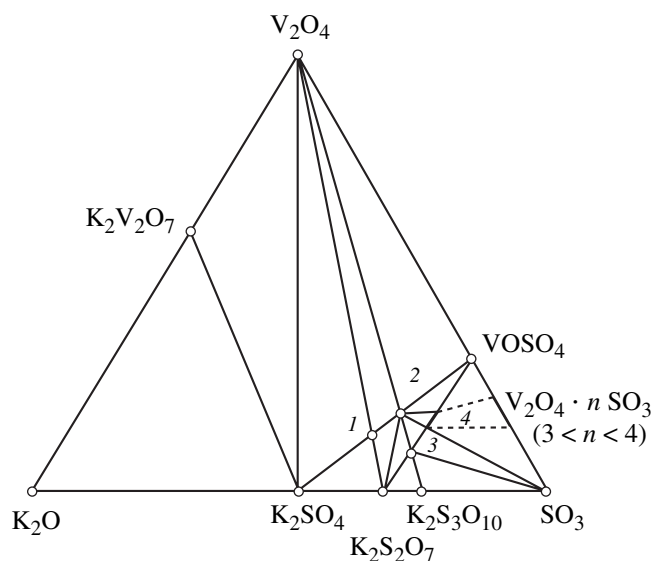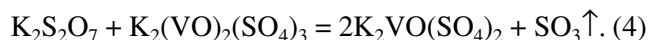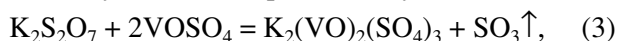Above 350°C, the reaction of potassium disulfate with vanadyl sulfate is represented by

$$K_2S_2O_7 + 2VOSO_4 = K_2(VO)_2(SO_4)_3 + SO_3\uparrow, \quad (3)$$

$$K_2S_2O_7 + K_2(VO)_2(SO_4)_3 = 2K_2VO(SO_4)_2 + SO_3\uparrow. \quad (4)$$

Fig. 1. Phase diagram for the K_2SO_4–V_2O_4–SO_3 region of the K_2O–V_2O_4–SO_3 system: (*1*) $K_2VO(SO_4)_2$, (*2*) $K_2(VO)_2(SO_4)_3$, (*3*) $K_2VO(SO_4)S_2O_7$, and (*4*) $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ ($0 \leq x \leq 1.5$)5).

Both reactions may be used to prepare $K_2VO(SO_4)_2$ and $K_2(VO)_2(SO_4)_3$. Reaction (3) requires heating to 350–400°C; reaction (4), to 450°C. Another quite efficient route to synthesize $K_2VO(SO_4)_2$ is to alloy a stoichiometric mixture of vanadium(IV) oxide and potassium disulfate in sealed quartz ampoules at 550°:

$$K_2S_2O_7 + 1/2V_2O_4 = K_2VO(SO_4)_2. \quad (5)$$

Powdered potassium oxosulfatovanadates(IV) are blue, which is characteristic of practically all vanadyl complexes. $K_2VO(SO_4)_2$ crystals have a prismatic or acicular habit. A single crystal is faced with two pinacoids [(100), (001)] and a rhombic prism [(110)]. The cleavage is perfect parallel to (100) and weak parallel to (001). The refractive indices are $Ng = 1.556$ (intense blue), $Nm = 1.524$ (light blue), and $Np = 1.494$ (colorless). $K_2VO(SO_4)_2$ crystals are short prisms or platy with prominent pleochroism from blue in the direction of the optical indicatrix Ng to colorless in the direction oriented along Np. Their refractive indices are $Ng = 1.605$, $Nm = 1.595$, and $Np = 1.587$. Finely dispersed $K_2VO(SO_4)S_2O_7$ is light blue. Microscopic observation shows short-prismatic crystals with vertical or inclined (to 10°– 20°) extinction. The refractive indices are $Ng = 1.561$ (light blue), $Nm = 1.554$ (colorless), and $Np = 1.547$ (colorless). A $K_2(VO)_2(SO_4)_2S_2O_7$ powder is also blue. Microscopic examination shows well-edged short-prismatic crystals with vertical extinction in all directions and with the Ng axis oriented along the prism axis. The crystal system is orthorhombic; the unit cell parameters $a = 13.467$ Å, $b = 11.456$ Å, $c = 9.271$ Å. The refractive indices are $Ng = 1.568$ (blue), $Nm = 1.552$ (light

Table 1. Interplanar spacings (d) and relative intensities (I) for $K_2(VO)_2(SO_4)_2S_2O_7$ (**1**) and $K_2VO(SO_4)S_2O_7$ (**2**)

	1			2			
$h\,k\,l$	d, Å	d_{calcd}, Å	I, %	d, Å	I, %	d, Å	I, %
101	7.670	7.643	50	6.637	15	2.775	15
200	6.711	6.734	5	6.299	5	2.656	15
210	5.814	5.814	20	6.026	15	2.581	30
300	4.463	4.480	10	4.439	25	2.568	20
221	3.972	3.961	10	4.345	5	2.542	10
030	3.849	3.853	85	4.210	20	2.508	5
311	3.811	3.813	40	3.927	10	2.396	5
320	3.570	3.570	10	3.818	25	2.378	10
401	3.164	3.164	100	3.717	50	2.364	20
330	2.922	2.922	45	3.582	10	2.281	5
421	2.772	2.773	15	3.540	20	2.263	15
241	2.570	2.568	5	3.498	40	2.184	15
313	2.486	2.490	5	3.384	50	2.161	15
431	2.449	2.446	15	3.271	15	2.127	5
413	2.236	2.234	15	3.243	20	2.099	10
342	2.148	2.150	10	3.169	100	1.984	10
143	2.085	2.084	25	3.128	40	1.970	10
351	2.004	2.005	20	3.094	30	1.966	5
433	1.958	1.959	15	3.008	15	1.807	15
244	1.744	1.745	10	2.988	25	1.767	20
315	1.696	1.695	15	2.940	35	1.697	5
524	1.690	1.688	5	2.826	25	1.562	5

blue), and $Np = 1.534$ (colorless). The upper boundary of the homogeneous field of the $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ solid solution ($0 \le x \le 1.5$) was determined by microscopic analysis. The refractive indices determined at room temperature with an accuracy of ±0.002 for a sample with $x = 1.5$ are the following: $Ng = 1.593$, $Nm = 1.580$, and $Np = 1.559$. The X-ray spectra for $K_2(VO)_2(SO_4)_2S_2O_7$ and $K_2(VO)_{2+x}(SO_4)_{2+x}S_2O_7$ solid solution samples differ only insignificant over the entire homogeneous range. The absence of noticeable shifts or changing intensities of the spectral lines indicates that the formation of solid solutions does not significantly distort their $K_2(VO)_2(SO_4)_2S_2O_7$ base structure. This fact may be interpreted on the assumption of the bridging coordination mode of the disulfate groups: this coordination mode provides for the spatial looseness of the structure.

The character of the IR spectrum of $K_2VO(SO_4)S_2O_7$ (Fig. 2, Table 2) shows that SO_4 and S_2O_7 groups do exist in its crystal structure. The broad strong band with resolutions at 609, 590, 576, 563, and 545 cm^{-1} can be assigned to the antisymmetrical bending vibrations of the SO_3 groups in the $S_2O_7^{2-}$ ion [12]. 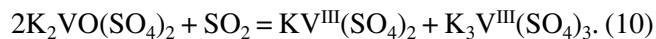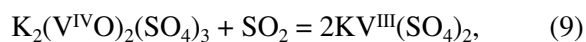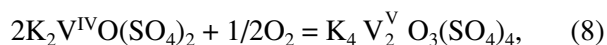The vibrat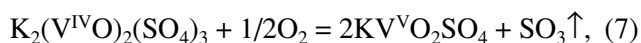ions of S–O–S and V–O–S bridges appear as strong, well resolved bands in the frequency range of 795–752 and 885–850 cm^{-1}. In the region of the stretching vibrations of SO_3 and SO_4 groups, at least 12 bands are observed. The strong, well resolved band at 1018 cm^{-1} is due to the symmetrical stretching vibrations of the sulfato group $\nu_1(SO_4)$. The bands with maxima at 667 and 650 cm^{-1} can be assigned to the antisymmetrical bending vibrations $\nu_4(SO_4)$, and the bands at 483 and 457 cm^{-1}, to the symmetrical mode $\nu_2(SO_4)$. The stretching vibrations of the multiple V–O bonds are responsible for the strong band at 985 cm^{-1}. The IR spectrum of $K_2(VO)_2(SO_4)_2S_2O_7$ differs from the spectrum considered above (Fig. 2) in the weak appearance of $S_2O_7^{2-}$ vibration bands and the low level of splitting of the SO_4^{2-} vibrational frequencies; these features indicate the higher symmetry of the crystal structure, which leads to the degeneracy of some vibrational frequencies. A similar structure may be built on the basis of $(VO)(SO_4)$ groups linked through $O_3S–O–SO_3$ bridges. That is, the weak appearance of the vibrational frequencies of the $S_2O_7^{2-}$ ions in the $K_2(VO)_2(SO_4)_2S_2O_7$ structure is due to their shielding by the $(VO)(SO_4)$

vibrations. An even stronger effect is observed in the IR spectra of K$_2$(VO)$_{2+x}$(SO$_4$)$_{2+x}$S$_2$O$_7$ solid solutions (the relative S$_2$O$_7^{2-}$ concentration in the structure of the solid solution decreases with increasing x): the S$_2$O$_7^{2-}$ vibrational frequencies almost do not appear for high x.
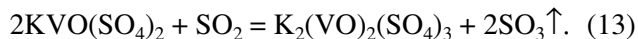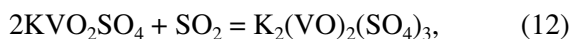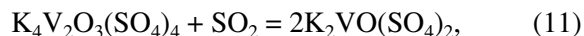
Due to the low thermal stability of K$_2$VO(SO$_4$)S$_2$O$_7$ and K$_2$(VO)$_2$(SO$_4$)$_2$S$_2$O$_7$, it is unlikely that they would form during the catalytic reaction of sulfur dioxide oxidation, but K$_2$VO(SO$_4$)$_2$ and K$_2$(VO)$_2$(SO$_4$)$_3$ formation is quite possible [3, 4]. In an inert medium, K$_2$VO(SO$_4$)$_2$ melts without decomposition at 550 ± 5°C; K$_2$(VO)$_2$(SO$_4$)$_3$ decomposes under the same conditions above 450°C with sulfur trixide evolution:

$$K_2(VO)_2(SO_4)_3 \longrightarrow K_2VO(SO_4)_2 + 1/2V_2O_4 + SO_3\uparrow. \quad (6)$$

Being exposed in air at 410–350°Cor under a sulfur dioxide atmosphere at 450°C, both compounds experience the following transformations:

$$K_2(V^{IV}O)_2(SO_4)_3 + 1/2O_2 = 2KV^VO_2SO_4 + SO_3\uparrow, \quad (7)$$

$$2K_2V^{IV}O(SO_4)_2 + 1/2O_2 = K_4V_2^VO_3(SO_4)_4, \quad (8)$$

$$K_2(V^{IV}O)_2(SO_4)_3 + SO_2 = 2KV^{III}(SO_4)_2, \quad (9)$$

$$2K_2VO(SO_4)_2 + SO_2 = KV^{III}(SO_4)_2 + K_3V^{III}(SO_4)_3. \quad (10)$$

K$_2$VO(SO$_4$)$_2$ and K$_2$(VO)$_2$(SO$_4$)$_3$ may be prepared by exposing K$_4$V$_2$O$_3$(SO$_4$)$_4$, KVO$_2$SO$_4$, and KVO(SO$_4$)$_2$ to air-diluted sulfur dioxide [3, 4]:

$$K_4V_2O_3(SO_4)_4 + SO_2 = 2K_2VO(SO_4)_2, \quad (11)$$

$$2KVO_2SO_4 + SO_2 = K_2(VO)_2(SO_4)_3, \quad (12)$$

$$2KVO(SO_4)_2 + SO_2 = K_2(VO)_2(SO_4)_3 + 2SO_3\uparrow. \quad (13)$$

As a result of prolonged (about 50-h) exposure in vacuo at 300°C, KVO(SO$_4$)$_2$ converts to K$_2$(VO)$_2$(SO$_4$)$_2$S$_2$O$_7$:

$$2KV^VO(SO_4)_2 \longrightarrow K_2(V^{IV}O)_2(SO_4)_2S_2O_7 + 1/2O_2. \quad (14)$$

The reaction of potassium oxosulfatovanadates(V) with sulfur dioxide in accordance with reactions (11) and (12) starts at about 350°C; in order for K$_2$VO(SO$_4$)$_2$ and K$_2$(VO)$_2$(SO$_4$)$_3$ to be oxidized with atmospheric oxygen, they should be heated above 400°C.

Under a water-saturated atmosphere at room temperature, K$_2$VO(SO$_4$)$_2$ converts to its monohydrate K$_2$VO(SO$_4$)$_2 \cdot$ H$_2$O; Ivakin and colleagues [13] isolated this monohydrate from K$_2$SO$_4$–VOSO$_4$–H$_2$SO$_4$–H$_2$O solutions. The compounds containing S$_2$O$_7$ groups decompose by the reaction

$$\begin{aligned} K_2VO(SO_4)S_2O_7 + 4H_2O \\ = 2KHSO_4 + VOSO_4 \cdot 3H_2O. \end{aligned} \quad (15)$$
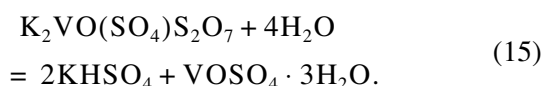
K$_2$(VO)$_2$(SO$_4$)$_3$ is not noticeably affected by water vapor. This compound slowly dissolves in water to
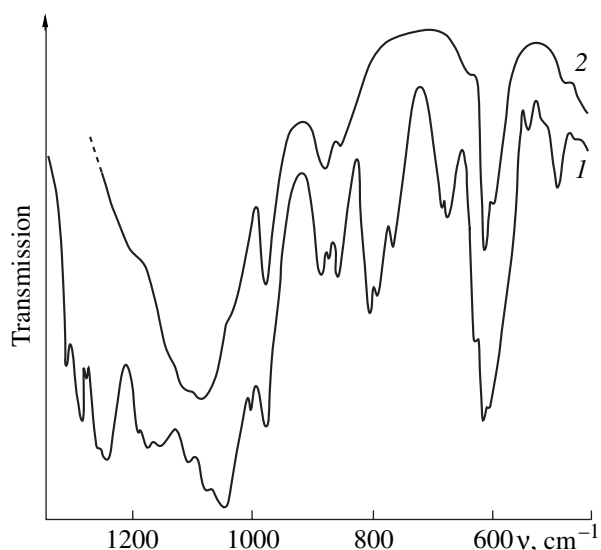
Fig. 2. IR spectra for (*1*) K$_2$VO(SO$_4$)S$_2$O$_7$ and (*2*) K$_2$(VO)$_2$(SO$_4$)$_2$S$_2$O$_7$.

yield a blue solution, which turns green as a result of hydrolysis and partial vanadium oxidation.

Powdered K$_2$VO(SO$_4$)$_2 \cdot$ H$_2$O is bright blue. Under a microscope, irregular shaped grains with wavy extinction are seen. Cleaved fragments resemble short prisms. The refractive indices are $Ng = 1.563$ (blue), $Nm = 1.540$ (colorless), and $Np = 1528$ (colorless). The interplanar spacings (d, Å) and relative intensities (I, %) for

Table 2. Wavenumbers (cm^{-1}) of absorption peaks in the IR spectrum of K$_2$VO(SO$_4$)S$_2$O$_7$

Band	Assignment	Band	Assignment
1351	$\nu(SO_3)$, $\nu_3(SO_4)$	885	ν(V–O–S),
1330		872*	ν(S–O–S)
1324*		850	
1316		795	
1300		770	
1280		752	
1260*		667	$\nu_4(SO_4)$
1220		650	
1206		609	
1178		590	$\nu(SO_3)$
1135		576*	
1100		563	
1065		545*	
1018	$\nu_1(SO_4)$,	510	
994*	ν(V=O)	483*	ν(V–O)
985		457	$\nu_2(SO_4)$

* Weak appearance as a shoulder.

Table 3. Wavenumbers (cm^{-1}) of absorption peaks in the IR spectrum of K$_2$VO(SO$_4$)$_2 \cdot$ H$_2$O

Vibrations of SO$_4^{2-}$ ion				V–O vibrations		H$_2$O vibrations	
ν_1	ν_2	ν_3	ν_4			ν	δ
1010 vs	448 w	1249 vs	684 s	994 vs	ν(V=O)	3450 s	1620 s
		1225 vs	621 m	972 vs		3300 m	
		1210 vs	598 s			3180 m	
		1140 vs		510 m	ν(V–O)		
		1119 vs					
		1050 vs					
		1026 vs					

K$_2$VO(SO$_4$)$_2$ · H$_2$O are the following: 6.841 (10), 6.042 (15), 5.265 (35), 4.552 (15), 4.144 (20), 3.811 (5), 3.584 (15), 3.515 (20), 3.435 (20), 3.351 (60), 3.295 (30), 3.085 (20), 2.988 (20), 2.931 (100), 2.876 (75), 2.782 (20), 2.647 (20), 2.588 (15), 2.533 (15), 2.278 (20), 2.154 (15), 2.112 (25), 2.073 (15), 1.901 (10), 1.760(10). Powdered VOSO$_4 \cdot$ 3H$_2$O is also bright blue. When viewed under a microscope, the crystals and their chips have a well-defined isometric shape; short prisms and elongated platelets are less frequent. The refractive indices are Ng = 1.574 (greenish-yellow), Nm = 1.560 (light blue), and Np = 1.542 (bright blue). Colorless KHSO$_4$ crystals usually have no cleavage. The refractive indices are Ng = 1.491, Nm = 1.460, and Np = 1.445. Potassium hydrosulfate crystals are very easy to distinguish against the background of colored vanadium compounds.

In the IR spectrum of K$_2$VO(SO$_4$)$_2$ · H$_2$O, there is the set of bands that indicates the bidentate coordination of the sulfato groups to the vanadium atoms (Table 3). The frequency of the antisymmetrical stretching vibrations of the sulfato group ν_3(SO$_4$) is split to seven components; $\Delta\nu_3$= 223 cm^{-1}. In the spectral region of the antisymmetrical bending vibrations ν_4(SO$_4$), there are three quite strong bands: 684, 621, and 598 cm^{-1}. The symmetrical stretching vibrations ν_1(SO$_4$) and bending vibrations ν_2(SO$_4$) appear as a strong narrow band at 1010 cm^{-1} and a weak band at 448 cm^{-1}, respectively. The bands at 994 and 972 cm^{-1} can be assigned to the vibrations of multiple V–O bonds and the band at 510 cm^{-1} to the vibrations of ordinary bands. The stretching vibrations of water molecules ν(H$_2$O) appear as three bands (3450, 3300, and 3180 cm^{-1}); their intensity decreases with decreasing wavenumber. The bending vibrations δ(H$_2$O) are characterized by a strong narrow band at 1620 cm^{-1}. The nonappearance of the bands due to the rocking and wagging vibrations ρ(H$_2$O) [14, 15] in the

IR spectrum of K$_2$VO(SO$_4$)$_2$ · H$_2$O implies that the water molecules in the crystal structure are not coordinated to vanadium atoms; rather, they are in interlayer spaces.

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