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Synthesis and Properties of Rubidium Salts of Phosphotungstic Acid

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Abstract: The work is devoted to the study of the influence of synthesis conditions on the properties of water-insoluble rubidium salts of phosphotungstic acid (PTA). Such heteropoly compounds have a wide range of applications, including in the field of electrocatalysts and solid electrolytes for various electrochemical devices. The acid salts of PTA with high activity of acid sites on the particle surface are of particular interest. It is known that the properties of water-insoluble PTA salts strongly depend on synthesis conditions, such as the ratio of reagents, temperature, concentrations, and other parameters. The work examines the influence of the ratio and concentration of reagents on the sizes of crystallites and agglomerates, specific surface area (SSA), porosity, water content, and ionic conductivity of the synthesized PTA salts. The SSA value of the obtained samples varied in the range of 84–123 m² g^{−1}, and the ionic conductivity was 13–90 mS cm^{−1} at room temperature and 75% RH. An increase in the acid concentration and the degree of proton substitution led to an increase in SSA, accompanied by an increase in particle sizes without changing the size of crystallites. The results of the work may be useful for the development of new materials based on the obtained salts in many fields, including hydrogen energy.



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Keywords: rubidium salts; phosphotungstic acid; heteropoly compounds; synthesis; morphology; ionic conductivity

1. Introduction

Rubidium salts of phosphotungstic acid (PTA) are one of the classes of heteropoly compounds that can be used in various fields, including the development of effective materials for electrochemical devices, such as fuel cells, gas sensors, and redox flow batteries [1–10]. Water-insoluble salts of PTA are widely used in organic catalysis [11–13], electrocatalysis [14], doping of polymer membranes [1,2,15,16], and various other fields due to an excellent combination of properties: high acidity, specific surface area (SSA), porosity, thermal stability, proton conductivity, and low solubility in water [17–24]. Water-insoluble salts of PTA (containing cations such as cesium, rubidium, ammonium, or silver) have improved properties compared with the initial acid. Insoluble salts of PTA self-assemble into large particles (with an average size of 100–2000 nm) during the synthesis process. These agglomerates are composed of small crystallites 10–50 nm in size [21,23–30]. This structure determines the developed surface and high porosity. Acid salts of PTA are of greatest interest since they have the maximum specific concentration of acid sites per unit surface area of particles [31,32].

Among the water-insoluble PTA salts, rubidium salts are promising for various applications. Thus, in [33], it was shown that rubidium salts have a larger SSA and pore volume compared with cesium salts; therefore, they can be used as catalysts in organic

synthesis [34], including in the reactions of hydrogenation and dehydrogenation of organic compounds [35]. The catalytic effect of rubidium salts of PTA promotes the activation of the bond between hydrogen and organic molecules, which allows reactions to be carried out with high efficiency [36]. Hybrid Nafion membranes doped with the rubidium salt of PTA show higher values of conductivity and strength compared with membranes doped with cesium salt [15]. It is worth noting that the ionic conductivity of rubidium and cesium salts of PTA has similar values and is the highest among other insoluble salts of PTA [20,22]. At the same time, the solubility of these salts in water is the lowest among other insoluble PTA salts [37]. Thus, rubidium salts of PTA are promising compounds for the development of hydrogen energy. Like cesium salts, they can be used to create effective electrocatalysts for water electrolysis [38,39] or for polymer membrane modification [15,40].

The properties of insoluble PTA salts strongly depend on synthesis conditions. Thus, by varying the synthesis parameters, it is possible to change the sizes of crystallites and particles/agglomerates, SSA, porosity, composition, ionic conductivity, etc. [18,21,23,24,41,42]. To obtain the most active catalysts, different synthesis parameters are varied: the type of initial reagents, their concentration and ratio, precipitate washing modes, synthesis temperature, and subsequent annealing temperature. From this point of view, cesium salts of PTA have been most widely studied [19,23,24,32]. In addition, there are a number of publications on ammonium [19,21,43,44], potassium [32,45,46], and silver [30,47,48] salts. Rubidium salts of PTA remain the least studied. For example, in [37], a number of samples of rubidium salts of PTA with different degrees of proton substitution from 1.8 to 3 were obtained. However, only data on the solubility, water content, and composition of the resulting salts were presented. Data on ionic conductivity, SSA, and particle size of rubidium salts of PTA are not available in the literature.

Therefore, the purpose of this work was to study the influence of synthesis conditions (ratios and concentrations of reagents) on the physicochemical and ion-conducting properties of rubidium salts of PTA. Studying the influence of synthesis conditions on the properties of rubidium salts of PTA will expand scientific knowledge about such compounds and their potential for various applications.

2. Experimental

2.1. Synthesis of the Rubidium Salts of PTA

The synthesis of $\text{Rb}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($1 \leq x \leq 3$) was carried out by neutralizing an aqueous solution of PTA with a solution of RbCl . All chemicals were purchased from Nevareaktiv LLC (Saint-Petersburg, Russia) at 99.9% purity without additional purification. PTA was obtained using a well-known method [49]. Two series of “ kmM-x ” samples were obtained (k is the concentration of PTA, x is the stoichiometric degree of proton substitution). PTA concentrations (k) were 2.5 and 14 mM; the concentration of the rubidium chloride solution was 1.5 times higher than the concentration of PTA. The volumes of mixed solutions were determined from stoichiometric ratios to obtain a salt with the required value of the degree of proton substitution (x). The obtained milky-white suspensions were centrifuged to separate insoluble salts, followed by decantation of the mother liquor. The resulting precipitate was washed using ultrasound and centrifugation 7 times and dried in an oven at 60 °C for 3 days; the powders thus obtained were white or white-gray in color.

2.2. Sample Characterization

Microphotographs of the samples were obtained using a scanning electron emission microscope (SEM) LEO SUPRA 25 (Carl Zeiss, Jena, Germany). Energy-dispersive X-ray spectroscopy analysis (EDX) was also performed alongside the microscopy.

Particle size distribution was determined on the “Analysette 22 Next” laser diffractometer (Fritsch, Idar-Oberstein, Germany).

The specific surface area (SSA) of the samples was determined by the nitrogen adsorption–desorption method on a QUADRASORB SI instrument (Anton Paar Quantachrome Instruments, Boynton Beach, FL, USA). Samples were degassed for 3 h at 300 °C

in a helium atmosphere. Sample preparation and calculation of the specific surface area were carried out in accordance with the methodology of [50].

The crystalline structure of the obtained samples was studied using X-ray diffraction (XRD) analysis at room temperature. The measurements were carried out in the range $2\theta = 5\text{--}80^\circ$ in 0.04° increments on an Aeris instrument (Malvern Panalytical B.V., Almelo, The Netherlands) using $\text{CuK}\alpha$ radiation. For the identification of crystalline phases, the PDF-4+ ICDD database was used. Calculation of the crystalline parameters was performed using the Rietveld refinement method in Topas software. The coherent scattering region (CSR) was determined using the Sherer equation in the Fityk-1.3.1 software.

The Fourier-transform infrared (FTIR) spectra of the prepared samples were recorded at ambient pressure on the spectrometer Vertex 70 V (Germany) at room temperature using a Bruker diamond attachment in the $50\text{--}4500\text{ cm}^{-1}$ range (resolution 4 cm^{-1} , 50 scans).

The amount of water in the samples was determined by simultaneous thermal analysis (STA) on Netzsch STA 409 PC Luxx and QMS 403 C Aëolos instruments (Netzsch, Selb, Germany). The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were recorded in the temperature range of $25\text{--}300^\circ\text{C}$ under an argon atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

The ion conductivity of the samples was measured by impedance spectroscopy in a symmetric two-electrode cell on an Elins P40X potentiostat with an FRA module (Russia) in the frequency range of $2\text{ MHz--}1\text{ Hz}$ with an amplitude of 10 mV . The samples were pressed between titanium electrodes at a pressure of 3 MPa in a cell with a diameter of 5 mm . The temperature was controlled using a Huber Pilot One CC 805 thermostat (Germany). The Nyquist plots were analyzed by a graphoanalytical method.

3. Results and Discussion

3.1. Sample Composition and Morphology

Figure 1 shows typical SEM images of the obtained acidic rubidium salts $\text{Rb}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$. All particles have a spherical shape and sizes in the range of 0.1 to $2\text{ }\mu\text{m}$. There is a tendency for particle sizes to increase with higher concentrations of the PTA solution, which contrasts with the data obtained for cesium salts in [24]. The distribution of particles in all studied salts has a monomodal form and is well described by the lognormal equation (Figure 2). The average particle size varies in the range of $0.3\text{--}0.5\text{ }\mu\text{m}$ (Table 1). Along with an increase in the stoichiometric degree of substitution of protons x , an increase in the average particle size (except for the 14 mM-1 sample) and SSA are observed, regardless of the PTA concentration. As in the case of cesium salts [24], the rubidium content determined by the EDX method is higher than the theoretically expected value (Table 1). The typical EDX spectrum with corresponding SEM image is shown in Figure 2. Neutral rubidium salt of PTA can be obtained only by increasing the ratio of reagents. The samples with the highest degree of proton substitution $x = 3$ have the largest $\text{SSA} = 123\text{ m}^2$ and 120 m^2 , respectively. In general, the increase in SSA with x increasing correlates with literature data for cesium salts [19,31,51]. However, the SSA of cesium salts prepared using the same method, which was used in this work, does not depend on x and is 103 and $136\text{ m}^2\text{ g}^{-1}$ for PTA concentrations of 2.5 and 14 mM , respectively [24].

The nitrogen adsorption–desorption isotherms for the studied rubidium salts are presented in Figure 3a. According to the IUPAC classification, such isotherms are of different types. The isotherms of samples with an $\text{SSA} < 100\text{ m}^2\text{ g}^{-1}$ are of the type IV; hysteresis loop at relative pressure p/p_0 between 0.4 and 1.0 exhibits an H2 type. In these cases, capillary condensation takes place in mesopores, and the distribution of pore size and shape is not well defined. This is confirmed by the character of the differential pore size distribution, obtained by the density functional theory (DFT) method (Figure 3b). The average pore size calculated by the Barrett–Joyner–Halenda method is 3.4 and 4.3 nm for the salts, synthesized at PTA concentrations of 14 and 2.5 mM , respectively.

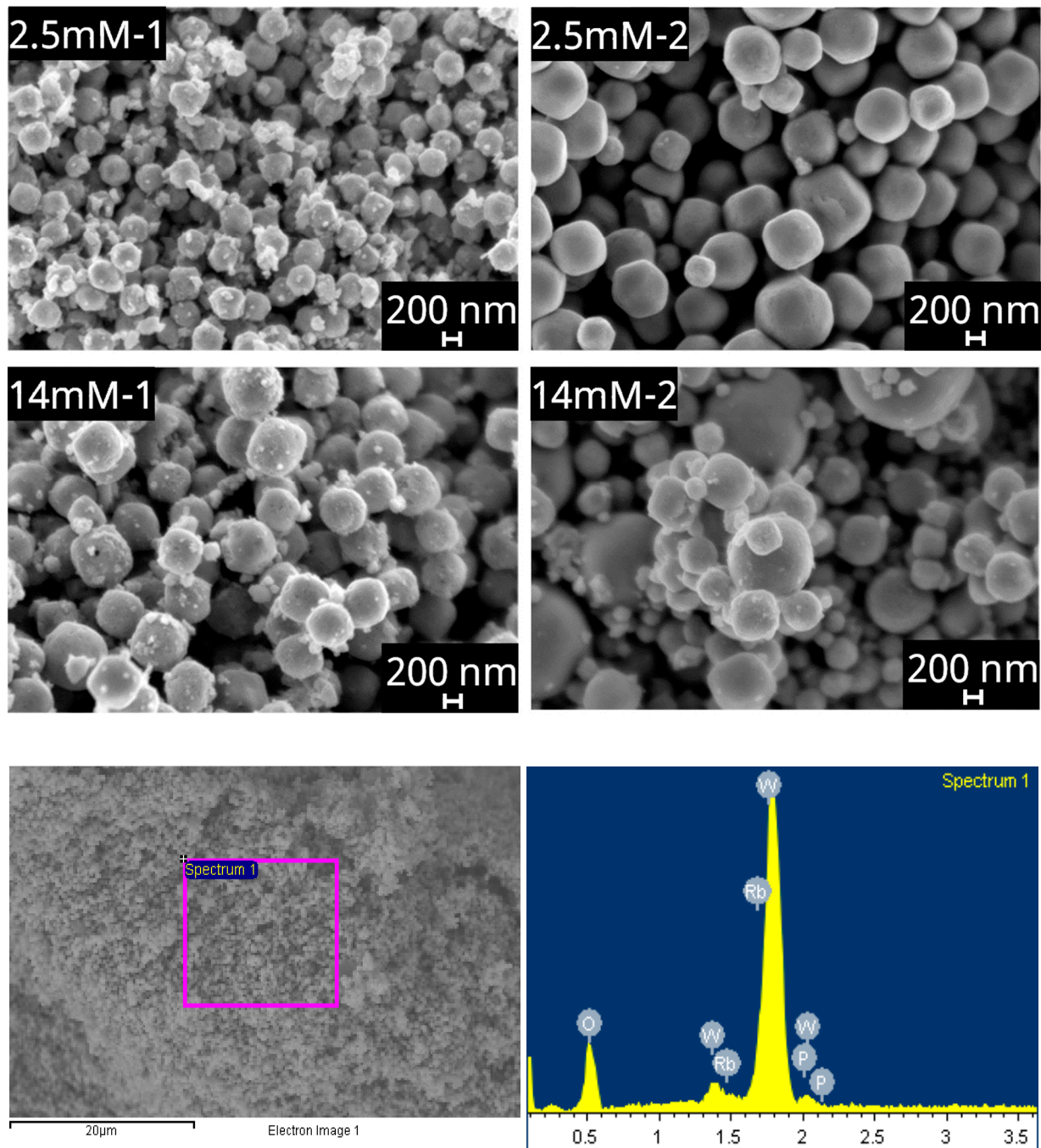


Figure 1. SEM images of the obtained samples with different degrees of proton substitution and SEM image and corresponding EDX spectra of sample 2.5mM-2.

The isotherm of the 14mM-2.5 sample is type II, corresponding to the case of poly-molecular adsorption. The absence of a hysteresis loop indicates the absence of capillary condensation and, accordingly, the absence of mesopores. A steep rise in the isotherm in the low-pressure region and a high value of the C parameter indicate the presence of micropores. To estimate the volume of micropores (V_{micro}), a comparative t -plot method was used; the analyzed isotherm was rearranged into a dependence of the adsorption value not on p/p_0 but on t (the statistical thickness of the adsorption film). It allowed for the determination of V_{micro} , excluding adsorption on the outer surface, which is equal to $0.01 \text{ cm}^3 \text{ g}^{-1}$ (Table 1).

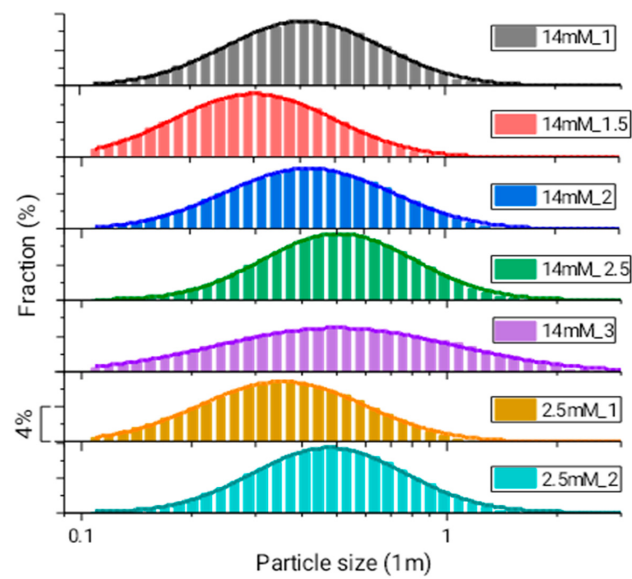


Figure 2. Particle size distributions of the obtained rubidium salts.

Table 1. Degrees of proton substitution (x), average particle sizes, SSA, pore (V), and micropore (V_{micro}) volumes of the obtained samples.

Sample	Theoretical x	x by EDX	Particle Size, μm	SSA, $\text{m}^2 \text{g}^{-1}$	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V ($\text{cm}^3 \text{g}^{-1}$)	
						BET	DFT
14mM-1	1	2.2	0.40	83.9	0.01 ^t	0.11	0.091
14mM-1.5	1.5	2.2	0.30	84.1	0.011 ^t	0.15	0.130
14mM-2	2	2.2	0.42	98.6	0.010 ^t	0.074	0.061
14mM-2.5	2.5	2.0	0.49	114	0.010 ^t	—	—
14mM-3	3	2.6	0.50	123	0.048 ^{DR}	—	0.060
2.5mM-1	1	1.7	0.34	70.6	0.007 ^t	0.10	0.086
2.5mM-2	2	2.9	0.47	120	0.040 ^{DR}	—	0.057

^t—Calculated by the t-plot method; ^{DR}—calculated by the DR method.

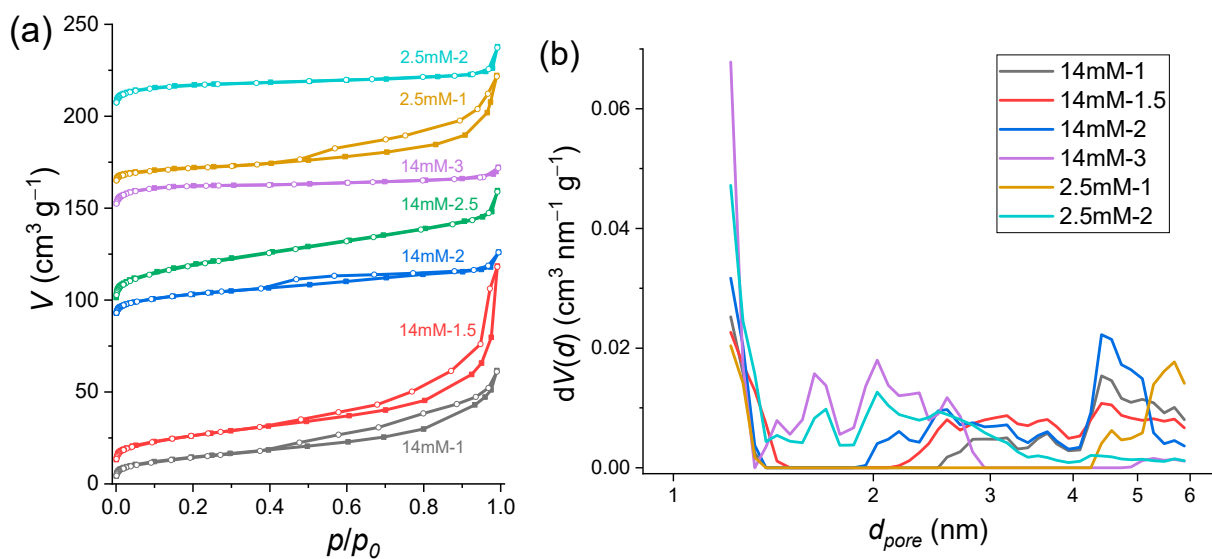


Figure 3. Nitrogen adsorption (solid points)—desorption (open points) isotherms (a) and differential pore size distribution (b) for studied salts.

The adsorption–desorption isotherms for the salts with the highest SSA value are of type I. This type of isotherm is typical for adsorption on microporous adsorbents. Due to a different adsorption mechanism (volumetric filling of micropores instead of polymolecular adsorption), the BET theory is not applicable to microporous samples. The Dubinin–Radushkevich (DR) method of microporosity calculation was used. The V_{micro} for these two samples is four times higher than for the other studied samples and is $0.04\text{--}0.05\text{ cm}^3\text{g}^{-1}$ (Table 1), with an average pore size of 1.2–1.3 nm.

3.2. Crystalline Phases

The obtained samples of PTA salts with different degrees of proton substitution have similar XRD peak positions (Figure 4c). The corresponding diffraction maxima are characteristic of the rubidium salt of PTA with the general formula $\text{Rb}_3(\text{PO}_4)(\text{W}_{12}\text{O}_{36})$ PDF #01-076-4195, of unsubstituted PTA $\text{H}_3(\text{PO}_4)(\text{W}_{12}\text{O}_{36})$ PDF #01-070-4202, and of acid salts with intermediate degrees of proton substitution. PTA, as well as its acidic and fully substituted rubidium salts, have a cubical crystal lattice belonging to the space group $Pn\bar{3}m$ (Figure 3a). A model image of the structure of a fully substituted rubidium salt of PTA is shown in Figure 3b. The intensity of the diffraction maximum, which belongs to the crystallographic plane with Miller indices (110), decreases as the rubidium content in the resulting salts increases. According to the diffraction patterns of the reference structures, the intensity of the diffraction maximum (110) for unsubstituted PTA reaches the highest value in comparison with the fully substituted salt (Figure 4a). This is in good agreement with the increase in the intensity of the diffraction maximum (110) along with the decrease in the degree of proton substitution, which was observed in the XRD patterns of the experimental samples (Figure 3b). The crystallographic plane (110) intersects predominantly the positions of rubidium atoms in the crystal lattice of the resulting substances (Figure 4b), so the intensity of this reflection is directly related to the rubidium content.

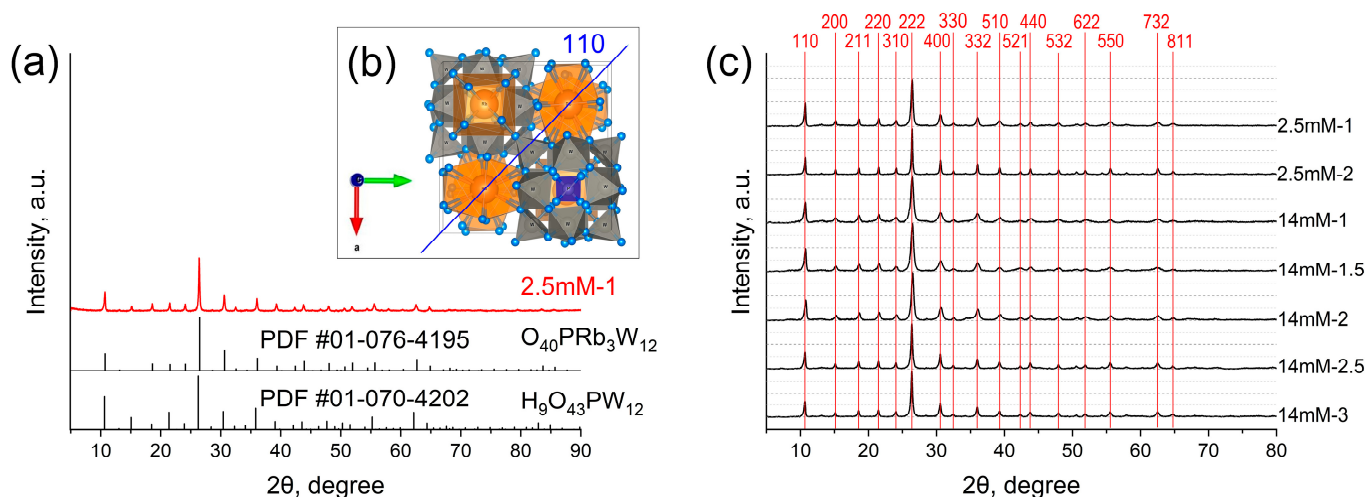


Figure 4. XRD pattern of the 2.5mM-1 sample (a), a model image of the $\text{Rb}_3(\text{PO}_4)(\text{W}_{12}\text{O}_{36})$ structure (b), and XRD patterns of the obtained salts (c).

Table 2 shows the values of the crystalline parameters of the obtained samples of rubidium salts of PTA, calculated by the Rietveld method. The weighted deviation factor R_2 during the calculation did not exceed 10%. The crystal lattice parameter a does not depend on the salt synthesis conditions and is varied in the range of $a = 11.67\text{--}11.68\text{ Å}$, which is slightly higher than the literature data ($a = 11.63 \pm 0.03\text{ Å}$) [22]. The calculated value of the crystal lattice parameter a is comparable to the value of a for ammonium salts of PTA (11.7 Å) [21,43,52]. However, the calculated value of a is lower than the value of the lattice parameter for cesium and silver salts of PTA ($11.8\text{--}11.9\text{ Å}$) [23,24,28,51,53–55]. As the degree of substitution of protons x increases, the occupancy of positions corresponding

to rubidium atoms also increases. The calculation of the CSR (L_{XRD}) was carried out using the Scherrer formula with the coefficient $K = 0.9$, corresponding to spherical particles. The L_{XRD} value varies in the range of 19–46 nm (Table 2), which is slightly higher than the literature data ($L_{XRD} = 12$ nm according to [22]). In general, this crystallite size value is characteristic of water-insoluble PTA salts (12–70 nm).

Table 2. Crystalline properties of the obtained rubidium salts.

Sample	Lattice Parameter $a = b = c, \text{\AA}$	Occupancy of Rb Atoms	L_{XRD}, nm	Unit Cell Volume V, nm^3
14mM-1	11.681	0.8773	21.7	1.594
14mM-1.5	11.684	0.8773	41.4	1.595
14mM-2	11.682	0.9463	25.2	1.594
14mM-2.5	11.672	0.9982	20.4	1.590
14mM-3	11.669	1.0410	18.8	1.589
2.5mM-1	11.677	0.8812	45.9	1.589
2.5mM-2	11.682	0.9891	19.7	1.589

3.3. FTIR Spectra

The FTIR spectra of the obtained samples of rubidium salts of PTA with different degrees of proton substitution are presented in Figure 5. The most intense changes in the absorption bands of FTIR spectra are observed in the range of 500–1100 cm^{-1} . According to the literature data, this range corresponds to the Keggin anion $\text{PW}_{12}\text{O}_{40}^{3-}$ [23,56]. The Keggin anion is a very rigid structural formation. Its structure does not depend on the degree of substitution of protons by other cations or on the degree of hydration of the salt. Consequently, the band intensities and the frequencies of vibrational transitions are also practically independent of these parameters. Therefore, the Keggin anion is suitable for use as an internal standard. In this regard, the intensities of the $\nu(\text{OH})$ and $\delta(\text{HOH})$ bands of H_2O molecules and proton hydrates can be normalized to the intensities $\nu(\text{WO})$. In the present study, the FTIR spectra were normalized to the most intense band at 781 cm^{-1} (Figure 4a), corresponding to the Keggin anion.

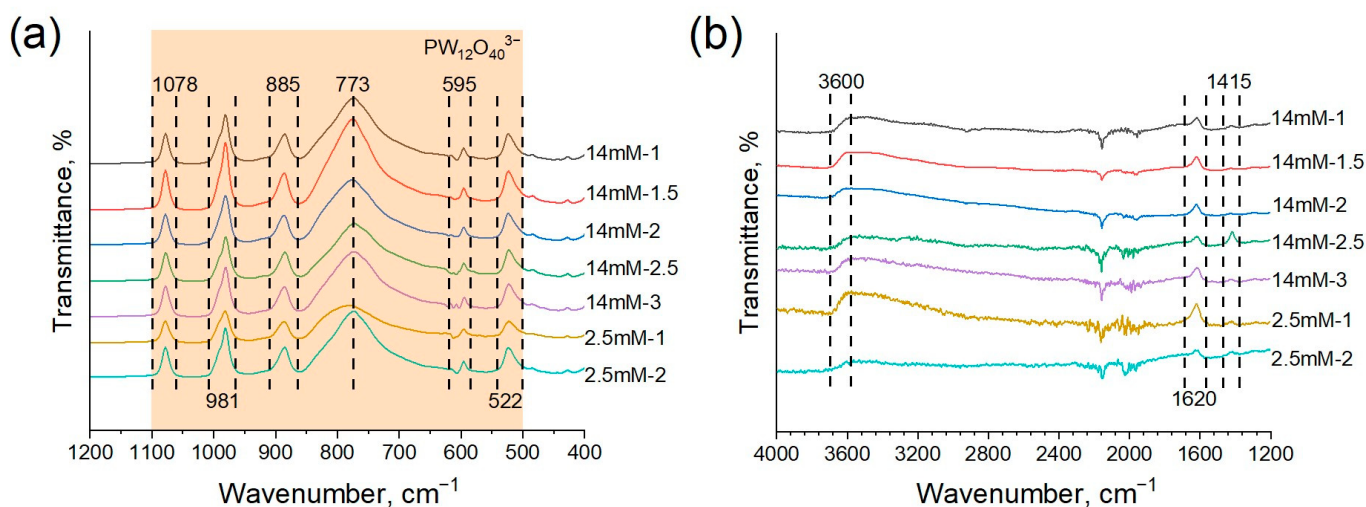


Figure 5. FTIR spectra of the obtained rubidium salts in the 1200–400 cm^{-1} range (a) and in the 4000–1200 cm^{-1} range (b).

High-intensity bands at 773 cm^{-1} , 885 cm^{-1} , 981 cm^{-1} , and 1078 cm^{-1} correspond to stretching vibrations of the P–O, W=O, and W–O–W bonds. Medium-intensity bands at 522 cm^{-1} and 595 cm^{-1} characterize bending vibrations of the O–P–O and W–O–W bonds.

The presence of a narrow band at 1620 cm^{-1} in the FTIR spectra (Figure 4) indicates bending vibrations of the H–O–H bond. This is explained by the adsorption of water molecules in the pore space of rubidium salts of PTA with the formation of intermolecular hydrogen bonds. The peak at 1415 cm^{-1} can be explained by the presence of rubidium chloride impurities. As can be seen from Figure 5b, this peak is observed only in the FTIR spectrum of sample 14mM-2.5. A continuous broad shoulder toward low frequencies from the maximum at 3600 cm^{-1} is caused by vibrational transitions of hydrates of higher protons [57].

3.4. Water Content

Typical STA curves for the obtained samples of PTA salts with different degrees of proton substitution have a similar appearance (Figure 6b). Heating the samples to a temperature of $145\text{--}190\text{ }^{\circ}\text{C}$ is accompanied by a loss of mass in one stage due to the dehydration of the salts (Figure 6a). This is confirmed by the mass spectra of the outlet gases, in which there are ion currents with ratios $m/z = 18$ and $m/z = 17$, characteristic of water molecules H_2O and OH^- particles, respectively. The total mass loss for the obtained samples with different degrees of rubidium substitution varies in the range of $95.2\text{--}97.8\%$. At the same time, samples obtained from solutions with a PTA concentration of $k = 2.5\text{ mM}$, as well as samples with high degrees of proton substitution x , have larger total mass losses. The dehydration of these samples is also completed at a higher temperature. The position of the maximum endothermic peak on the DSC curves does not depend on the synthesis conditions of the studied rubidium salts and lies in the region of $65\text{--}90\text{ }^{\circ}\text{C}$.

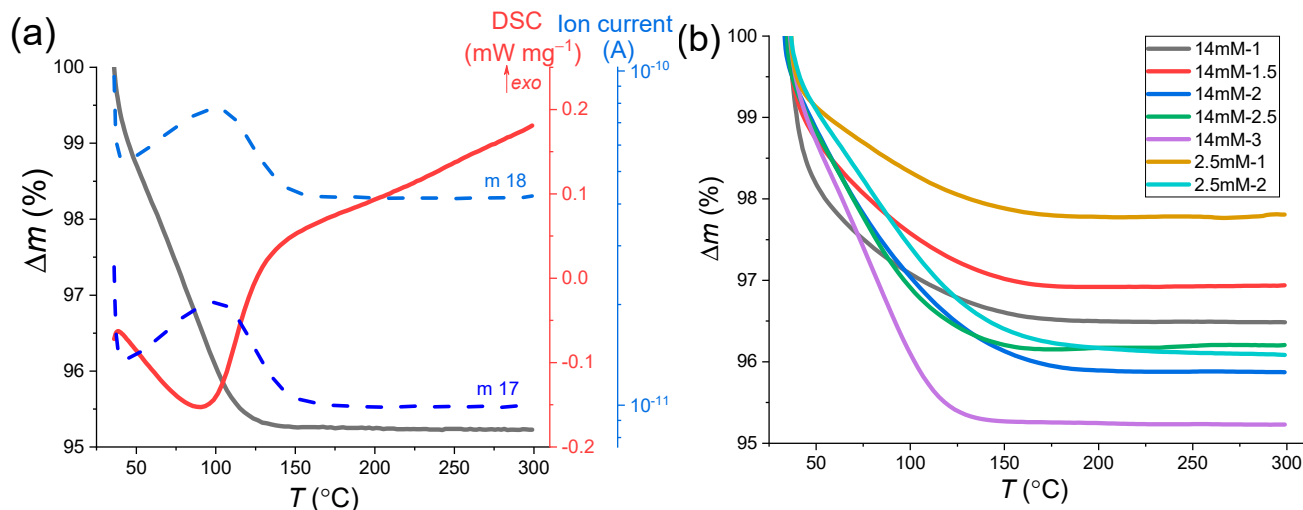


Figure 6. STA and ion current flow curves for 14mM-1 sample (a), and TGA curves for the obtained samples (b).

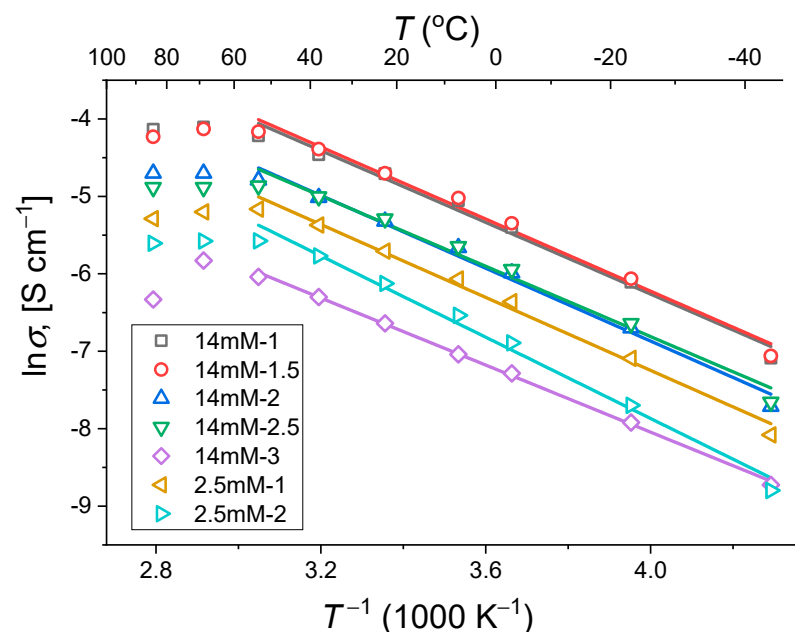
Based on the data from STA, the number of water molecules per salt molecule was calculated (Table 3). The total mass loss for synthesized PTA salts varies in the range of $2\text{--}5\%$ (Figure 5b), which corresponds to $n = 4\text{--}9$ water molecules per salt molecule (Table 3). With an increase in the concentration of PTA k during synthesis and the degree of proton substitution x , an increase in water content n in the obtained samples is also observed. This observation correlates well with an increase in SSA (Table 1). Since the observed dehydration process is a one-stage process (Figure 6), it can be assumed that the water contained in the samples is adsorbed on their surface and not bound in the crystal structure of the studied rubidium salts of PTA.

Table 3. Amount of water per molecule of salt (n), specific ionic conductivity at 25 °C ($\sigma^{25^\circ\text{C}}$), and activation energy of conductivity (E_σ) of the obtained samples.

Sample	n	$\sigma^{25^\circ\text{C}}, \text{mS cm}^{-1}$	E_σ, eV
14mM-1	6.2	9.0	0.20
14mM-1.5	5.4	9.1	0.20
14mM-2	6.7	4.9	0.20
14mM-2.5	6.8	5.0	0.19
14mM-3	8.6	1.3	0.19
2.5mM-1	3.8	3.3	0.20
2.5mM-2	7.1	2.2	0.22

3.5. Ionic Conductivity

The ionic conductivity of samples kept at RH = 75% was determined from the impedance spectra. Figure 7 shows a graph of the temperature dependence of the specific ionic conductivity of the studied samples. In the temperature range from -40 to $+55$ °C, the curves are well described by the Arrhenius equation. As the ambient temperature increases above 55 °C, a deviation from linearity σ in Arrhenius coordinates is observed with a decrease in conductivity, which is apparently due to the removal of water from the samples, as confirmed by TGA data (Figure 6b). The activation energy of conductivity, calculated from the slope of the straight lines, does not depend on the synthesis conditions and is $E_\sigma = 20 \pm 2$ eV (Table 3), which indicates the same nature of ionic conductivity in this temperature range.

**Figure 7.** Temperature dependences of the specific ionic conductivity of the studied rubidium salts.

At room temperature (25 °C), the specific ionic conductivity of the studied rubidium salts lies in the range of 9 to 1.3 mS cm^{-1} , which is consistent with the literature data (5 mS cm^{-1} at RH = 90% [22]). In the series of samples from 14mM-1 to 14mM-3 (Table 3), a decrease in ionic conductivity is observed (Table 3), even though the water content increases. In addition, a decrease in the concentration of PTA samples also leads to a decrease in the value of ionic conductivity. As was shown in [28], the main charge carriers in water-insoluble PTA salts are protons, and their transfer occurs mainly along the surface of crystallites and large particles or agglomerates consisting of them. In the studied samples,

the number of protons in this series changes insignificantly, but it can be assumed that their number can vary greatly on the surface and volume of the crystallite, depending on the synthesis conditions. Therefore, a number of additional studies are required to accurately describe the reasons for this behavior and the mechanism of ionic conduction.

4. Conclusions

For the first time, the influence of such synthesis conditions as the ratio of reagents and the concentration of PTA on the most important properties of rubidium salts $\text{Rb}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ (composition, particle morphology, crystalline structure, water content, and ion conductivity) was studied. The degree of proton substitution by rubidium ions weakly depends on the ratio of the reagents; rubidium salts of the composition $\text{RbH}_2\text{PW}_{12}\text{O}_{40}$ and $\text{Rb}_3\text{PW}_{12}\text{O}_{40}$ could not be obtained under the synthesis conditions studied. An increase in the ratio of reagents and a decrease in the concentration of the PTA solution leads to a decrease in the CSR, while the crystal lattice parameter a remains unchanged. An increase in SSA and the average particle size of the resulting salts is observed with higher ratios of reagents and lower PTA concentrations. The presence of adsorption water in the samples is confirmed by the direct dependence of the water content in the samples on the SSA value. An anomalous decrease in specific ionic conductivity with an increase in the number of water molecules per salt molecule and similar values of the degree of proton substitution x indicates a significant contribution of charge carriers and their distribution in the crystallites of rubidium salts. We recommend synthesizing salts in high concentrations and with the addition of a small amount of cesium chloride (2.5–3 mole per 1 mol of PTA). In this case, salts with a larger SSA and water content will be obtained. All these factors will positively affect the catalysis of reactions or water retention in polymer membrane modification. Optimization of parameters for the synthesis of rubidium salts of PTA can contribute to the creation of effective functional materials for various fields of application.

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