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MODELING OF EQUILIBRIA IN ACIDIFIED SOLUTIONS OF SODIUM ORTHOTUNGSTATE IN THE PRESENCE OF CALCIUM(II) IONS

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The interactions of the $Ca^{2+}-WO_4^{2-}-H^+-H_2O$ system initially acidified to the molar ratio (acidity) $Z=\nu(H^+)/\nu(WO_4^{2-})=1.00$ were studied by the methods of pH-potentiometry, mathematical modeling and conductometry in the interval $Z=0.60-2.00$ at 298 ± 0.1 K with $NaNO_3$ ($I=0.05-0.30$ mol·l^{-1}) as the supporting electrolyte. The logarithms of the equilibrium concentration constants were calculated by the Newton's method, and previously unknown logarithms of the thermodynamic constants and Gibbs energy of the reactions of the formation of ion associates $Ca^{2+},[W_4O_{14}(OH)_2]^{4-}$; $Ca^{2+},[W_6O_{20}(OH)_2]^{6-}$; $Ca^{2+},[W_{12}O_{40}(OH)_2]^{10-}$; $Ca^{2+},H[W_{12}O_{40}(OH)_2]^{9-}$; $Ca^{2+},H_2[W_{12}O_{40}(OH)_2]^{8-}$; $Ca^{2+},H_3[W_{12}O_{40}(OH)_2]^{7-}$; $[W_{12}O_{38}(OH)_2]^{6-}$; and $H[W_{12}O_{38}(OH)_2]^{5-}$ were calculated using the Pitzer method. The formation of particles with a ratio of $Ca^{2+}:[W_{12}O_{40}(OH)_2]^{10-}=1:1$ and $Ca^{2+}:[W_6O_{20}(OH)_2]^{6-}=1:1$ in the solutions was shown by the conductometric titration method. The crystals of calcium paratungstate B $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$ were synthesized from Na_2WO_4 solution acidified to acidity $Z=1.00$. By using ATR-FTIR and Raman spectroscopies, it was shown that the isopolyanion in the composition of the salt belongs to the structural type of paratungstate B. The structure of $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$ was determined by single crystal X-ray diffraction: monoclinic, $P2_1/n$, $a=15.3619(4)$ Å, $b=11.7537(3)$ Å, $c=18.1471(5)$ Å, $\beta=109.2950(10)^0$, $V=3092.58(14)$ Å^3, $R_1=0.0298$, $wR(F^2)=0.1387$.

Keywords: coordination compound, mathematical modeling, ion pair equilibrium, polyoxometalates, thermodynamics of solutions, calcium, ATR-FTIR and Raman spectroscopy, single crystal X-ray diffraction.

Introduction

From the analysis of literature sources concerning the state of tungsten(VI) ions in solution [1,2], it follows that within the low acidity range ($Z=\nu(H^+)/\nu(WO_4^{2-})=1.00-1.25$), where $\nu(H^+)$ stands for the initial molar amount of a strong acid (e.g. hydrochloric or nitric acid), and $\nu(WO_4^{2-})$ is the initial molar amount of sodium tungstate, the equilibrium solution contains WO_4^{2-}, $[W_6O_{20}(OH)_2]^{6-}$, $[W_7O_{24}]^{6-}$, and $[H_aW_{12}O_{40}(OH)_2]^{(10-a)-}$ ($a=0-1$) anions. In the high acidity region ($Z=1.25-1.65$), the solution contains $[HW_7O_{24}]^{5-}$, $[H_aW_{12}O_{40}(OH)_2]^{(10-a)-}$ ($a=2-3$), and $[H_aW_{12}O_{38}(OH)_2]^{(6-a)-}$ ($a=0-2$) anions in an aqueous solution, with additional $[H_aW_{10}O_{32}]^{(4-a)-}$ and $[W_6O_{19}]^{2-}$ anions in a mixed aqueous-organic solution.

Despite the extensive ion distribution outlined across the broad acidity range ($Z\geq1.00$), it is noteworthy that only paratungstate B $[W_{12}O_{40}(OH)_2]^{10-}$ salts are synthesized from solutions containing an equilibrium mixture of various isopolytungstates [3]. This observation emphasizes the notable stabilization of $[H_aW_{12}O_{40}(OH)_2]^{(10-a)-}$ in the solution, facilitated by the presence of cations during the synthesis process.

It is crucial to highlight that, notwithstanding the high dielectric permeability of aqueous solutions, the electrostatic interaction between isopolytungstate anions (IPTA) and calcium(II) cations, facilitated by the substantial charges of polyoxometalate anions, appears highly plausible. Recent investigations into the state of IPTA have moved beyond the consideration of reactions resulting solely in individual IPTA

formation. These studies within the framework of ionic equilibrium models, have included reactions for the formation of ion associates, such as [M^{n+}, IPTA], [$M(H_2O)_m^{n+}$, IPTA] [4,5].

Isopolyoxotungstates of alkaline-earth metals exhibit a pronounced sensitivity to surface photoelectric voltage and electric field-induced surface photoelectric voltage. This observation underscores their semiconducting characteristics, suggesting promising applications as photocatalysts and in devices for the conversion of light into electricity [6]. The remarkable sensitivity to these surface photoelectric phenomena indicates the potential for further advancements in the utilization of compounds with IPTA, expanding their applicability in future technologies.

Nevertheless, there is limited information available in the literature regarding the synthesis of calcium(II) isopolytungstates. This is somewhat surprising given that the ionic radius of calcium (0.099 nm) suggests its potential suitability as an affective precipitating reagent for IPTA.

Thus, in work [7], a colorless ammonium-sodium salt with an unconventional anion structure, $(NH_4)_{10}Na_2\{[Ca(H_2O)]_6[P_4W_6O_{34}]_2\}\cdot14H_2O$, was synthesized. This compound was derived from $Na_2WO_4\cdot2H_2O$, $Na_2HPO_4\cdot12H_2O$, $CaCl_2$ and NH_4Cl within a weakly acidic aqueous medium (pH 6.5) at a temperature ranging from 353 K to 363 K. The structural characterization was conducted using X-ray crystallography and IR spectroscopy.

Another synthesized calcium-containing heteropolytungstate is $[Ca_4(H_2CyDTA)_2(H_2O)_{22}][SiW_{12}O_{40}]\cdot8H_2O$. This compound was isolated through the reaction involving $CaCl_2\cdot2H_2O$, H_4CyDTA and $(NH_4)_4[SiW_{12}O_{40}]\cdot4H_2O$ in an aqueous medium. The synthesis occurred under sufficiently acidic conditions with a pH of 1.8 and at a temperature of 343 K. The structural characterization of the compound was carried out using X-ray crystallography [8].

Information on the methods of synthesizing double calcium salts of paratungstate B is notably limited. Currently available data pertains primarily to the isolation of a double sodium-calcium paratungstate B with the molecular formula $Ca_2Na_6[H_2W_{12}O_{42}]\cdot30H_2O$. This compound was synthesized in a rather unconventional manner through the reaction involving $Na_{12}[Bi_2W_{22}O_{74}(OH)_2]\cdot44H_2O$, $CaCl_2\cdot2H_2O$, and $Na_9[BiW_9O_{33}]\cdot16H_2O$. The synthesis occurred at 343 K with a pH of 6.5, maintained by a Na_2CO_3 solution [6].

The limited literature addressing the synthesis of calcium polyoxotungstates underscores the need for comprehensive research in this domain. Notably,

the absence of detailed insights into the behavior of tungstate ions (WO_4^{2-}) in acidified solutions in the presence of Ca^{2+} highlights the necessity to explore the potential interaction between Ca^{2+} cations and IPTA. Such an investigation holds significance due to its potential impact on the extraction efficiency of Ca-containing isopolytungstates from acidified aqueous solutions of sodium tungstate under conditions of low acidity.

These studies are inherently tied to the existing knowledge of the aqueous phase behavior of tungsten (VI) anions. To address these research gaps, the pH-potentiometric and conductometric studies were conducted to elucidate equilibria in acidified solutions of sodium tungstate. The thermodynamic characteristics of these equilibria were rigorously determined. Additionally, solid phases were synthesized and isolated from solution at Z=1.00. The resulting crystals were thoroughly characterized using elemental analysis, ATR-FTIR and Raman spectroscopy, and X-ray crystallography.

Materials and methods

Initial solutions of salts were prepared from crystalline $Na_2WO_4\cdot2H_2O$ (p.a.), $Ca(NO_3)_2\cdot H_2O$ (p.a.), and $NaNO_3$ (p.a.) by dissolving them in bidistilled water purified from CO_2. The working acid solution was prepared by diluting concentrated HNO_3 (puriss.). The precise concentrations of the solutions were established following the methods described in ref. [9].

pH-potentiometric titration

pH-Potentiometric titration was employed to investigate the interaction of ions in the $Ca^{2+}-WO_4^{2-}-H^+-H_2O$ system. The titration was conducted using an ionometer «I-160 MI» in solutions thermostated at 298.15±0.10 K. The indicator electrode utilized was a proton-selective glass electrode «HI 1131B», and any minor temperature fluctuations were compensated for by a thermal compensator TDL-1000. The initial ion concentrations were set as follows: $C(WO_4^{2-})$=0.010 mol·l^{-1}, $C(H^+)$=0.006 mol·l^{-1}, $C(Ca^{2+})$=0.0017 mol·l^{-1}. Titration proceeded with continuous, vigorous stirring of the system, employing a titration step of ΔZ=0.02. Titration experiments were conducted at various ionic strengths (I=0.05; 0.10; 0.15; 0.20; 0.25; 0.30 mol·l^{-1}), which were achieved by adjusting the amount of 2 mol·l^{-1} sodium nitrate.

Conductometric titration

Conductometric titration, involving the continuous monitoring of electrical conductivity ($\varkappa$, µS·cm^{-1}), was performed using a laboratory conductometer DDS-308A (ULAB) at a controlled temperature of 298.15 K, with an error margin of

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0.5%. The apparatus was equipped with a TDS thermal compensator for accurate measurements. The initial concentrations of ions were set as follows: $C(WO_4^{2-})=0.10$ moll^{-1}, $C(H^+)=0.10$ mol·l^{-1} and 0.17 mol·l^{-1}. Throughout the titration, the system underwent vigorous mixing. The titration process concluded when the ratio $n=v(Ca^{2+}):v(WO_4^{2-})$ reached the value of 0.4.

Mathematical modeling of equilibrium

Mathematical modeling of equilibrium in the $Ca^{2+}-WO_4^{2-}-H^+-H_2O$ system was carried out using the CLINP 2.1 software (quasi-Newton method). When calculating, the law of mass action and the equations of material balance were used, and charge balance was also monitored, which made it possible to construct calculated titration curves [10]. Initially, a set of complex formation reactions (chemical model) was selected, representing the most likely reactions under the study conditions. Subsequent optimization steps involved adjusting the model by iteratively adding reactions that minimized discrepancies in calculated parameters or removing reactions that increased deviations compared to the experimentally obtained values.

At each point of the curve, Δ_k (the difference between the calculated ($[H^+]^{(calc)}$) and experimental ($[H^+]^{(exp)}$) equilibrium concentration of protons) was calculated in the following way:

$$\Delta_k=[H^+]^{(calc)}-[H^+]^{(exp)},$$

and the value of the criterion function (CF) was minimized for the entire dependence:

$$CF = \sum_{k=1}^{N} F\left(w_k \Delta_k^2\right),$$

where F is some function; N is the number of points of the studied series, $k=1, 2, ..., N$, and w_k is the statistical weight of the kth measurement associated with the estimate of the dispersion $S^2(\Delta_k)$:

$$w_k = \frac{1}{S^2(\Delta_k)} = \frac{1}{\left(\left[H^+\right]_k^{(e)}\right)^2} \cdot \frac{1}{S_r^2},$$

where $S(\Delta_k)$ is the standard deviation of Δ_k.

The relative error S_r of pH measurements is taken to be equal to 0.05. Models were considered adequate if the following inequality was satisfied [11]:

$$\chi_{exp.}^2 = S_0^2 \cdot f < \chi_f^2(\alpha),$$

where S_0^2 is residual variance; $\chi_f^2(\alpha)$ is the statistical distribution criterion for f degrees of freedom at a given level of significance δ ($\delta=0.05$) [11]:

$$S_0^2 = \frac{1}{f}\sum_{k=1}^{N} w_k \Delta_k^2.$$

To mathematically replicate the experimental data (pH vs. Z dependences), a model representing the most probable interactions between isopolyoxotungstate anions (IPTA) and calcium cations was computed using theoretical data. The goal was to achieve convergence between calculated and experimental results. The optimized model facilitated the calculation of equilibrium concentration constants (lgK_C) and the construction of ion distribution diagrams contingent on the concentration of the supporting electrolyte (ionic strength I).

The logarithms of the thermodynamic constants (lgK^0) were defined by Pitzer's method [12,13] by extrapolating the dependence of lgK_C vs. I to I=0 mol·kg^{-1}. This extrapolation was based on the set of lgK_C obtained at different values of ionic strength. The molar concentration (C_m) was calculated according to the equation:

$$C_m = \frac{C(NaNO_3)}{\rho - \dfrac{C(NaNO_3) \cdot M(NaNO_3)}{1000}},$$

where ρ is the experimentally measured density of the solution (g·cm^{-3}).

Synthesis

Nitric acid was added into an aqueous solution of sodium orthotungstate ($C_W=0.01$ mol·l^{-1}) with vigorous stirring to achieve the specified acidity level of Z=1.00. Subsequently, a calcium nitrate solution was added dropwise to maintain the ratio $C(Ca^{2+}):C(WO_4^{2-})=1:12$. The resulting homogeneous solutions were stirred at a temperature of 298 K for 1 hour. Following this, the system was left exposed to the air, and after approximately one week, nucleation was observed. After 3-4 weeks from the system's preparation, colorless crystals were collected for subsequent analysis.

ATR-FTIR and Raman spectroscopy

The identification of anions in the synthesized salts was conducted through ATR-FTIR and Raman spectroscopic analyses of air-dried samples. Infrared (using single-bounce diamond ATR) and Raman (utilizing a vacuum-sealed capillary with a 1064 nm excitation laser) spectra were recorded on a Nicolet iS50 FTIR spectrometer, which was equipped with a Raman iS50 module. The spectral resolution employed for both FTIR and Raman measurements was 4 cm^{-1} (with a data spacing of 0.482 cm^{-1}). FTIR spectra were captured in the wave number range of 200−

1800 and 400−4000 cm^{-1}, while Raman spectra covered the range of 0−4000 cm^{-1}. The determination of vibrations in the IR spectra was carried out based on existing data [1−3,14].

Determination of crystal structure

Full sets of diffraction data were collected at 150(2) K with a Bruker D8-Venture diffractometer equipped with Cu (Cu/K$_\alpha$ radiation; λ=1.54178 Å) or Mo (Mo/K$_\alpha$ radiation; l=0.71073 Å) microfocus X-ray (IμS) sources; Photon III CMOS detector and Oxford Cryosystems cooling device were used for data collection. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). Obtained data were treated with the software XT version 2019/1 and SHELXL-2019/3 implemented in the APEX4 v2022.2-0 (Bruker AXS) system.
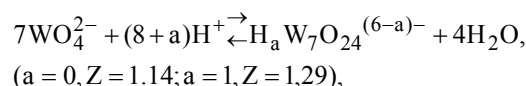
Chemical analysis

The tungsten content (WO$_3$, δ=0.5%) was determined gravimetrically following the procedure outlined in ref. [9]. The water content was determined by calcining dry samples at T=773 K for 2 hours. The calcium content was determined through complexometric titration, as per the method described elsewhere [9]. The potential sodium content was calculated as Na$_2$O by the difference after accounting for the percentages of WO$_3$, H$_2$O, and CaO.
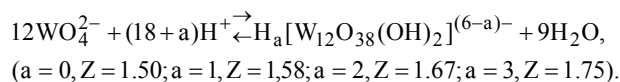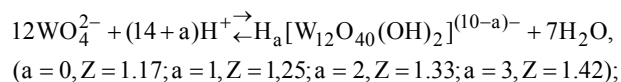
Results and discussions

It is well known that the formation of isopolytungstate anions in acidified aqueous solutions of tungstate anions occurs due to polycondensation according to the following general scheme [1−3]:

$$nWO_4^{2-} + mH^+ \underset{\leftarrow}{\rightarrow} [H_{m-2k}W_nO_{4n-k}]^{(2n-m)-} + k \cdot H_2O;$$

$$Z = m/n = C(H^+)/C(WO_4^{2-}).$$
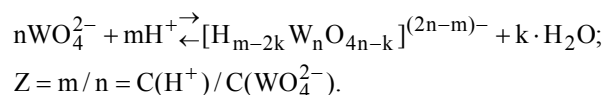
Since the reagents are hydrogen ions and tungstate ions, it is convenient to operate with the concept of acidity $Z(C(H^+)/C(WO_4^{2-}))$, which allows fixing the zones of predominance of a specific isopolytungstate anion in the system and, unlike pH, does not depend on the concentration of solutions. Usually interesting for research is the area of acidity Z=0−1.5, which covers weakly alkaline, neutral and weakly acidic pH. In this zone, the formation of protonated heptatungstates is usually observed:

$$7WO_4^{2-} + (8+a)H^+ \underset{\leftarrow}{\rightarrow} H_aW_7O_{24}^{(6-a)-} + 4H_2O,$$
$$(a = 0, Z = 1.14; a = 1, Z = 1,29),$$

as well as dodecatungstate anions [1]:

$$12WO_4^{2-} + (14+a)H^+ \underset{\leftarrow}{\rightarrow} H_a[W_{12}O_{40}(OH)_2]^{(10-a)-} + 7H_2O,$$
$$(a = 0, Z = 1.17; a = 1, Z = 1,25; a = 2, Z = 1.33; a = 3, Z = 1.42);$$

$$12WO_4^{2-} + (18+a)H^+ \underset{\leftarrow}{\rightarrow} H_a[W_{12}O_{38}(OH)_2]^{(6-a)-} + 9H_2O,$$
$$(a = 0, Z = 1.50; a = 1, Z = 1,58; a = 2, Z = 1.67; a = 3, Z = 1.75).$$

On the other hand, the hydroheptatungstate anion, as a result of hydrolysis over a relatively extended period that surpasses the synthesis time, can transform into protonated anions of paratungstate B according to the following reaction [2]:

$$12HW_7O_{24}^{5-} + (7x-4)H_2O \underset{\leftarrow}{\rightarrow} 7H_x[W_{12}O_{40}(OH)_2]^{(10-x)-} + (7x-10)OH^-, (x = 0-3).$$
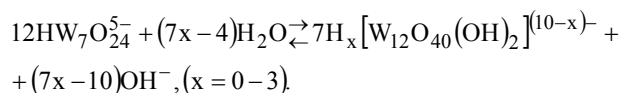
Previously, at the Department of Inorganic, Organic, and Analytical Chemistry of Vasyl' Stus Donetsk National University, it was demonstrated [2,3] that in the presence of M^{2+} cations (M=Mn, Co, Ni), the state of tungsten ions undergoes significant changes, leading to the formation of ion associates (ion pairs) between these cations and hydroparatungstate-B anions in the solution. It is theoretically plausible that calcium cations may also form ion pairs with isopolytungstate anions. To test this hypothesis, a conductometric titration at the acidity of 1.17 was conducted. The dependence of the change in electrical conductivity on the ratio of the number of calcium cations to tungstate anions (Fig. 1) consists of decreasing and increasing parts. Linear dependences were established for both parts by the method of least squares:

$$\varkappa_1 = -200.19n + 1099 \text{ and } \varkappa_2 = 120.58n + 1071.3.$$

The intersection of these lines corresponds to the value of $\nu(Ca^{2+}):\nu(WO_4^{2-})=0.086\approx1/12$, indicating the possibility of forming a bond not with ortho-, hexa-, or heptatungstate anions, but with the paratungstate B anion $[W_{12}O_{40}(OH)_2]^{10-}$. Taking into account the contribution of its high charge and size, it could be suggested the formation of ion pair between it and the Ca^{2+} cation.
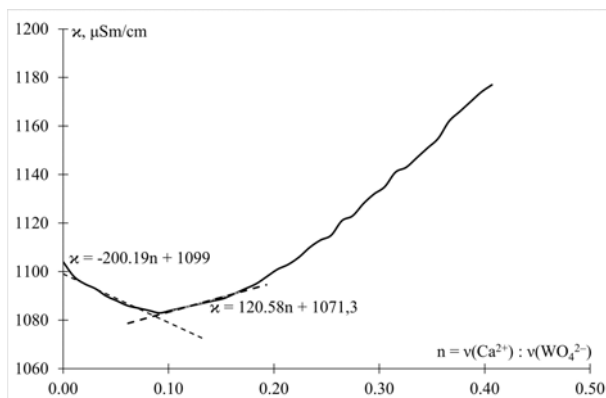

Fig. 1. Results of conductometric titration at Z=1.17

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The study of interactions in the $Ca^{2+}-WO_4^{2-}-H^+-H_2O$ system using the pH-potentiometric titration method resulted in a series of integral pH vs. Z and differential $\Delta pH/\Delta Z$ vs. Z curves (Fig. 2) at various ionic strengths (I=0.05−0.30). The differential curve exhibits distinct extrema in the acidity range corresponding to the formation of paratungstate and metatungstate anions. Considering potential processes involving both polycondensation and the formation of ion associates, the wide acidity range observed does not correspond to the formation of only one or two isopolyanions. Instead, it indicates the formation of a larger number of particles through series-parallel reactions, consistent with findings in acidified tungstate solutions lacking calcium cations [1−3].
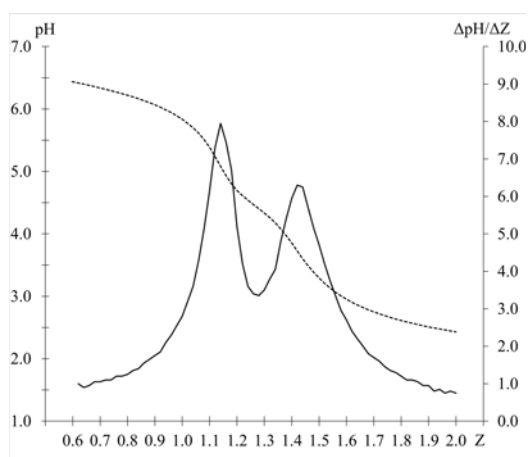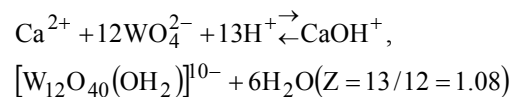

Fig. 2. Integral (---) and differential (−) titration curves of the system $Ca^{2+}-WO_4^{2-}-H^+-H_2O$ at T=298 K, I=0.2 mol·l^{-1}

The information gathered from pH-potentiometric titration served as the foundation for computer modeling of polycondensation process equilibria, given the influential role of hydrogen ions in these processes. Moreover, the experimental determination of the equilibrium concentration of H^+ ions, actively engaged in the reactions, provided a precise parameter for quality control in the model, in accordance with the law of charge balance.
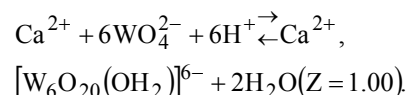
Considering prior research conducted at the department, which indicated the inadequacy of the traditional model [1,2] in the presence of cations and suggested that the model with ion associates $[M^{n+},$ IPTA], $[M(H_2O)_m^{n+},$ IPTA] [3] more accurately describes the system, the initial *model 1* incorporated the following associates: $CaOH^+,[W_{12}O_{40}(OH)_2]^{10-}$; $Ca^{2+},[W_{12}O_{40}(OH)_2]^{10-}$; $Ca^{2+},H_2[W_{12}O_{40}(OH)_2]^{8-}$; $Ca^{2+},H_3[W_{12}O_{40}(OH)_2]^{7-}$; and $[W_{12}O_{38}(OH)_2]^{6-}$. Despite favorable statistical indicators (CF=22.81), where $\chi^2_{exp}>\chi^2_{f,\alpha=0.05}$ (3.6<84.8), the *model 1* was rejected due to the low probability of a sufficient

concentration of $CaOH^+$ particles in the corresponding pH zone. Taking into account the second dissociation constant of calcium hydroxide ($K_2=4.3\cdot10^{-2}$) and the initial concentration of $C(Ca^{2+})=1.7\cdot10^{-3}$ mol·l^{-1}, the content of the $CaOH^+$ cation can be estimated as $5\cdot10^{-4}$% at pH 5.40.

At acidity Z≈1.00, the competitor of the reaction of the formation of paratungstate:

$$Ca^{2+}+12WO_4^{2-}+13H^+\underset{\leftarrow}{\rightarrow}CaOH^+,$$
$$[W_{12}O_{40}(OH_2)]^{10-}+6H_2O\left(Z=13/12=1.08\right)$$

can be reaction:

$$Ca^{2+}+6WO_4^{2-}+6H^+\underset{\leftarrow}{\rightarrow}Ca^{2+},$$
$$[W_6O_{20}(OH_2)]^{6-}+2H_2O\left(Z=1.00\right).$$

The possibility of the formation of ion associates with the hexatungstate anion is confirmed by the results of conductometric titration, which indicate the formation of an ion pair with a ratio of $\nu(Ca^{2+}):\nu(WO_4^{2-})$ close to 1/6 (Fig. 3).
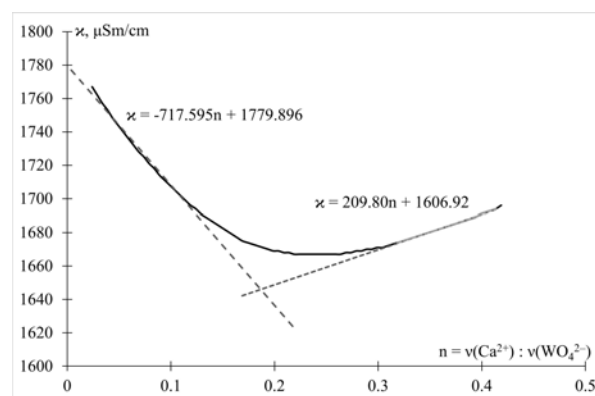

Fig. 3. Results of conductometric titration at Z=1.00

After extensive approbation of numerous potential combinations of ion pairs, *model 2* was formulated, including associates $Ca^{2+},[W_4O_{14}(OH)_2]^{4-}$; $Ca^{2+},[W_6O_{20}(OH)_2]^{6-}$; $Ca^{2+},[W_{12}O_{40}(OH)_2]^{10-}$; $Ca^{2+},H[W_{12}O_{40}(OH)_2]^{9-}$; $Ca^{2+},H_2[W_{12}O_{40}(OH)_2]^{8-}$; $Ca^{2+},H_3[W_{12}O_{40}(OH)_2]^{7-}$; $[W_{12}O_{38}(OH)_2]^{6-}$; and $H[W_{12}O_{38}(OH)_2]^{5-}$. This model adequately described the experimental results with satisfactory statistical characteristics, including CF=23.44 and $\chi^2_{exp}<\chi^2_{f,\alpha=0.05}$ (4.5<90.5). Furthermore, it is not redundant based on the elements of the Jacobi matrix [10].

An essential observation is that the qualitative composition of *model 2* differs from the compositions of models describing polycondensation processes of orthotungstate anions in acidified solutions without doubly charged cations [1,2]. It is noteworthy that

the inclusion of «low-acid» particles such as $[W_4O_{14}(OH)_2]^{4-}$ and $[W_6O_{20}(OH)_2]^{6-}$ reduced deviations in the acidity range $Z<1.00$. Additionally, in the interval Z from 1.00 to 1.35, protonated heptameric $[W_7O_{24}]^{6-}$ particles were not utilized in the model, even considering that the monoprotonated form of $H[W_7O_{24}]^{5-}$ is stable enough in solution and has the tendency to transform into protonated paratungstates over time. Furthermore, the introduction of a calcium cation into the solution was found to stabilize only highly charged paratungstate anions $H_a[W_{12}O_{40}(OH)_2]^{(10-a)-}$ ($a=0-3$) in the acidity zone $Z=1.00-1.50$ due to the formation of ion pairs.

Based on the logarithms of the concentration constants for the formation of ion pairs from monomer ions calculated for *model 2* (Table 1), a diagram illustrating the distribution of ion pairs was constructed as a function of Z (Fig. 4).
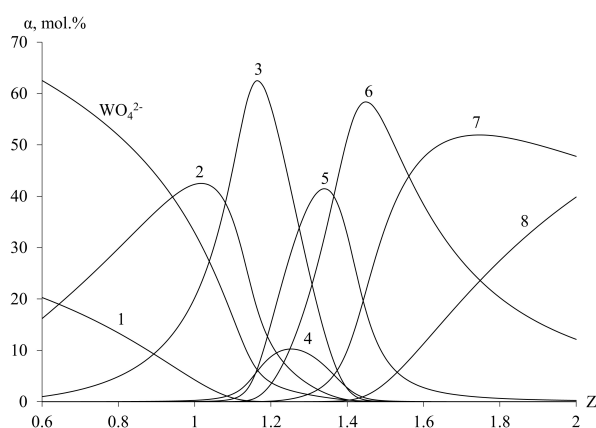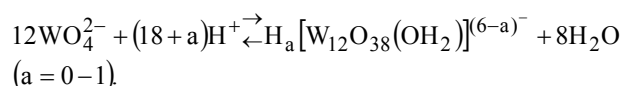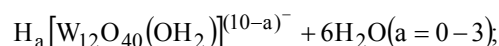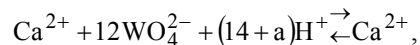

Fig. 4. Diagram of the distribution of particles in the $Ca^{2+}-WO_4^{2-}-H^+-H_2O$ system for the ionic strength (I) of 0.15 mol·l^{-1}: $1 - Ca^{2+}, [W_4O_{14}(OH)_2]^{4-}$; $2 - Ca^{2+}, [W_6O_{20}(OH)_2]^{6-}$; $3 - Ca^{2+}, [W_{12}O_{40}(OH)_2]^{10-}$; $4 - Ca^{2+}, H[W_{12}O_{40}(OH)_2]^{9-}$; $5 - Ca^{2+}, H_2[W_{12}O_{40}(OH)_2]^{8-}$; $6 - Ca^{2+}, H_3[W_{12}O_{40}(OH)_2]^{7-}$; $7 - [W_{12}O_{38}(OH)_2]^{6-}$; and $8 - H[W_{12}O_{38}(OH)_2]^{5-}$

Therefore, within the acidity range of $Z=1.00\div1.50$, the presence of a calcium cation

significantly alters the state of IPTA, focusing mainly on two types of reactions. These reactions encompass the polycondensation and protonation processes specifically involving dodecameric IPTA, along with the formation of ion pairs:

$$Ca^{2+}+12WO_4^{2-}+(14+a)H^+ \underset{\leftarrow}{\rightarrow} Ca^{2+},$$

$$H_a[W_{12}O_{40}(OH_2)]^{(10-a)-}+6H_2O(a=0-3);$$

$$12WO_4^{2-}+(18+a)H^+ \underset{\leftarrow}{\rightarrow} H_a[W_{12}O_{38}(OH_2)]^{(6-a)-}+8H_2O$$
$$(a=0-1).$$

An analogous outcome, where only metatungstate and paratungstate anions were observed in this range, was previously noted when acetic acid was utilized for acidification. This was explained by the formation of a buffer solution containing a weak acid, mitigating the rise in acidity by adjusting the pH and thereby stabilizing the presence of the aforementioned anions in the solution [3].

The results obtained suggest that the formation of paratungstates can take place in a surprisingly broad range of acidity, $Z=1.00-1.50$, both when utilizing acetic acid and due to the formation of ionic associates. This observation may partially elucidate the prevalence of synthesized salts containing the paratungstate B anion among isopolytungstates, even at acidities that frequently deviate from the theoretical $[W_{12}O_{40}(OH)_2]^{10-}$ ($Z=1.17$).

Calculation of thermodynamic characteristics

The logarithms of the equilibrium concentration constants (lgK_C) obtained from the modelling of ion pair formation reactions (Table 1) are influenced not only by the concentrations of the initial substances but also by the concentration of the supporting electrolyte, which is added in excess relative to the starting substances. To accurately calculate thermodynamic characteristics from the lgK_C values at different ionic strengths, the logarithms of the thermodynamic equilibrium constants (lgK^0), which

Table 1

Logarithms of concentration constants for ion pair formation reactions

Ion pair	lgK_C for the value of ionic strength I (mol·l^{-1})					
	0.05	0.10	0.15	0.20	0.25	0.30
$Ca^{2+}, [W_4O_{14}(OH)_2]^{4-}$	24.05	24.01	23.93	23.88	23.78	23.64
$Ca^{2+}, [W_6O_{20}(OH)_2]^{6-}$	54.95	54.80	54.78	54.70	54.66	54.67
$Ca^{2+}, [W_{12}O_{40}(OH)_2]^{10-}$	120.88	120.72	120.67	120.66	120.67	120.72
$Ca^{2+}, H[W_{12}O_{40}(OH)_2]^{9-}$	125.22	124.75	124.62	–	124.59	124.77
$Ca^{2+}, H_2[W_{12}O_{40}(OH)_2]^{8-}$	130.18	129.82	129.62	129.50	129.43	129.48
$Ca^{2+}, H_3[W_{12}O_{40}(OH)_2]^{7-}$	134.32	133.79	133.74	133.44	133.47	133.58
$[W_{12}O_{38}(OH)_2]^{6-}$	134.18	133.71	133.85	133.45	133.82	133.84
$H[W_{12}O_{38}(OH)_2]^{5-}$	136.86	136.39	136.20	135.98	135.91	135.84

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are independent of the nature and concentration of ions in the solution, were determined by extrapolating the lgK_C vs. I dependence to the I=0 mol·kg^{-1} (Fig. 5) using the Pitzer method [12,13] and are shown in Table 2.
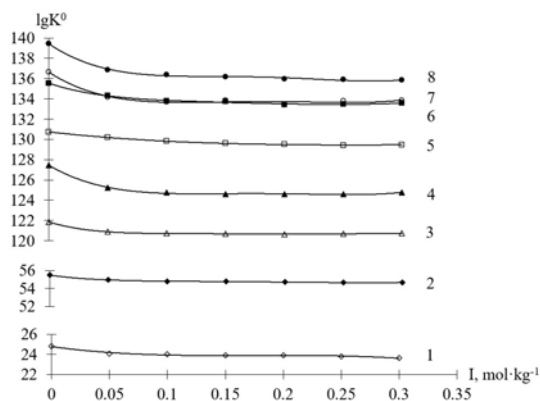

Fig. 5. Calculation of logarithms of thermodynamic constants of ion pair formation: $1 - Ca^{2+}, [W_4O_{14}(OH)_2]^{4-}$; $2 - Ca^{2+}, [W_6O_{20}(OH)_2]^{6-}$; $3 - Ca^{2+}, [W_{12}O_{40}(OH)_2]^{10-}$; $4 - Ca^{2+}, H[W_{12}O_{40}(OH)_2]^{9-}$; $5 - Ca^{2+}, H_2[W_{12}O_{40}(OH)_2]^{8-}$; $6 - Ca^{2+}, H_3[W_{12}O_{40}(OH)_2]^{7-}$; $7 - [W_{12}O_{38}(OH)_2]^{6-}$; and $8 - H[W_{12}O_{38}(OH)_2]^{5-}$

The presence of thermodynamic constants allows calculating the Gibbs energy of formation reactions of ion pairs from monomer ions using the formula:

$$\Delta_r G^0 = -RT \cdot \ln K^0.$$

Synthesis, analysis and structure determination

The modeling indicates that only paratungstate anions are stabilized in the acidified solution of sodium tungstate in the presence of calcium cations. It was shown that a possible reason for this is the interaction between calcium cations and these anions with the formation of ion pairs. To validate the modeling results, a solid-phase synthesis was conducted to determine which salt with which anion would be obtained from a solution in which an ion associate could potentially form.

To obtain calcium-containing polytungstate, a solution was prepared with a concentration of tungstate anion $C(WO_4^{2-})=0.1000$ mol·l^{-1}, $C(H^+)=0.1000$ mol·l^{-1}). With intensive stirring, a solution of calcium cation was added dropwise to $C(Ca^{2+})=0.0083$ mol·l^{-1}. The system was kept at a temperature of 298 K for 3−4 weeks until the formation of a colorless crystalline precipitate, and then additionally for a week at T=278 K for the thickening of the precipitate. After that, the precipitate was filtered, washed with cold distilled water, and air-dried to a constant weight. The resulting crystalline powder underwent elemental analysis, and the results allowed establishing the molar ratio between the elements in the synthesized crystals. Found (calculated) wt.%: CaO 7.65 (7.73), WO$_3$ 75.82 (76.86), H$_2$O 14.83 (15.41).

A compound with a similar molar ratio has been synthesized previously in ref. [9]. It is noteworthy that the authors isolated such a compound under different synthesis conditions. The crystals were obtained after 2 months from a solution with an acidity of 1.29, in contrast to our approach, where crystals were obtained after 1 month from a solution with an acidity of 1.00.

To identify the anion in these compounds, ATR-FTIR and Raman spectroscopies were employed. The results (Fig. 6) exhibit characteristic absorption bands of FTIR (375(s), 392(s), 431(s), 463(s) (δ(O−W−O)), 689(s), 774(m) (ν(O−W−O)$_c$ (octahedral corner sharing)), 854(m), 865(m) (ν(O−W−O)$_e$ (octahedral edge sharing)); 932(w), 944(w) (ν(O−W−O)$_t$ (terminal)), 960(w) (ν(W=O)$_t$

Table 2

Thermodynamic constants and Gibbs free energies for ion pair formation reactions from monomer ions

Reaction	lgK^0	$\Delta_r G^0$, kJ·mol^{-1}
$Ca^{2+}+4WO_4^{2-}+2H^+ \rightleftarrows Ca^{2+},[W_4O_{14}(OH)_2]^{4-}$	24.82	−141.54
$Ca^{2+}+6WO_4^{2-}+6H^+ \rightleftarrows Ca^{2+},[W_6O_{20}(OH)_2]^{6-}+2H_2O$	55.48	−316.41
$Ca^{2+}+12WO_4^{2-}+14H^+ \rightleftarrows Ca^{2+},[W_{12}O_{40}(OH)_2]^{10-}+6H_2O$	121.86	−694.99
$Ca^{2+}+12WO_4^{2-}+15H^+ \rightleftarrows Ca^{2+},H[W_{12}O_{40}(OH)_2]^{10-}+6H_2O$	127.46	−726.91
$Ca^{2+}+12WO_4^{2-}+16H^+ \rightleftarrows Ca^{2+},H_2[W_{12}O_{40}(OH)_2]^{9-}+6H_2O$	130.75	−745.65
$Ca^{2+}+12WO_4^{2-}+17H^+ \rightleftarrows Ca^{2+},H_3[W_{12}O_{40}(OH)_2]^{7-}+6H_2O$	135.55	−773.04
$12WO_4^{2-}+18H^+ \rightleftarrows [W_{12}O_{18}(OH)_2]^{6-}+8H_2O$	136.65	−779.33
$12WO_4^{2-}+19H^+ \rightleftarrows H[W_{12}O_{18}(OH)_2]^{5-}+8H_2O$	139.45	−795.29

(terminal), 1618(br) ($\delta(H_2O)$), 3298(br) ($\nu(H_2O)$)) and Raman spectroscopy 346(m), 361(m) 426(w), 444(w), 493(w) ($\delta(O-W-O)$), 645(m), 682(w), 767(w) ($\nu(O-W-O)_c$), 840(m), 874(m), 887(w) ($\nu(O-W-O)_e$), 944(vs) ($\nu(O-W-O)_t$), 963(vs) ($\nu(W=O)_t$), 1637(vw) ($\delta(H_2O)$), 3371(w), 3425(w) ($\nu(H_2O)$)) that correlate well with the known spectra of isopolytungstates [1−3,14]. It can be concluded that the anion present in the crystals can be identified as the paratungstate B-anion.
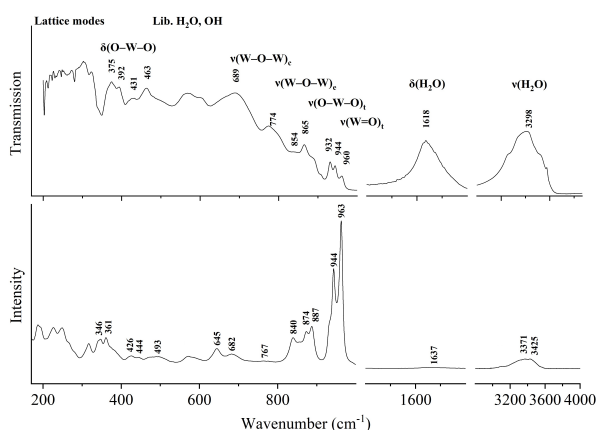

Fig. 6. ATR-FTIR and Raman spectra for $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$

Direct single crystal X-ray diffraction analysis was carried out for the obtained single-crystal samples of the synthesized crystals. The main crystallographic data and the results of refinement of the crystal structure are presented in Table 3. The coordinates of the basic W, O, Ca atoms of the framework of the structure were determined by the direct method, the positions of the hydrogen atoms were not identified. The numbering scheme of atoms in the structure and the structure of a crystallographically independent moiety are shown in Fig. 7, and the projection of the structure along the x axis is shown in Fig. 8.
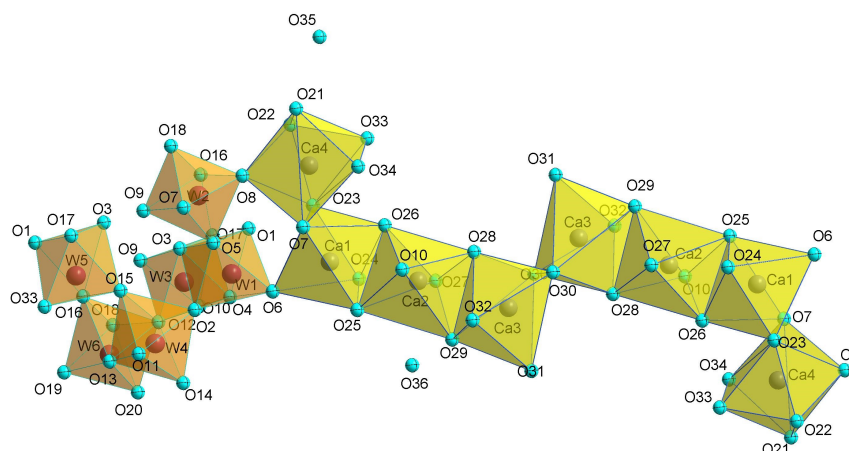
Table 3

Crystallographic data and refinement results for $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$

Empiric formula	$Ca_5O_{72}W_{12}$
Molecular weight	3590.68
Crystal system	Monoclinic
Space group	$P2_1/n$
Temperature (K)	150
a (Å)	15.3618(4)
b (Å)	11.7537(3)
c (Å)	18.1471(5)
α (°)	90
β (°)	109.2950(10)
γ (°)	90
Unit cell volume (Å³)	3092.58(3)
Density (g/cm³)	3.822
Absorption coefficient, μ/mm⁻¹	22.402
No. of reflections measured	11568
No. of independent reflections	5422
R(int)	0.0712
Final indexes (I>2σ(I))	R_1=0.0510, $wR(F^2)$=0.0798
Final indexes (all data)	R_1=0.0863, $wR(F^2)$=0.0911

Based on the analytical results, it can be proposed that the synthesized compound is calcium paratungstate-B 30-hydrate with the stoichiometric formula $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$. The formation of the paratungstate B anion is likely attributed to the predominance of ion pair formation in the solution, contributing to the stabilization of the $[W_{12}O_{40}(OH)_2]^{10-}$ anion even at an unusual acidity of 1.00 during the synthesis. Additionally, the result of X-ray crystallography indicates that the cation of the ion pair becomes the outer-sphere, and the ion associate itself is not preserved in the synthesized salt.
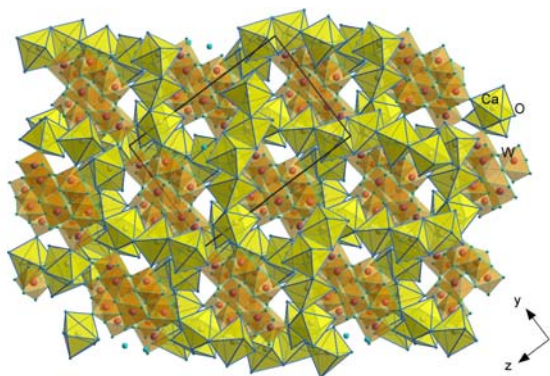

Fig. 7. The numbering scheme for crystallographically independent moiety of the $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$ structure

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Fig. 8. Polyhedral representation of $Ca_5[W_{12}O_{40}(OH)_2]\cdot 30H_2O$ along *x* axis. Color codes: {WO_6}, orange octahedra; {CaO_n}, yellow polyhedra; and O (from uncoordinated H_2O molecules), turquoise balls

Conclusions

Modeling of chemical equilibria in the solutions of sodium orthotungstate under acidic conditions in the presence of calcium cations revealed the stabilization of paratungstate B anions through the formation of ion pairs (associates). Logarithms of thermodynamic constants and standard free Gibbs energies of formation from monomeric ions were calculated for these ion pairs. The synthesis and analysis of calcium-containing paratungstate B $Ca_5[W_{12}O_{40}(OH)_2]\cdot 30H_2O$, isolated from a solution with acidity of 1.00, further confirm the possibility of ion pair formation between calcium cations and the stabilized paratungstate B in the solution.

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МОДЕЛЮВАННЯ РІВНОВАГ У ПІДКИСЛЕНИХ РОЗЧИНАХ НАТРІЙ ОРТОВОЛЬФРАМАТУ ЗА ПРИСУТНОСТІ ІОНІВ КАЛЬЦІЮ(II)

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Методами pH-потенціометрії, математичного моделювання та кондуктометрії вивчено взаємодію в системі $Ca^{2+}-WO_4^{2-}-H^+-H_2O$, початково підкислений до мольного співвідношення (кислотності) $Z=\nu(H^+)/\nu(WO_4^{2-})=1,0$, в інтервалі $Z=0,60-2,00$ за температури $298\pm0,1$ K з фоновим електролітом $NaNO_3$ (іонна сила $I=0,05-0,30$ моль·л$^{-1}$). Методом Ньютона обчислено логарифми концентраційних констант рівноваги, методом Пітцера розраховано раніше невідомі логарифми термодинамічних констант і енергії Гіббса реакцій утворення іонних асоціатів $Ca^{2+},[W_4O_{14}(OH)_2]^{4-}$; $Ca^{2+},[W_6O_{20}(OH)_2]^{6-}$; $Ca^{2+},[W_{12}O_{40}(OH)_2]^{10-}$; $Ca^{2+},H[W_{12}O_{40}(OH)_2]^{9-}$; $Ca^{2+},H_2[W_{12}O_{40}(OH)_2]^{8-}$; $Ca^{2+},H_3[W_{12}O_{40}(OH)_2]^{7-}$; $[W_{12}O_{38}(OH)_2]^{6-}$; $H[W_{12}O_{38}(OH)_2]^{5-}$. Методом кондуктометричного титрування показано утворення частинок зі співвідношенням $Ca^{2+}:[W_{12}O_{40}(OH)_2]^{10-}=1:1$ та $Ca^{2+}:[W_6O_{20}(OH)_2]^{6-}=1:1$ у розчинах. Запропоновано схему взаємних переходів між іонними парами в водному розчині. Із підкисленого розчину Na_2WO_4 ($Z=1,00$) синтезовано кальцій паравольфрамат Б: $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$. Методами ІЧ-БППВВ і КР-спектроскопії підтверджено, що ізополіаніон у складі солі відноситься до структурного типу паравольфрамату Б. Методом рентгеноструктурного аналізу досліджено кристалічну будову $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$: моноклінна сингонія, пр.гр. $P2_1/n$, a=15,3619(4) Å, b=11,7537(3) Å, c=18,1471(5) Å, β=109,2950(10)^0, V=3092,58(14) Å^3, R_1=0,0298, $wR(F^2)$=0,1387.

Ключові слова: координаційні сполуки, математичне моделювання, рівноваги іонних пар, поліоксометалати, термодинаміка розчинів, кальцій, ІЧ-БППВВ та КР-спектроскопія, рентгеноструктурний аналіз.

MODELING OF EQUILIBRIA IN ACIDIFIED SOLUTIONS OF SODIUM ORTHOTUNGSTATE IN THE PRESENCE OF CALCIUM(II) IONS

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The interactions of the $Ca^{2+}-WO_4^{2-}-H^+-H_2O$ system initially acidified to the molar ratio (acidity) $Z=\nu(H^+)/\nu(WO_4^{2-})=1.00$ were studied by the methods of pH-potentiometry, mathematical modeling and conductometry in the interval $Z=0.60-2.00$ at 298 ± 0.1 K with $NaNO_3$ ($I=0.05-0.30$ mol·l^{-1}) as the supporting electrolyte. The logarithms of the equilibrium concentration constants were calculated by the Newton's method, and previously unknown logarithms of the thermodynamic constants and Gibbs energy of the reactions of the formation of ion associates $Ca^{2+},[W_4O_{14}(OH)_2]^{4-}$; $Ca^{2+},[W_6O_{20}(OH)_2]^{6-}$; $Ca^{2+},[W_{12}O_{40}(OH)_2]^{10-}$; $Ca^{2+},H[W_{12}O_{40}(OH)_2]^{9-}$; $Ca^{2+},H_2[W_{12}O_{40}(OH)_2]^{8-}$; $Ca^{2+},H_3[W_{12}O_{40}(OH)_2]^{7-}$; $[W_{12}O_{38}(OH)_2]^{6-}$; and $H[W_{12}O_{38}(OH)_2]^{5-}$ were calculated using the Pitzer method. The formation of particles with a ratio of $Ca^{2+}:[W_{12}O_{40}(OH)_2]^{10-}=1:1$ and $Ca^{2+}:[W_6O_{20}(OH)_2]^{6-}=1:1$ in the solutions was shown by the conductometric titration method. The crystals of calcium paratungstate B $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$ were synthesized from Na_2WO_4 solution acidified to acidity $Z=1.00$. By using ATR-FTIR and Raman spectroscopies, it was shown that the isopolyanion in the composition of the salt belongs to the structural type of paratungstate B. The structure of $Ca_5[W_{12}O_{40}(OH)_2]\cdot30H_2O$ was determined by single crystal X-ray diffraction: monoclinic, $P2_1/n$, a=15.3619(4) Å, b=11.7537(3) Å, c=18.1471(5) Å, β=109.2950(10)^0, V=3092.58(14) Å^3, R_1=0.0298, $wR(F^2)$=0.1387.

Keywords: coordination compound; mathematical modeling; ion pair equilibrium; polyoxometalate; thermodynamics of solutions; calcium; ATR-FTIR and Raman spectroscopy; single crystal X-ray diffraction.

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