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ABOUT INFLUENCE OF TUNGSTEN AND MOLYBDENUM AT EDUCATION HETEROPOLYARSENATES WITH THE MIXED STRUCTURE OF LIGANDS

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The complication of arsenate in the system «molybdate-tungstate-sulfuric acid» has studied. Spectrophotometric method is showed the formation of binary and mixed ternary heteropolyarsenates with varying ratios of ligands. The conditions of formation, composition, size of the initial oxidation potentials and conditional instability constants for unfirmness of complexes are defined. The method of determining micro-concentration of arsenic in the form of binary tungstenarsenate is proposed.

Keywords: molibdoarsenaty, volframoarsenaty, mixed heteropoliarsenaty, spectrophotometry, determination of arsenate

Heteropolycomplexs (HPC) found a wide use for determination of elements - typical complexesformers, such as phosphorus, silicon, arsenic and germanium. Their formation flows in the difficult multicomponent systems and depends on a number of factors: pH environment, processes of hydrolysis and polymerization, spatial coordination of central atom and ligands, presence in solution of ions of extraneous electrolytes. Therefore receipt of new data about conditions formation and properties of double molybdenum- or tungsten-, and also mixed triple heteropolyarsenates, which while are studied not enough, is an actual task for an analysis.

At high-quality and quantitative determination of arsenic (V), as a rule, the highly sensitive reaction of renewal of molybdenumarsenate in a sour environment different repairers are used. A reaction is related to possibility of receipt of connection with intensively blue color, which is characteristic that takes in light in the visible area of spectrum with a maximum of absorption at the wave-length ~830 nm and it is investigated by an accessible photometric method.

However the receipt of the unrecovered form of double arsenatemolybdenum complex (AMC), which appears at heating of mixture of arsenate with a molybdate in a sulfuric environment, is preceded the process of renewal for molybdenumarsenate. A reaction flows in time and characterized by appearance of connection, painted in yellow, with maximal absorption in the visible area of spectrum at lengths of wave ~375-400 nm. Therefore formation of AMC is investigated by a photometric method.

It is set that at co-operating of arsenate with the analogue of molybdenum is tungsten (VI) in a sour environment is formation of other double connection - arsenatetungsten complex (ATC). As opposed to molybdenumarsenate, ATC appears instantly; his solutions are colorless and take in light in the near ultraviolet area of spectrum, with a maximum at the wave-length ~260 nm. A complex is investigated

by less accessible, what photometric variant, but by more exact spectrophotometry method.

Task of investigations are study influence of ligand-substituent on co-operation in the systems «molybdenumarsenate-tungstate» and «tungstatearsenate-molybdate» with the purpose of receipt of mixed heteropolyarsenate, and also investigation of composition, properties and application possibility of heteropolyarsenates for determination of arsenic (V) in his containing objects.

From unrecovered heteropolymolybdates the phosphorus complex (PMC) of composition of PMo_{12} is most well studied [1]. It was necessary to expect that an arsenic (V), being the analogue of phosphorus (V), also forms a double complex, however a it is unsteady and at dissolution grows into connection of composition of $AsMo_9$ [2].

It is set that if the receipt of AMC is realized in presence a tungstate, a reaction is accompanied by formation of triple arsenatemolybdenumtungsten (AMTC) complex.

Registration of absorbency of solutions was conducted by means of photometer at the wave-length of 410 nm, that eliminates absorption of surplus molybdate fully. An area, isochromatic fringes of which are locked, is educed, that testifies to formation in the system not alone, and a few mixed connections. For determination of correlation for components in complexes there are used the photometric variant of methods of satiation and isomolecular carouses. Both methods allowed to get conciliate results and showed education in solution of AMTC for connections of two compositions which can be described by the formulas $[AsMo_{10}W_2O_{40}]^{3-}$ and $[AsMo_9W_3O_{40}]^{3-}$, that corresponds to formation of steady connections of the saturated type of $AsMo_{10}W_2$ and $AsMo_9W_3$ [3].

Data about formation of phosphotungate complex (PTC) of composition of PW_{12} are described in-process [1]. It was of interest to get similar information for arsenic (V) connections. Really, at co-operating of arsenate with a tungstate formation of double ATC is shown, and at adding to ATC of molybdate - triple ATMC. By the methods of satiation and isomolecular cereous, that double AMC answer two connections of AsW_{12} and AsW_{24} , and triple - $AsW_{11}Mo$ and $AsW_{23}Mo$ [4]. Formation of $AsW_{11}Mo$ takes place substitutionally tungsten-ion in $[AsW_{12}O_{40}]^{3-}$ on the ion of molybdate with the receipt $[AsW_{11}MoO_{40}]^{3-}$. All investigational complexes appear at a room temperature in a sulfuric environment with the interval of pH 1.5-2.0 practically instantly.

The spectrum of tungstate was got in the conditions of formation of complexes at pH 2. The spectrums of AsW_{12} and $AsW_{11}Mo$, have like disposition and differ from the spectrum of tungstate. In a spectrum ATC is observed at most at 260 nm, and in the spectrum of triple complex a maximum is smoothed out, in him a ground appears at 240-270 nm. Composition of complexes is defined the methods of satiation, isomolecular carouses and method of Adamovich, formation of connections goes in a sulfuric environment at pH 1.5-2.0.

Reactions of formation of heteropolytungstates are highly sensitive and characterized by the high molar coefficients of redemption (ϵ_{\max} = from 38750 to 75000), therefore exactly heteropolytungstates present exceptional interest for an

analysis at determination of arsenic (V) microconcentrations in objects, containing arsenates.

Quantitative determination of durability of heteropolyarsenates is performed with the use of method of change of equilibrium [3]. Applying the known chart of method, it was succeeded to find out influence of surplus of tungstate on plenitude of formation of ATC and ATMC, to define the degree of influence of n for bodied m times of tungstate-polyion $[W_m]^n$, to calculate the relative constants of unfirmness of AsW_{12} and $AsW_{11}Mo$. The numeral values of constants of unfirmness of double ATC and triple ATMC correspond to the sizes $1.14 \cdot 10^{-14}$ and $1.25 \cdot 10^{-18}$, that testifies to education in solution of steady and durable complexes. Measuring of initial oxidizing potentials of E_{init} specifies on a large capacity for renewal more rich by molybdenum (VI) of complexes: the increase of part for molybdenum (VI) strengthens oxidizing properties, and increase of stake of tungsten (VI) - weakens.

Likeness of properties of PTC and ATC testifies that at application for HPC of arsenic for an analysis complexes must be divided. Its division succeeded to be carried out by an extraction method by means of ethyl-acetate, which does not take in light in the ultraviolet spectrum area and preferentially extracts from solution of heteropolycomplexes only ATC, that allows to determine arsenic in his containing objects by a highly sensitive spectrophotometry method.

Conclusions. The conditions of two mixed triple complexes ($AsMo_{10}W_2$ and $AsMo_9W_3$), got at co-operating of molybdenumarsenate with a tungstate are defined is found. The conditions of two double complexes of AsW_{12} and AsW_{24} and two mixed triple connections of $AsW_{11}Mo$ and $AsW_{23}Mo$, got at co-operating of tungstenarsenate with a molybdate are defined. Possibility of the analytical use of tungstenarsenate composition of AsW_{12} is shown for determination of arsenic (V) microconcentrations by a spectrophotometry method.

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