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Abstract

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STUDY OF AQUEOUS SOLUTIONS OF SODIUM PARATUNGSTATE

The mechanism of the reactions that occur upon acidification of solutions of normal tungstates has still been studied comparatively little. In the pH region 8—6, paratungstates are formed—the most important representatives of the class of aquopolycompounds. One of us (^{1}) has suggested that, for this process, an essential role is played by the simultaneous presence of hydroxonium ions, tungstate ions, and molecules of tungstic acid, interacting in solution through the formation of hydrogen bonds.

Water plays an important constitutional role in the compound obtained (^{2}—^{4}).

We have studied the properties of solutions of sodium paratungstate as a function of the conditions of their preparation, the heating temperature, and the storage time. For this purpose, the methods of dialysis, polarography, chromatography, and light absorption were used.

The molecular weights of the ions present in 0.01 M solutions of tungstates were determined by dialysis through a cellophane membrane at 25°. The molecular weight of the hydrated ion of normal tungstate, $WO_4^{2-} \cdot 2H_2O$ ($M = 284$), was taken as the unit of comparison. A freshly prepared solution of crystalline paratungstate, $Na_{10}W_{12}O_{41} \cdot 28H_2O$, was characterized by a molecular weight of about 3000, which closely corresponds to the ion $W_{12}O_{41}^{10-} \cdot 28H_2O$ ($M = 3368$). After boiling the solution, the molecular weight of the anions decreases to 1500—1600, i.e., practically by a factor of two (Table 1).

Table 1

Dialysis coefficients and molecular weights of certain tungstate ions in solution

Compound	Characteristic of the solution	pH	Dialysis coefficient, λ	Molecular weight, M
$Na_2WO_4 \cdot 2H_2O$		8.0	0.236	284
$Na_{10}W_{12}O_{41} \cdot 28H_2O$	Freshly prepared	6.1	0.072	3000
$Na_{10}W_{12}O_{41} \cdot 28H_2O$	Heated for 8 h at 100°	6.2	0.098	1600

Compound	Characteristic of the solution	pH	Dialysis coefficient, λ	Molecular weight, M
$Na_2W_4O_{13} \cdot 10H_2O$		3.6	0.033	14000

The phenomenon taking place may be expressed by the equation

$$Na_{10}W_{12}O_{41} \cdot 28H_2O \rightleftarrows 2Na_5[H_3O \cdot W_6O_{21}] \cdot 12.5H_2O.$$

Evaporation leads to the formation of crystalline paratungstate, which in solution again exhibits a doubled molecular weight.

When a solution of Na_2WO_4 is acidified with nitric acid, the composition of the anions obtained depends on the pH and the duration of the reactions (Table 2). Only in the ob-

in the pH range 7.0–6.6 hexatungstate ions are formed immediately. At pH 6.3–6.1 ions with molecular weight 5000–10000 appear at first. The latter, after 10 days, decreases to 1500. Apparently, here

Table 2

Change in dialysis coefficients and molecular weights of anions on standing of acidified Na_2WO_4 solutions

pH	Time of standing of the solutions, days	Dialysis coefficients: immediately after acidification of the solution	Dialysis coefficients: after standing of the solution	Molecular weight, M: immediately after acidification of the solution	Molecular weight, M: after standing of the solution
6.6	19	0.186	0.219	1500	1300
6.3	19	0.102	0.174	5000	1600
6.1	14	0.072	0.180	9900	1500
5.8	6	0.029	0.062	55000	14000
5.6	11	0.016	0.058	120000	14000

high-molecular-weight ions of the type $[H_3O \cdot W_6O_{21}]^{5-} \cdot nH_2WO_4 \cdot aq$ are formed, which over time undergo disaggregation, splitting off lighter hexatungstate ions. This phenomenon is revealed still more sharply upon further acidification. If the pH of the solution is brought to 5.8–5.6, the molecular weight of the anions formed initially reaches the enormous value 55000–120000 and, after standing for

Fig. 1. Polarography in a background of 12 N HCl; 1 –$2.0 \cdot 10^{-3}$ mol/l $Na_2WO_4 \cdot 2H_2O$; 2 –$1.7 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$; 3 –$1.67 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$ (solution was heated to boiling for 8 h); 4 –$4.18 \cdot 10^{-4}$ mol/l $Na_2W_4O_{13} \cdot 10H_2O$. Sensitivity 1/100

Figure 1: Fig. 1. Polarography in a background of 12 N HCl; 1 –$2.0 \cdot 10^{-3}$ mol/l $Na_2WO_4 \cdot 2H_2O$; 2 –$1.7 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$; 3 –$1.67 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$ (solution was heated to boiling for 8 h); 4 –$4.18 \cdot 10^{-4}$ mol/l $Na_2W_4O_{13} \cdot 10H_2O$. Sensitivity 1/100

10 days, decreases only to 14000. The same molecular weight was shown under the conditions of our experiments by sodium metatungstate, $Na_2W_4O_{13} \cdot 10H_2O$, which corresponds to an ion polymerized approximately 12-fold, $[H_3O(HWO_4)_3 \cdot (H_2WO_4)(H_2O)_6]^{2-}$ or $[W_4O_{13} \cdot 10H_2O]^{2-}$.

Fig. 1. Polarography in a background of 12 N HCl;
1 –$2.0 \cdot 10^{-3}$ mol/l $Na_2WO_4 \cdot 2H_2O$;
2 –$1.7 \cdot 10^{-4}$ mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$;
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4 –$4.18 \cdot 10^{-4}$ mol/l $Na_2W_4O_{13} \cdot 10H_2O$. Sensitivity 1/100.

The transformations detected in tungstate solutions were also confirmed by the polarographic method using the Heyrovský micropolarograph. The capillary had the characteristic $m^{2/3}t^{1/6} = 3.083$ mg$^{2/3}$ sec$^{-1/2}$. The mercury drop time was 2.5-2.6 sec.

The results of the polarographic investigations are presented in Table 3 and in Fig. 1. It should be noted that in the strongly acidic medium in which tungstates are usually subjected to polarography, it is not the original tungstate ions that are present, but colloidal tungstic acid or metatungstic acid. In this respect Na_2WO_4 and a freshly prepared solution of paratungstate behave identically (half-wave potentials: –0.46 V), thus forming in an acidic medium one and the same product. A paratungstate solution that has been boiled already gives another polarogram with two waves ($E'_{1/2} = -0.26$ V, $E''_{1/2} = -0.44$ V), more similar to the polarograms of sodium metatungstate and metatungstic acid. Obviously, the hexatungstate ion in its structure is related

to metatungstate and, perhaps, is its structural unit. The indicated transformation of paratungstate is recorded polarographically starting at a temperature of 35° and is completed at 80°. At pH 5.0–5.6 (acetate buffer) and against a background of K_2SO_4, the same differences are observed in the behavior of freshly prepared and heated solutions of paratungstate. It has long been known that tungstate compounds that are more acidic (with respect to WO_3 content) are more readily reduced to the 5-valent state. In this way one can explain the lower initial reduction potential (–0.26 V) of metatungstic acid (experiments 3, 4, Table 3) compared with ordinary tungstic acid (experiments 1, 2, Table 3).

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

The latter, however,

Fig. 2. Absorption spectra: **1** –2.5 · 10^{-2} mol/l $Na_2WO_4 \cdot 2H_2O$; **2** –freshly prepared solution 2.5 · 10^{-5} mol/l $Na_{10}W_{12}O_{41} \cdot 28H_2O$; **3** –after 4 days; **4** –after 10 days; **5** –after 15 days; **6** –after 18 days; **7** –after 30 days; **8** –after 1 year; **9** –2.5 · 10^{-5} mol/l $Na_2W_4O_{13} \cdot 10H_2O$

Fig. 3. Change in the absorption spectra of sodium paratungstate as a function of the boiling time of the solution: **1** –1 hour; **2** –2 hours; **3** –3 hours; **4** –4 hours; **5** –6 hours; **6** –8 hours; **7** –16 hours.

apparently appears during polarography, as a partial decomposition product, also in solutions of metatungstic acid, giving a wave with a half-wave potential of −0.44 or −0.40 V. The presence of several waves on polarograms recorded in acetate buffer and against a background of K_2SO_4 is evidently connected with the presence of several equilibrium forms of tungstate anions, reduced ($W^{6+} \rightarrow W^{5+}$) at different half-wave potentials. For a neutral or weakly acidic medium, the occurrence of successive stages of deeper reduction of one and the same anion is unlikely.

The kinetics of the transformation of paratungstate ions into hexatungstate ions can also be followed with the aid of absorption spectra. The studies were carried out in the ultraviolet region (220–290 mμ). Freshly prepared solutions of sodium paratungstate give a curve that falls steeply downward with increasing wavelength (Fig. 2). On standing of the solutions, the fall of the curve in the 245–260 mμ region slows down; a plateau appears here, and then a maximum at a wavelength of 256–257 mμ. The indicated maximum slowly increases with time and reaches a constant value one month after preparation of the solution. Subsequent observations over the course of a year showed the absence of further changes in the optical properties of the solutions.

Analogous phenomena, but faster, occur when paratungstate solutions are heated to boiling (Fig. 3). After 3 hours there appears

maximum in the wavelength region 256-257 mμ. Its height reaches a constant value after 10-16 hours of boiling the solution. The coincidence of the light-absorption maximum for solutions that had stood for a long time or had been heated makes it possible to assert that in both cases one and the same process occurs–the conversion of paratungstate ions into hexatungstate ions, to which the indicated maximum corresponds. It is interesting

Table 3

Polarographic study of tungstate solutions

Experiment No.	Compound	Solution concentration, mol/l	Characteristic of the solution	Half-wave potentials on various backgrounds, V	Half-wave potentials on various backgrounds, V	Half-wave potentials on various backgrounds, V
				12 N HCl	CH_3COOH – CH_3COONa, pH 4.6–5.6	1 N K_2SO_4
1	$Na_2WO_4 \cdot 2H_2O$	10^{-3}	Freshly prepared	−0.46		
2	$Na_{10}W_{12}O_{41} \cdot 28H_2O$	10^{-4}	Freshly prepared	−0.46	−0.46 −0.92	−0.44
3	$Na_{10}W_{12}O_{41} \cdot 28H_2O$	10^{-4}	Heated 8 hours to boiling	−0.26 −0.44	−0.40 −0.90	−0.44 −0.84 −1.04
4	$Na_2W_4O_{13} \cdot 10H_2O$	10^{-4}		−0.26 −0.44	−0.40 −0.90	−0.44 −0.84 −1.04
5	$H_2W_4O_{13} \cdot 9H_2O$	10^{-4}		−0.26 −0.40	–	−0.45 −0.72 −0.98

to note that in this case as well a similarity between hexatungstate and metatungstate is observed: their absorption spectra are very close (see Fig. 2).

Acidified Na_2WO_4 solutions, immediately after preparation, give absorption spectra in the form of curves that fall steeply downward with increasing wavelength. With time a plateau appears on the curves, and then a maximum. However, this process proceeds more slowly than in solutions of sodium paratungstate.

Finally, it should be noted that freshly prepared and boiled solutions of paratungstate behave somewhat differently with respect to anion exchangers. Sorption of hexatungstate ions occurs to a noticeably smaller extent, especially at low concentrations (Fig. 4).

Fig. 4. Absorption of paratungstate by EDE-10 anionite: 1—freshly prepared solution $Na_{10}W_{12}O_{41} \cdot 28H_2O$, 2—solution heated for 16 hours to boiling.

Fig. 4. Absorption of paratungstate by EDE-10 anionite: 1—freshly prepared solution $Na_{10}W_{12}O_{41} \cdot 28H_2O$, 2—solution heated for 16 hours to boiling.

Figure 3: Fig. 4. Absorption of paratungstate by EDE-10 anionite: 1—freshly prepared solution $Na_{10}W_{12}O_{41} \cdot 28H_2O$, 2—solution heated for 16 hours to boiling.

The similarity of the studied properties of hexatungstate and metatungstate deserves great attention. It is possible that the transition of paratungstate into hexatungstate on boiling the solution represents an important intermediate stage in the formation of metatungstates. On the other hand, the closest products of hydrolysis of metatungstates should probably be hexatungstates.

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Note: Figure translations are in progress. See original paper for figures.