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L. I. YURANOVA, L. N. KOMISSAROVA, and V. E. PLYUSHCHEV

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Abstract

Full Text

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L. I. YURANOVA, L. N. KOMISSAROVA, and V. E. PLYUSHCHEV

NEW DATA ON THE BEHAVIOR OF ZIRCONIUM AND HAFNIUM OXYNITRATES IN AQUEOUS SOLUTIONS AND SOME ORGANIC SOLVENTS

(Presented by Academician V. I. Spitsyn, April 25, 1961)

At the present time the existence of two stable oxynitrates of zirconium and hafnium has been proven—dihydrates $MeO(NO_3)_2 \cdot 2H_2O$ and hexahydrates $MeO(NO_3)_2 \cdot 6H_2O$. The conditions of synthesis and some properties of these compounds were described earlier ([1,2]). The existence of zirconium and hafnium nitrates of another composition requires verification. The literature contains data on the chemistry of nitric-acid solutions of zirconium. However, almost all investigations in this area carried out in recent years have been performed with microquantities of zirconium and with very dilute solutions. Such are the works of V. I. Paramonova ([3]), McDonald ([4]), and others ([5,6]). In practice, however, often—especially in the study of extraction methods for separating zirconium and hafnium—one has to deal with fairly concentrated solutions. In this connection, it is of interest to clarify the behavior of zirconium and hafnium oxynitrates when they dissolve in water and to obtain certain characteristics of nitric-acid solutions in which zirconium and hafnium are present in macroconcentrations.

In the present communication are given the results of a study of the dependence of pH, specific electrical conductivity, density, and viscosity of solutions of zirconium and hafnium oxynitrates on the concentration of the latter in aqueous solutions, as well as data from the study of their solubility in some organic solvents.

Experimental Part

The starting substances used were $ZrO(NO_3)_2 \cdot 2H_2O$, $ZrO(NO_3)_2 \cdot 6H_2O$, and $HfO(NO_3)_2 \cdot 2H_2O$, $HfO(NO_3)_2 \cdot 6H_2O$. The zirconium and hafnium dioxides used for the synthesis of the oxynitrates contained, respectively, 0.03% HfO_2 and 2% ZrO_2. The concentration of nitric-acid solutions of zirconium (hafnium) was varied within the range from 0.001 to 1 mole/liter, calculated as MeO_2. The results

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Fig. 1. Dependence of pH (1) and specific electrical conductivity (2) on the concentration of zirconium oxynitrate solutions at 20°

Figure 1: Fig. 1. Dependence of pH (1) and specific electrical conductivity (2) on the concentration of zirconium oxynitrate solutions at 20°

Fig. 2. Dependence of pH (1) and specific electrical conductivity (2) on the concentration of hafnium oxynitrate solutions at 20°

Figure 2: Fig. 2. Dependence of pH (1) and specific electrical conductivity (2) on the concentration of hafnium oxynitrate solutions at 20°

Table 1

Values of pH and specific electrical conductivity of nitric-acid solutions of zirconium and hafnium at $20 \pm 0.1^\circ$

Concentration of solutions as MeO_2, M/l	Nitric-acid solutions of zirconium pH	Nitric-acid solutions of zirconium $\chi \cdot 10^3$, $ohm^{-1} \cdot cm^{-1}$	Nitric-acid solutions of hafnium pH	Nitric-acid solutions of hafnium $\chi \cdot 10^3$, $ohm^{-1} \cdot cm^{-1}$	Concentration of solutions as MeO_2, M/l	Nitric-acid solutions of zirconium pH	Nitric-acid solutions of zirconium $\chi \cdot 10^3$, $ohm^{-1} \cdot cm^{-1}$	Nitric-acid solutions of hafnium pH	Nitric-acid solutions of hafnium $\chi \cdot 10^3$, $ohm^{-1} \cdot cm^{-1}$
1.0	0.26	92.49	0.31	56.48	0.05	1.37	20.18	1.43	14.00
0.5	0.39	82.21	0.51	55.49	0.01	2.11	3.90	2.25	3.65
0.2	0.78	56.19	0.87	42.69	0.005	2.27	2.36	2.38	1.86
0.1	1.19	34.68	1.25	21.00	0.001	2.80	0.60	2.87	0.47

measurements of pH and specific electrical conductivity of zirconium and hafnium oxynitrate solutions, presented in Table 1 and in Figs. 1 and 2, show that as the concentration increases, the pH decreases and the specific electrical conductivity increases. This is explained by the fact that dissolution of zirconium and hafnium oxynitrates in water is accompanied by hydrolysis, which proceeds rather intensively: in all cases low pH values were obtained. With increasing concentration, the pH of the corresponding solutions decreases, although the degree of hydrolysis is reduced. The latter is confirmed by calculating the number of hydrogen ions per

Fig. 1. Dependence of pH (**1**) and specific electrical conductivity (**2**) on the concentration of zirconium oxynitrate solutions at 20°.

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Fig. 2. Dependence of pH (**1**) and specific electrical conductivity (**2**) on the concentration of hafnium oxynitrate solutions at 20°.

each metal ion, for solutions of different concentrations. It turns out that at high concentrations this quantity is considerably smaller than in the case of low concentrations. The decrease in pH, however, is determined only by an increase in the absolute amount of dissolved salts. The increase in the concentration of hydrogen ions also causes an increase in electrical conductivity.

Table 2

Change in the pH of zirconium and hafnium oxynitrate solutions with time at 20 ± 0.1°

Concentration of solution, mol/liter as MeO_2	pH of zirconium oxynitrate solutions, freshly prepared	pH of zirconium oxynitrate solutions, after 14 days	pH of zirconium oxynitrate solutions, after 8 months	pH of hafnium oxynitrate solutions, freshly prepared	pH of hafnium oxynitrate solutions, after 14 days	pH of hafnium oxynitrate solutions, after 8 months	Concentration of solution, mol/liter as MeO_2	pH of zirconium oxynitrate solutions, freshly prepared	pH of zirconium oxynitrate solutions, after 14 days	pH of zirconium oxynitrate solutions, after 8 months	pH of hafnium oxynitrate solutions, freshly prepared	pH of hafnium oxynitrate solutions, after 14 days	pH of hafnium oxynitrate solutions, after 8 months
1.0	0.26	0.25	0.25	0.31	0.30	0.30	0.05	1.37	1.27	1.27	1.43	1.35	1.35
0.5	0.39	0.39	0.38	0.51	0.48	0.50	0.01	2.11	2.08	2.10	2.25	2.15	2.16
0.2	0.78	0.69	0.70	0.87	0.85	0.86	0.005	2.27	2.15	2.14	2.38	2.20	2.22
0.1	1.19	1.04	1.05	1.25	1.15	1.14	0.001	2.80	2.74	2.74	2.87	2.78	2.77

In order to determine the influence of time on the hydrolysis process, pH measurements of the solutions were carried out 2 weeks and 8 months after their preparation (Table 2). To determine the influence of temperature on the hydrolysis process, freshly prepared solutions of selected concentrations were kept for one hour at a specified temperature, after which pH measurements were made immediately (Table 3).

The hydrolysis process of zirconium and hafnium oxynitrates in aqueous solutions proceeds with time. The equilibrium state is established 2 weeks after preparation of the solutions. An increase in temperature also intensifies the hydrolysis process. Comparison of the results on hydrolysis,

Table 3

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Change in pH of nitric-acid solutions of zirconium and hafnium as a function of temperature

Solution concentration in terms of MeO_2, mol/l	pH of nitric-acid zirconium solutions, 20°	pH of nitric-acid zirconium solutions, 40°	pH of nitric-acid zirconium solutions, 100°	pH of nitric-acid hafnium solutions, 20°	pH of nitric-acid hafnium solutions, 40°	pH of nitric-acid hafnium solutions, 100°
0.5	0.39	0.40	0.05	0.51	0.45	0.30
0.05	1.37	1.31	1.05	1.43	1.45	1.25
0.005	2.27	2.16	1.84	2.38	2.25	2.14

obtained for nitric-acid solutions of zirconium and hafnium, as was to be expected, indicates the somewhat more basic character of hafnium oxynitrates in comparison with the corresponding zirconium compounds.

Fig. 3. Dependence of density (1) and viscosity (2) on the concentration of nitric-acid zirconium solutions at 20°

Fig. 4. Dependence of density (1) and viscosity (2) on the concentration of nitric-acid hafnium solutions at 20°

The results of measuring the density and viscosity of nitric-acid solutions of zirconium and hafnium are presented in Table 4 and in Figs. 3 and 4. With increasing concentration of zirconium and hafnium, the values of the density and viscosity of the solutions increase almost linearly.

Table 4

Values of density (d) and viscosity (η) of nitric-acid solutions of zirconium and hafnium at 20 ± 0.1°

Solution concentration in terms of MeO_2, mol/l	Nitric-acid zirconium solutions, d	Nitric-acid zirconium solutions, η	Nitric-acid hafnium solutions, d	Nitric-acid hafnium solutions, η	Solution concentration in terms of MeO_2, mol/l	Nitric-acid zirconium solutions, d	Nitric-acid zirconium solutions, η	Nitric-acid hafnium solutions, d	Nitric-acid hafnium solutions, η
1.0	1.185	1.533	1.278	1.744	0.05	1.006	1.046	1.011	1.042

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Solution concentration in terms of MeO_2, mol/l	Nitric-acid zirconium solutions, d	Nitric-acid zirconium solutions, η	Nitric-acid hafnium solutions, d	Nitric-acid hafnium solutions, η	Solution concentration in terms of MeO_2, mol/l	Nitric-acid zirconium solutions, d	Nitric-acid zirconium solutions, η	Nitric-acid hafnium solutions, d	Nitric-acid hafnium solutions, η
0.5	1.092	1.283	1.139	1.303	0.01	1.001	1.042	1.005	1.030
0.2	1.035	1.092	1.067	1.127	0.005	0.998	1.037	1.001	1.022
0.1	1.018	1.066	1.029	1.067	0.001	0.994	1.014	0.999	1.021

To study the solubility of zirconium and hafnium oxynitrates ($MeO(NO_3)_2 \cdot 2H_2O$ and $MeO(NO_3)_2 \cdot 6H_2O$) in organic solvents, we selected 15 organic compounds of various classes. Before use, the solvents were additionally purified by distillation, and the alcohols and ketones were absolutized.

The solubility was determined at 20 and 30° in ordinary glass vessels with a stirrer. Mercury was used for the aqueous solutions. In co-

a certain amount of the corresponding oxynitrate and 30–50 ml of solvent were loaded into the vessel. The vessel prepared in this way was placed in a water thermostat adjusted to the specified temperature. The temperature fluctuation was $±$0.1°. It was found experimentally that equilibrium in all cases was established after 7 days. The liquid and solid phases were separated using a cotton filter. The samples were analyzed for MeO_2 content. The results obtained are presented in Table 5.

Table 5

Solubility data for $MeO(NO_3)_2 \cdot 2H_2O$ and $MeO(NO_3)_2 \cdot 6H_2O$ in organic solvents (wt. % MeO_2) at 20 and 30°

Solvent	$ZrO(NO_3)_2 \cdot 2H_2O$, 20°	$ZrO(NO_3)_2 \cdot 2H_2O$, 30°	$ZrO(NO_3)_2 \cdot 6H_2O$, 20°	$ZrO(NO_3)_2 \cdot 6H_2O$, 30°	$HfO(NO_3)_2 \cdot 2H_2O$, 20°	$HfO(NO_3)_2 \cdot 2H_2O$, 30°	$HfO(NO_3)_2 \cdot 6H_2O$, 20°	$HfO(NO_3)_2 \cdot 6H_2O$, 30°
Methyl alcohol	19.39	20.13	17.32	19.12	18.21	–	17.99	18.47
Ethyl alcohol	18.03	19.20	15.30	17.01	11.95	13.51	10.98	11.65

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Solvent	$ZrO(NO_3)_2 \cdot 2H_2O$, 20°	$ZrO(NO_3)_2 \cdot 2H_2O$, 30°	$ZrO(NO_3)_2 \cdot 6H_2O$, 20°	$ZrO(NO_3)_2 \cdot 6H_2O$, 30°	$HfO(NO_3)_2 \cdot 2H_2O$, 20°	$HfO(NO_3)_2 \cdot 2H_2O$, 30°	$HfO(NO_3)_2 \cdot 6H_2O$, 20°	$HfO(NO_3)_2 \cdot 6H_2O$, 30°
n-Propyl alcohol	3.52	5.62	0.35	0.37	1.96	5.87	–	–
iso-Butyl alcohol	0.26	0.50	–	–	0.20	–	–	–
iso-Propyl alcohol	0.07	0.10	n.s.	n.s.	n.s.	–	n.s.	n.s.
iso-Butyl alcohol	n.s.*	0.16	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Acetone	20.65	–	12.30	–	18.90	–	4.78	–
Ethyl acetate	10.35	14.07	7.10	7.73	8.48	11.90	3.68	8.58
Butyl acetate	n.s.	0.19	n.s.	0.19	n.s.	n.s.	n.s.	n.s.

* n.s. –solubility less than 0.001 wt.%.

Polar organic solvents, in particular alcohols and acetone, have the best dissolving power. It is interesting to note that, with an increase in the number of carbon atoms in the molecules of alcohols of the normal series, the solubility of zirconium and hafnium oxynitrates decreases. It also decreases on going to alcohols with a branched chain of carbon atoms. This type of change in the solubility of inorganic salts in alcohols, although not general, is observed often. It was previously noted, for example, in the study of the solubility of alkali-metal chlorides in aliphatic alcohols ([7]). In addition, the dihydrates of zirconium and hafnium oxynitrates have a somewhat higher solubility than the hexahydrates, and for all compounds it increases with increasing temperature. We have experimentally established that the zirconium and hafnium compounds studied do not dissolve in acetophenone, dibutyl and benzyl ethers, chloroform, carbon tetrachloride, or dichloroethane.

Thus, it may be concluded that, in low-polarity and nonpolar organic solvents, zirconium and hafnium oxynitrates, as a rule, dissolve only to a slight extent or

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do not dissolve at all. Other conditions being equal, zirconium oxynitrates are characterized by higher solubility in organic substances than the corresponding hafnium compounds.

Moscow Institute of Fine Chemical Technology
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