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Abstract

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CHEMISTRY

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ON CERTAIN REGULARITIES IN THE COMPLEX FORMATION OF PENTAVALENT ACTINIDE ELEMENTS

(Presented by Academician I. I. Chernyaev, 29 X 1962)

In recent years, in studies of complex formation by metal ions in aqueous solutions using various physicochemical methods, numerous quantitative data have been accumulated on the stability of the compounds formed in them. In a number of cases certain regularities of complex formation have been noted, for example, that of actinide elements with acid anions. Thus, for the first time I. Hindman (1,2), on the basis of qualitative information, expressed the idea that the arrangement of anions in order of decreasing tendency to interact with hydrogen ions corresponds to the order of decreasing tendency to form complexes with plutonium(IV). Somewhat later A. D. Gelman and co-workers, and the authors of the present communication (3–13), using the instability constants obtained by them for complexes of actinide-element ions in different valence states with acid anions, drew a number of conclusions about the influence of the charge Z, the ionic radius r, and the structure of the central atom and the addend on their complex-forming properties.

Quite recently new data were obtained on the composition and instability constants of complexes formed by pentavalent protactinium, neptunium, and plutonium with the anions of a number of acids; therefore it seems of interest to consider the question of certain regularities in their complex formation.

It is generally accepted that pentavalent actinides have the least tendency toward complex formation in comparison with other element ions. However, one of us, together with Yu. A. Zolotov (14), expressed the view that this tendency is not as small as might be expected for large singly charged ions. In our opinion, this is confirmed by the data we have obtained. Below, Table 1 gives the composition and instability constants of the complexes of Pa(V), Np(V), and Pu(V) with the anions of certain acids, found by the ion-exchange method. These data, which are undoubtedly of great importance for the chemistry of the corresponding elements, make it possible to draw certain conclusions about the nature of the change in the complex-forming properties of pentavalent actinide ions with increasing atomic number of the element.

As is evident from comparison of the constants, the ions of pentavalent actinides —Pa, Np, and Pu—with the indicated anions form complexes of one and the same composition and of approximately equal stability; i.e., in their tendency toward complex formation they differ very little from one another.

It is interesting to note that the nonmonotonicity, observed earlier (15), in the change of the chemical properties of pentavalent actinide ions with increasing atomic number of the element does not occur in the present case. Apparently, the influence of the ionic potential φ has little effect on the stability of their complexes with one and the same acid anion.

Table 1

Instability constants K_n of complex ions of Pa(V), Np(V), and Pu(V)*

No.	Acid	Composition of complex ion on M:A**	K_n for Pa(V), $\mu = 0.25$	K_n for Pa(V), $\mu = 0$***	Mean effective charge, $\bar{Z}$	Literature	Composition of complex ion (M = Np and Pu)	μ	K_n for Np(V), $\mu \neq 0$	K_n for Np(V), $\mu = 0$	Literature	K_n for Pu(V), $\mu = 0.05$	K_n for Pu(V), $\mu = 0$	Literature
1	Lactic	1 : 1	$5.7 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	1.3	(12)	MO_2Lact^0	0.05	$2.0 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	****	–	–	–
1	Lactic	1 : 1	$5.7 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	1.3	(12)	»	0.20	$2.8 \cdot 10^{-2}$	–	****	–	–	–
1	Lactic	1 : 1	$5.7 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	1.3	(12)	$MO_2(Lact)_2^-$	0.05	$3.3 \cdot 10^{-3}$	$2.6 \cdot 10^{-3}$	****	–	–	–
1	Lactic	1 : 1	$5.7 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	1.3	(12)	»	0.20	$5.9 \cdot 10^{-3}$	–	****	–	–	–
2	α-Oxyisobutyric	1 : 2	$3.3 \cdot 10^{-4}$	$3.3 \cdot 10^{-5}$	1.9	(13)								
2	α-Oxyisobutyric	1 : 3	$1.0 \cdot 10^{-7}$	–	–	(13)								
3	Mandelic	1 : 1	$1.1 \cdot 10^{-3}$	$1.83 \cdot 10^{-4}$	1.0	(13)								
4	Malic	1 : 1	$1.2 \cdot 10^{-3}$		4.5	(11)								

No.	Acid	Composition of complex ion on M:A**	K_n for Pa(V), $\mu = 0.25$	K_n for Pa(V), $\mu = 0$***	Mean effective charge, $\bar{Z}$	Literature	Composition of complex ion (M = Np and Pu)	μ	K_n for Np(V), $\mu \neq 0$	K_n for Np(V), $\mu = 0$	Literature	K_n for Pu(V), $\mu = 0.05$	K_n for Pu(V), $\mu = 0$	Literature
4	Malic	1 : 2	$1.9 \cdot 10^{-5}$	–	3.5	(11)								
5	Tartaric	1 : 1	$4.6 \cdot 10^{-3}$	$7.7 \cdot 10^{-3}$	1.5		MO_2tart^{-}	0.05	$4.8 \cdot 10^{-3}$	$2.2 \cdot 10^{-3}$***	(18)			
5	Tartaric	1 : 2	$4.8 \cdot 10^{-5}$	–			$MO_2(tart)_2^{3-}$	0.05	$5.0 \cdot 10^{-5}$	–	(18)			
6	Trioxyglutaric	1 : 1	$1.1 \cdot 10^{-3}$	$3.0 \cdot 10^{-4}$	4	(11)								
6	Trioxyglutaric	1 : 2	$1.3 \cdot 10^{-8}$	–	10									
7	Oxalic	1 : 1	$2.8 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$	10	(11)	$MO_2C_2O_4^{-}$	0.05	$9.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-4}$	(14)	$3.0 \cdot 10^{-5}$	–	(3)
7	Oxalic	1 : 2	$1.2 \cdot 10^{-6}$	–	4		$MO_2(C_2O_4)_2^{3-}$	0.05	$4.1 \cdot 10^{-8}$	$4.4 \cdot 10^{-8}$	(14)	$4.2 \cdot 10^{-8}$	–	(3)
8	Citric	1 : 1	$2.2 \cdot 10^{-4}$	–	8.7	(11)	MO_2Cit^{2-}	0.05	$2.1 \cdot 10^{-4}$	$6.5 \cdot 10^{-5}$***	(18)			
8	Citric	1 : 2	$1.2 \cdot 10^{-6}$	–	2.0									
8	Citric	1 : 3	$1.6 \cdot 10^{-9}$	–										
9	Aconitic	1 : 1	$6.6 \cdot 10^{-3}$	–	7	(13)								
10	Ethylenediaminetetraacetic	1 : 1	$6.5 \cdot 10^{-8}$	10^{-9}	–	(11)	MO_2Y^{3-}	0.05	$2.0 \cdot 10^{-10}$	$1.7 \cdot 10^{-11}$	(14)	$6.8 \cdot 10^{-11}$	$1.3 \cdot 10^{-11}$	(7)
10	Ethylenediaminetetraacetic	1 : 2	$1.1 \cdot 10^{-12}$	–	–		MO_2Y^{3-}	0.05	$2.0 \cdot 10^{-10}$	$4.2 \cdot 10^{-11}$	(14)	$6.8 \cdot 10^{-11}$	$1.3 \cdot 10^{-11}$	(7)
11	Acetic	–	–	–	–		MO_2Ac^{0}	1.5	$8.4 \cdot 10^{-2}$	$4.7 \cdot 10^{-2}$***	(10)			
11	Acetic	–	–	–	–		$MO_2(Ac)_2^{-}$	1.5	$2.8 \cdot 10^{-2}$	$1.6 \cdot 10^{-2}$***	(10)			
12	Carbonic	–	–	–	–		MO_2HCO_3	0.15	$6.7 \cdot 10^{-3}$	$3.7 \cdot 10^{-3}$	****			
13	Phosphoric	–	–	–	–		MO_2HPO_4	0.20	$1.4 \cdot 10^{-3}$	$4.2 \cdot 10^{-4}$	(10)			

Figure 1. Dependence of the instability constants of ethylenediaminetetraacetate (1), citrate (2), oxalate (3), lactate (4), and tartrate (5) complexes of pentavalent actinides on the atomic number of the element, at $\mu = 0$

Figure 1: Figure 1. Dependence of the instability constants of ethylenediaminetetraacetate (1), citrate (2), oxalate (3), lactate (4), and tartrate (5) complexes of pentavalent actinides on the atomic number of the element, at $\mu = 0$

* The composition and instability constants of acetate complexes were determined by Yu. I. Gryazn and G. I. Simakin.
** By the composition of the complex is meant only the found ratio M:A, where M is a hydrolyzed and partially polymerized, at the corresponding pH, form of Pa(V); A is an addend, which may be in the form of an undissociated or undissociated part of the acid.
*** The thermodynamic values of the constants were calculated by us with the aid of the Davies equation (17).
**** A. I. Moskvin, M. P. Mefod' eva, A. D. Gel' man (unpublished).

The addends, in terms of relative tendency toward complex formation with pentavalent actinides, are arranged (see Table 1) in the following series

$$\gamma^{4-} > \mathrm{Cit}^{3-} > \mathrm{HPO}_4^{2-} > \mathrm{tart}^{2-} > \mathrm{Ac}^{-} \simeq \mathrm{Lact}^{-}.$$

Taking into account data on the stability of Pa(V) complexes with hydroxy acids (11), this series may be represented in a more generalized form: EDTA > citric > oxalic > phosphoric > trihydroxyglutaric > α-hydroxyisobutyric > tartaric > malic > mandelic > acetic $\gg$ lactic. Although quantitative data on the stability of Np(V) and Pu(V) complexes with such hydroxy acids as α-hydroxyisobutyric, mandelic, malic, and trihydroxyglutaric are still lacking, the fact that the instability constants of their complexes with other acids coincide (see Table 1) gives grounds to regard the above series as also valid for these elements. A correspondence is observed between the order of decreasing tendency of Me(V) toward complex formation with acid anions and the increase in the degree of dissociation of the corresponding acids, as was also observed for other cations of transuranium elements of the type M^{3+}, M^{4+}, and MO_2^{2+} (3–10). It should be noted, however, that the position of the $C_2O_4^{2-}$ ions in the given series does not correspond to the value of the degree of dissociation of oxalic acid; that is, a difference is observed in its complex-forming properties as compared with other addends. In our opinion, a more or less satisfactory explanation of this anomaly can be given on the basis of considering the structure of the oxalate ion and its behavior in the present case as a hydroxy acid.

Fig. 1. Dependence of the instability constants of ethylenediaminetetraacetate (1), citrate (2), oxalate (3), lactate (4), and tartrate (5) complexes of pentavalent actinides on the atomic number of the element, at $\mu = 0$.

From a comparison (3) of the instability constants of complexes formed by different plutonium ions with one and the same addend, one may conclude that in the pentavalent state they have the least tendency toward complex formation.

It should be noted that, as yet, information on the composition and stability of complexes of pentavalent uranium with the anions of the indicated acids is completely lacking. Proceeding from the analogy indicated above in the complex-forming properties of Pa(V), Np(V), and Pu(V), and from the available quantitative data (see Table 1), conclusions may also be drawn regarding the composition and stability of complexes of pentavalent uranium with a number of acids.

Interpolation on the curves of the dependence of pK_{H} on the atomic number of the element (Z) (see Fig. 1) makes it possible to estimate approximately the values of the instability constants, for example, of the oxalate, ethylenediaminetetraacetate, tartrate, lactate, and citrate complexes of U(V) with a Me:addend ratio of $1:1$. They were found to be, respectively, pK_{H}: 3.2; 9.7; 2.6; and 4.0.

As is known, various physical and chemical properties of the actinides are invoked to substantiate their position in the Periodic System of D. I. Mendeleev.

One of the most convincing chemical proofs of the position of the actinides is provided by data on their ion-exchange separation using various eluents. The arrangement of the elution curves indicates a striking chemical similarity between the rare-earth and actinide elements. There are numerous data on the influence of various physicochemical factors on the process of ion-

exchange separation of actinide and lanthanide elements in the trivalent state.

In the present communication we have presented data indicating a similarity in the ion-exchange behavior of protactinium, neptunium, and plutonium in the pentavalent state.

We express our gratitude to Prof. A. D. Gel' man for valuable advice and guidance in this work.

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