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Sructural Parameters of the Nearest Surrounding of Tri- and Tetravalent Actinide Ions in Aqueous Solutions of Actinide Salts

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Abstract—Published data are generalized on different research methods for structural characterization of the nearest surrounding of trivalent and tetravalent actinide ions in aqueous solutions of their salts under standard conditions. The structural parameters such as coordination numbers, interparticle distances, the parameters of the second coordination sphere, and the types of ionic association are discussed. The quantitative characteristics of hydrated complexes of poorly known trivalent actinide ions are determined on the basis of comparative analysis with lanthanide ions.

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Data on the Knowledge of physical and chemical properties of actinide ions in aqueous solutions are necessary for the nuclear fuel industry. This is connected in particular with the problem of utilization of nuclear waste. Actinides attract considerable interest of researchers also as a special group of elements with unusual and very complex properties. Nevertheless, the number of studies concerning the structure of actinide solutions is relatively small, and some basic characteristics of the nearest surrounding of these elements have not yet been determined. This is due to a considerable experimental difficulties, not only because of the radioactivity of some of the elements, caused also by several other factors, like oxidative instability of light actinides and short lifetime of heavy cations. To date there are scanty information generalizing structural parameters of the nearest surrounding of actinide ions in aqueous solutions [1]. The present study is aimed at determining such short-range characteristics of these cations in aqueous solutions as coordination number, interparticle distances, the number of water molecules in the second coordination sphere, and the types of ionic associates. The diffusion coefficients and individual thermodynamic properties of some tri- and tetravalent actinide ions in aqueous solutions have been reported in the studies [2–4]. These works also discuss the hypothesis on the similarity of structural and dynamic properties of trivalent lanthanide and actinide ions of similar radii. Later on, in other studies the analogy of transport and structural properties of the 4f and 5f trivalent ions was confirmed [5, 6]. While analyzing the characteristics of the nearest surrounding of trivalent ions, we adhere to this concept. It is convenient to start the consideration of a series of these ions with the best studied Cm^{3+}cation rather than according to the order of the appearance of the elements.

Structure of the nearest surrounding of Cm^{3+} ion. The configuration of the outer electron shell of Cm^{3+} ion is $5f^7$, and it is an actinide analogous to Gd^{3+} ($4f^7$) among the lanthanides. Therefore, according to [7], we can expect that this cation may be boundary at the change of coordination number in the series of actinide ions. The curium ion is a strong source of α-particles. The Cm^{3+} ions are produced in nuclear reactors and cause a number of radiological and thermal problems in the removal of nuclear waste. Therefore, the structure of its hydrated complexes attracts increasing attention of researchers. A 0.01 M aqueous solution of curium chloride has been studied by EXAFS method in the presence of 0.2 M HCl (low content of chloride ions) and in the presence of 14 M LiCl (high content of chloride ions) [8]. In the first case it was found that the coordination number of Cm^{3+} ion was equal to 10.2, and the distance to the coordination sphere is 0.245 nm. In the case of high concentration of chloride ions the Cm^{3+} ion forms an inner-sphere complex with the chloride ions with the simultaneous loss of water molecules. The average number of anions in the complex $N = 2.4$ and the distance Cm^{3+}–Cl^- $R = 0.276$ nm.

From the data on the fluorescence lifetime the Cm^{3+} ion coordination number in 0.1–1.0 M aqueous solutions of perchloric acid was calculated: It was found to equal 9.2±0.5. Whereas in solutions of nitric, sulfuric and phosphoric acids the coordination number decreases with increasing acid concentration (from 10.1 to 8.7 in HNO_3, from 7.8 to 5.0 in H_2SO_4 and from 7.2 to 5 in H_3PO_4) due, as believe Kimura et al., to the complexation in solution [9, 10]. Based on the analysis of fluorescence lifetime the Cm^{3+} ion coordination number in aqueous solutions containing hydrochloric and nitric acid (0.1 M) was determined to be equal to nine [11]. Also a decrease was noted in the coordination number with increasing concentration of acid. Using the same method the same value of the coordination number was confirmed in a subsequent paper of the same team [12]. The calculated Cm^{3+}–OH_2 distance in the $[Cm (H_2O)_6]^{3+}$ cluster is 0.241 nm [13]. Unfortunately, in this work the clusters with the number of water molecules corresponding to that experimentally found were not investigated. By the method of laser fluorescence spectroscopy it was revealed that in solutions of curium perchlorate an equilibrium existed between the hydrated curium ions $[Cm(H_2O)_9]^{3+}$ and $[Cm(H_2O)_8]^{3+}$, the content of the latter in solution was about 10% [14]. The structural parameters of hydration of the curium ion were studied by the technique of quantum mechanics and molecular dynamics [15]. It was found that the coordination number of the discussed ion is nine, and the distance to the coordinated water molecules is 0.247–0.248 nm. The results of calculations show that the second coordination sphere of the cation may contain 21 water molecule at a distance of 0.465 nm. On the basis of quantum-chemical calculations and the molecular dynamics method it was found that the coordination number of the Cm^{3+} ion can be either eight or nine [16]. The first coordination sphere of the ion is located at an average distance of 0.255 nm. The second sphere includes on an average sixteen water molecules. By a combination of the high energy X-ray scattering and EXAFS study of curium perchlorate solutions (0.5 M Cm^{3+}) in 1 M aqueous perchloric acid [17] it was determined that the first coordination sphere of the Cm^{3+} ion consisted of 8.8±0.3 water molecules at a distance of 0.248±0.001 nm, and the second sphere included about 13±4 water molecules at a distance of 0.465±0.010 nm. In the work carried out using EXAFS spectroscopy it was revealed that Cm^{3+} in a dilute aqueous solution of curium trifluoromethanesulfonate coordinated nine water molecules that were arranged around it at an average distance of 0.2477 nm forming a three-cap trigonal prism [18]. By laser fluorescence spectroscopy it was proven that in aqueous solutions of curium chloride with a high content of chloride ions (up to 20 mol kg^{-1}) inner-sphere complexes formed [19]. Fanghanel et al. note that when the chloride ion concentration is less than 3 mol kg^{-1} such complexes are formed in solution in amount not exceeding 5%.

The above data show that the predominant coordination number of the Cm^{3+} ion is either eight or nine, with preference given to nine. The mean value of the distance to the coordinated water molecules in the first sphere is 0.247 nm. We believe that these findings confirm the similarity of the structural features of considered ion with similar-sized lanthanide ion Sm^{3+}, the characteristics of the nearest surrounding of which in aqueous solution are given in [20]. If so, then the Cm^{3+} ion is likely to form the first sphere of the nine water molecules arranged around it in the form of three-cap trigonal prism, as shown in [18]. The coordination number 8 obtained in several papers may be due to the complexity of the experimental fixation of all three water molecules located at greater distances. Following this logic, it may be assumed that the second coordination sphere of the discussed ion (as in the case of Sm^{3+} ion) in aqueous solutions with no solvent deficit is at a distance of 0.456 nm and includes eighteen water molecules. These parameters of the second sphere are different from those obtained in [15, 17]. It should be noted, however, that computational methods often produce excessive characteristics of quantitative parameters of the second coordination spheres of ions.

For predicting the ion association on the basis of comparison with lanthanide ions the following may be assumed. This cation does not form contact ion pairs with chloride and perchlorate ions. In aqueous solutions, curium nitrate can form both intra- and outer-sphere associates. In the sulfate solution the predominantly contact ion pairs are likely to be formed.

Since we adopted the concept of similarity between the structural characteristics of actinide ions and the

Table 1. Structural parameters of the hydrated ions of lanthanide complexes and related actinide ions in aqueous solutions of their salts

Lanthanide ion	Coordination number	Ln^{3+}–OH_2 distance, nm	Second coordination sphere	Ln^{3+}–OH_2(II) distance, nm	Actinide ion	An^{3+}–OH_2 distance, nm	Coordination number
			18	0.469	Ac^{3+}	0.260	9
			18	0.467	Th^{3+}	0.258	9
La^{3+}	6+3	0.252 0.265	18	0.465	Pa^{3+}	0.256	9
Ce^{3+}	6+3	0.250 0.263	18	0.465	U^{3+}	0.254	9
Pr^{3+}	6+3	0.248 0.260	18	0.463	Np^{3+}	0.252	9
Nd^{3+}	6+3	0.246 0.258	18	0.460	Pu^{3+}	0.250	9
Pm^{3+}	6+3	0.244 0.256	18	0.458	Am^{3+}	0.248	9
Sm^{3+}	6+3	0.242 0.254	18	0.456	Cm^{3+}	0.246	9
Eu^{3+}	8.8	0.244	18	0.454	Bk^{3+}	0.244	8.8
Gd^{3+}	8.7	0.242	18	0.453	Cf^{3+}	0.242	8.7
Tb^{3+}	8.6	0.239	16–18	0.452	Es^{3+}	0.240	8.6
Dy^{3+}	8.5	0.238	14–16	0.451	Fm^{3+}	0.238	8.5
Ho^{3+}	8.4	0.236	14–16	0.450	Md^{3+}	0.236	8.4
Er^{3+}	8.3	0.235	14–16	0.449	No^{3+}	0.235	8.3
Tm^{3+}	8.2	0.234	14–16	0.448	Lr^{3+}	0.234	8.2
Yb^{3+}	8.1	0.233	14–16	0.446			
Lu^{3+}	8.0	0.232	14–16	0.445			

lanthanide ions of similar size, then we suggest to compile the structural parameters of the nearest surrounding of the actinide ions directly from the corresponding lanthanide ions. Table 1 lists the structural characteristics of both series of the cations. It includes the parameters of the hydrated complexes of actinide ions corresponding to those of lanthanide ions given in [20]. Further, not following the order of the elements in the Periodical System, it is logical to consider the cations described in the literature.

Structure of the nearest surrounding of Np^{3+} ion. Neptunium is an artificial element produced in nuclear reactors. Study of its properties is necessary for optimization of nuclear fuel reprocessing. Neptunium can have five different oxidation states, from three to seven. Table 1 shows that, in accordance with our assumption, Np^{3+} ion probably coordinates nine water molecules at an average distance of 0.252 nm, which are located around it in the form of three-cap trigonal prism. The second sphere consisting of about eighteen water molecules must be located at a distance of 0.463 nm. Ion association can be manifested in the same way as by the curium ion. In this case we have only one publication to verify our assumptions. The results of combining EXAFS, density functional theory, and geometric modeling lead to the conclusion that the Np^{3+} ion coordination number is either eight or nine, with the distance to the coordinated molecules of 0.248±0.002 nm [21]. As can be seen, the experimental value of distance is close to the tabulated one, and the coordination number is expected to be equal to nine.

Structure of the nearest surrounding of Pu^{3+} ion. In [22] a theoretical analysis of XANES was carried out, and the hydrated Pu^{3+} ion was considered as a three-cap trigonal pyramid with the Pu^{3+}–OH_2 distance 0.248 nm. In the crystal hydrate $[Pu(H_2O)_9][CF_3SO_3]_3$ the Pu^{3+} ion forms three-cap trigonal prism with the distance to the six neighboring water molecules equal to 0.2476 nm, and to three more distant 0.2574 nm, as obtained by the single-crystal XRD [23]. In the same paper it was found that the coordination number of this cation in acidified aqueous solution of plutonium(III) trifluoromethanesulfonate is nine. Matonic et al. point out the similarity between the structural parameters of the coordination spheres of ions Pu^{3+} and Nd^{3+}, instead of the Sm^{3+}, as follows from their location in the Periodic System of elements. The structure of dilute aqueous solutions of plutonium(III) chloride (the content of Pu^{3+} 0.004 M) as a function of the chloride ion concentration (from 0.001 to 12.3 M) was investigated by XAFS in [8, 24]. At low concentrations of chloride ions the cation coordination number obtained was equal to 9.2 and the distance to the coordinated water molecules, 0.251 nm. Increasing the anion concentration leads to a decrease in the number of water molecules in the close environment of the Pu^{3+} cation to 5.2. The distance to water molecules remained almost unchanged (0.250 nm). The effect of reduced coordination number was ascribed by Allen et al. as a consequence of the strong decrease in water activity at a high ionic strength. It is strange that this effect was not observed in the lanthanide ions in the same studies. The formation of inner-sphere ion pairs was not detected up to the concentrations of Cl^- 14 M. The structural parameters of the coordination sphere of plutonium(III) ion have also been studied by density functional theory. It was established that the coordination number of the ion is either eight or nine, and the distance to the water molecules is in the range of 0.251–0.255 nm [25]. By EXAFS, the distance to 8–9 water molecules of the first coordination sphere is equal to 0.249 nm [26] or 0.248 nm [27]. The Pu^{3+}–OH_2 distance is less than the Np^{3+}–OH_2 distance, which is obviously due to the effect of compression in the series of actinide ions from Ac^{3+} to Lr^{3+}, similar to that of the lanthanide ions. The confirmations of this effect have been repeatedly published in the literature [28].

As is evident from these results, the distance from the cation to water molecules coordinated in the first sphere is similar to the hypothetical one presented in Table 1. The coordination number is found to be either eight or nine. We suggest that the light actinide ions have coordination number equal to nine. In the literature there is no information on the second coordination sphere of the ion. It is hypothetically possible to take its features the same as those of Nd^{3+} ion in the series of lanthanide ions (Table 1).

Structure of the nearest surrounding of Am^{3+}. The Am^{3+} coordination number in an aqueous solution of americium chloride was found equal to nine by spectroscopic method [29]. Analysis of fluorescence lifetime of Am^{3+} in a very dilute aqueous perchlorate solution also resulted in coordination number equal to nine [30]. 0.01 M aqueous solution of americium chloride was studied by EXAFS at both high and low content of chloride ions [8]. At the high content, the coordination number of Am^{3+} is found to be equal to 10.3, and the distance to the coordination sphere, to 0.248 nm. In this case the Am^{3+} ion forms an inner-sphere complex with the chloride ions, with simultaneous loss of the water molecules from the coordination sphere. The average number of anions in the complex $N = 1.8$, and the Am^{3+}–Cl distance $R = 0.281$ nm. More recent work using EXAFS spectroscopy revealed that in a dilute aqueous solution of americium trifluoromethanesulfonate the Am^{3+} ion is coordinated to nine water molecules arranged around it in the form of three-cap trigonal prism [18]. With the same method it was determined that the coordination number of this cation was either eight or nine, and the distance to the coordinated water molecules was 0.247–0.249 nm [31]. For this ion a similarity is also observed for the hypothetical parameters of the first coordination sphere listed in Table 1 with those experimentally obtained. We assume that the ion association of this ion will appear similarly to the described above for the curium ion. An additional information on this issue is that this cation forms only outer-sphere ion pairs with thiocyanate ions [32].

Structure of the nearest surrounding of the Bk^{3+} ion. We managed to find only one work devoted to the study of structure of the hydrated complex of berkelium(III) ion. By EXAFS, the coordination number of Bk^{3+} ion in aqueous solution acidified with 1 M $HClO_4$ was found to be equal to 9±1, and the distance to the coordinated water molecules, 0.243±0.002 nm [33]. The Bk^{3+} ion corresponds to the Eu^{3+} in the series of lanthanide ions. In solutions of Eu^{3+} besides the nine-coordinated hydrated complexes hydrated complexes with eight water molecules appear. Therefore, we assume that similar effect should also occur in the solutions of berkelium salts. Hence, the coordination number of this cation which reflects an average over the entire system will take a fractional value of 8.8. The logic of reasoning about quantitative description of the second coordination sphere and the manifestation of ion association is the same as was used above.

Structure of the nearest surrounding of Cf^{3+} ion. The Cf^{3+} ion is by far the heaviest of the studied triply charged actinide ions. By EXAFS, the coordination number of Cf^{3+} ion in aqueous solution acidified with 1 M HCl was found to equal 8.5±1.5, and the distance to the coordinated water molecules, 0.242±0.002 nm [34]. Later, by combined EXAFS and Monte Carlo methods the following parameters were found of the first coordination sphere of this cation [35]. According to the results of the EXAFS method, the coordination numbers 8 and 9 are equally probable. Only on the basis of a comparison with calculations using the

Monte Carlo method Galbis et al. prefer the smaller value of coordination number. Perhaps, the fractional value of the coordination number 8.7 in Table 1 just reflects this uncertainty. The distance to the coordinated water molecules was found to equal 0.243 nm. As can be seen, this distance is almost equal to the tabulated hypothetical value for this ion.

Thus, the available experimental results support the hypothesis of similarity of hydrated complexes of lanthanide and actinide ions of the same size. As shown above, this suggestion works in terms of quantitative description of the first coordination sphere. It allows us to predict the structural characteristics of the nearest surrounding of the remaining actinide ions (Table 1). It should be noted that, since Ac^{3+} and Th^{3+} ions do not have analogs of similar size in a series of lanthanide ions, the distance to the coordination spheres of these ions was determined by interpolation of the almost linear dependence of the distances vs. the atomic number of actinide ions. As for coordination number, we may only assume that the coordination number of each light actinide ion is nine. The number of water molecules in the second coordination sphere is also estimated approximately. As another proof, we note that the distance to the nearest environment of water molecules given in the Table 1 is in good agreement with those found using the density functional theory for all the ions in the hydrated complexes of actinides $[An^{III}(OH_2)_{h-1}OH_2]^{3+}$ ($h = 8, 9$) [36] . Parameters of the second coordination sphere of actinide ions are very poorly studied. We assume that, like at their formation in aqueous solutions without a deficit of the solvent, of primary importance is the ion charge and size, and structural characteristics of actinide ions are similar to those of the lanthanide ions (Table 1). Ion association for all actinide ions is assumed similar to that described for the Cm^{3+} ion.

Now we analyze the structural parameters of the nearest surrounding of tetravalent ions.

Structure of the nearest surrounding of Th^{4+} ion. The interest in the structural aspects of hydrated complexes of Th^{4+} ion from a practical point of view is due to the fact that it occurs naturally in ground water, and is a product of the decay of uranium and neptunium series. From the standpoint of basic science, the thorium(IV) ion hydration is interesting because of its high charge at a relatively small size. In recent years the interest of researchers to these problems increased [37, 38]. In the early X-ray study of 2 M aqueous solution of thorium(IV) nitrate the cation coordination number was found equal to 12±1 and the distance to the coordinated water molecules, 0.251 nm [39]. In addition, the presence of the second coordination sphere was determined at a distance of 0.450 nm. According to Johansson there is a third coordination sphere, at a distance of 0.650 nm. In subsequent work, also carried out using XRD, the coordination number of Th^{4+} ion in 2.3 M aqueous solution of thorium perchlorate (acidified with perchloric acid to suppress hydrolysis) was found equal to eleven with the distance to the coordinated water molecules of 0.250 nm [40]. Aqueous solutions of the thorium(IV) perchlorate (concentration 0.9–2.5 M), chloride (1.85 M) and nitrate (0.99–2.52 M) were studied [41], and it was found that in the solutions of thorium perchlorate and chloride the cation coordination number equals 8.0±0.5, with the distance to the water molecules 0.248±0.001 nm. In dilute solutions the presence was revealed of the second coordination sphere of the cation consisting of approximately 20 water molecules. The inner-sphere complexes were not found. On the contrary, in solutions of thorium chloride the inner-sphere complexes define the system structure and increase the total coordination number of the cation. They do not replace water molecules, but are built into the coordination sphere. In the thorium nitrate solutions complexes are formed where the nitrate ion interacts with the cation as a bidentate ligand. Bond lengths are similar to those found in the corresponding hydrates: Th^{4+}–O (NO_3^-) = 0.260 nm, Th^{4+}–O (H_2O) = 0.249 nm. The total coordination number of the discussed ion is more than eight, and in 1.0 M solution it is approaching ten. Johansson et al. conclude that the coordination number of Th^{4+} ion depends on the counterion. So, in the presence of perchlorate ion, the coordination number of the cation remains the same at different concentrations, in chloride solution it slightly increased due to the presence of chloride ions in the coordination sphere, and in solutions of nitrates the coordination number increases significantly. Note that the complexation of Th^{4+} and NO_3^- ions in aqueous solutions was revealed in the study of ultrasound absorption [42].

In a study using EXAFS of dilute aqueous solutions of thorium perchlorate and fluoride (of the concentration 0.003–0.3 M) acidified with 1.5 M $HClO_4$ [43] it was found that the first coordination sphere of the cation contained 10.8±0.5 water molecules located at a distance of 0.245±0.001 nm. The introduction of fluoride ions into the system leads to significant changes in the coordination sphere of the cation. Fluoride ions enter in the nearest surrounding of the cation. The distribution of distances in the first coordination sphere becomes unsymmetrical, which is due to the presence of the two sets of anions. The distance from the cation to the fluoride ion Th^{4+}–F is 0.214 nm, while to water molecules, Th^{4+}–O (H_2O) = 0.249 nm. But overall coordination number of the cation equal to 10±1 remains unchanged. These results were confirmed by another study, performed by the method of molecular dynamics, which established that the coordination number of Th^{4+} ion is close to ten, and the distance to the coordinated water molecules was 0.245±0.001 nm [44]. The combination of the methods of quantum mechanics and molecular dynamics revealed that the coordination number of this cation was nine with the distances of Th–O_I 0.254±0.001 nm and Th–H_I 0.322±0.001 nm [45]. Yang et al. note that due to the significant polarization of the first coordination sphere, strong hydrogen bonds are formed with the second sphere, consisting of 18.09 water molecules with distances Th–O_{II} 0.475 nm and Th–H_{II} 0.535 nm. Later the same group of authors found by the method of molecular dynamics that the coordination number of this ion in dilute solutions was equal to 9–10 [46]. The second coordination sphere is formed, that consists of about 20 water molecules. At high concentrations of chloride ions (5 M) the water molecules are replaced in the second coordination sphere by the anions. In a subsequent paper, Tsushima et al. by *ab initio* calculations found that the distances from Th^{4+} ion to water molecules in the second coordination sphere Th–O_{II} were different [38]. Each of the three water molecules of the first sphere located in the equatorial plane was bound with two water molecules in the second coordination sphere, which results in the Th–O_{II} distance 0.470 nm. Each of the six axial water molecules of the first sphere was connected with two water molecules in the second coordination sphere resulting in different Th–O_{II} distances, 0.445 and 0.500 nm. In another study by EXAFS it was determined that at 5.5×10^{-2} M aqueous solution of thorium containing 1.5 M $HClO_4$ the cation coordination number was 11±1, and the distance to the water molecules was 0.245±0.001 nm [47]. However, in today study by high energy XRD (synchrotron radiation) of aqueous solution of thorium(IV) bromide the coordination number of this ion was determined to be equal to ten, with the distance to the coordinated water molecules of 0.246±0.001 nm [48]. Note a slight decrease in the distance in the solution compared with the corresponding crystal hydrate (0.2498 nm). In addition, the existence was found of the second and third coordination spheres of the cation at the distances 0.460 and 0.660 nm, respectively. There was no evidence of formation of contact ion pairs of the cation with bromide ion. By EXAFS, the following parameters of the first coordination sphere of Th^{4+} ion in an 0.05 M aqueous solution of thorium perchlorate strongly acidified were found: coordination number 9.8, R = 0.244 nm [49]. In addition, it was found that three water molecules are located in the space between the first and second coordination sphere at a distance of 0.369 nm. In the same work it was shown that in thorium sulfate solutions both monodentate and bidentate complexes are formed, the number of the latter increases with increasing concentration. In a more recent study by EXAFS and XRD it was found that Th^{4+} ion in aqueous solutions of perchlorate coordinated nine water molecules at a distance of 0.245±0.001 nm. The second coordination sphere of the ion is formed, consisting of 12 water molecules (R = 0.455 nm) in 1.6 M solution and of 18 molecules (R = 0.466 nm) in 0.54 M solution [50]. Torapava et al. suggest that the coordination number of all actinide ions (both tri- and tetravalent) in water solutions is equal to nine. In addition, they note that while the distance to six water molecules of the first coordination sphere of trivalent cations differs significantly from the distance to three more remote, the tetravalent cations form a more regular structure due to a stronger electrostatic interaction. Using molecular dynamics it was determined that this ion has a well-structured first coordination sphere, which includes 8 to 9 water molecules at a distance of 0.245 nm. The cation also forms the second coordination sphere of 17–18 water molecules at a distance of 0.475 nm [51]. By processing the experimental XANES spectra with *ab initio* calculations it was found that Th^{4+} coordinates in aqueous solutions with nine water molecules arranged around it in the form of four-cap trigonal prism [52].

As seen from the considered material, in the most modern studies the coordination number obtained for this ion was between nine and ten (coordination numbers 11 and 12 were obtained mainly in the early X-ray studies). Perhaps this is due to the presence in these systems of both nine- and ten-coordinated thorium(IV) ions. In addition, the found openwork structure of the first coordination sphere can also lead

Table 2. Structural parameters of hydrated complexes of the four-charged actinide ions in aqueous solutions of their salts

Actinide ion	Coordination number	An^{4+}–OH_2 distance, nm	Second coordination sphere	An^{4+}–OH_2(II) distance, nm
Th^{4+}	9–10	0.248	20	0.462
U^{4+}	9–10	0.242	19–20	0.455
Np^{4+}	8–9	0.240	19	0.450
Pu^{4+}	8–9	0.239	18	0.450

to ambiguity in the determination of coordination number. We include both values in the summary Table 2 assuming them equally probable. As to the distances to the first sphere, most studies led to very consistent results, namely, 0.245 nm. In addition, it is safe to conclude that the cation forms a second coordination sphere. Due to the high ionic charge the number of molecules in it can be relatively large. In the above studies the number of solvent molecules in the second sphere was estimated at the range of 18 to 20, at the distance 0.460–0.475 nm. We assume that on the average twenty molecules are in the second coordination sphere of Th^{4+} ion in a solution with no deficit of the solvent. Due to the higher ionic charge of Th^{4+} than Th^{3+}, the distance to the second sphere should be slightly shorter than for the latter (R_{II} = 0.467 nm). Therefore, we assume that the average distance of 0.462 nm will correctly reflect the actual short-range order around the cations in the solution. It is also obvious that for the cation the ionic association is typical. Polyatomic oxygen-containing anions may be coordinated to the cation as a monodentate or bidentate ones.

Structure of the nearest surrounding the U^{4+} ion. The U^{4+} ion is one among the few four-charged ions remaining stable in acidified aqueous solution. In the early X-ray study of 2 M aqueous solution of uranium perchlorate it was found that the cation coordination number was eight [53]. Coordinated water molecules are located at a distance of 0.243 nm from the U^{4+} ion. Also the existence of the second coordination shell was established at an average distance of 0.440 nm, which, according to the opinion of Pocev and Johansson, includes both water molecules and the oxygen atoms of perchlorate ions. The U^{4+}–Cl distance is found to equal 0.570 nm. Dilute aqueous solutions of uranium perchlorate and fluoride (concentration 0.003–0.3 M) acidified with 1.5 M solution of $HClO_4$ were investigated by EXAFS [43]. It was found that the first coordination sphere of the cation included 10.8±0.5 water molecules located at a distance of 0.242± 0.001 nm. The introduction of the fluoride ions leads to significant changes in the coordination sphere of the cation. Distribution of distances becomes unsymmetrical because of the existence of two sets of the distances: between the cation and the fluoride ion U^{4+}–F 0.210 nm and the water molecule U^{4+}–O (H_2O) 0.245 nm. In addition, fluoride ions enter the inner sphere of the U^{4+} ion, but the overall coordination number of the cation remains unchanged, namely 10±1. Later by the molecular dynamics calculation the value of coordination number of U^{4+} ion equal to ten was confirmed, and the distance to the coordinated molecules was found to equal 0.242±0.001 nm [44]. However, calculations using density functional theory led to the coordination number of U^{4+} ion equal to nine [54]. The 0.01 M aqueous solutions of uranium(IV) with various concentrations of chloride ions (0, 3, 6, and 9 M) were investigated by EXAFS [55]. In the absence of chloride ions the cation was found to coordinate nine water molecules at a distance of 0.241±0.002 nm. The total coordination number (N_{Cl} + N_O) was reduced from nine to eight with an increase in the concentration of the Cl^- ions. The number of chloride ions in the coordination sphere of the cation increased from 0.3 to 2.7, and the distance to them was taken as constant, equal to 0.271±0.002 nm. By the same method, the following parameters of the first coordination sphere of the ion U^{4+} in 0.01 M aqueous solution of uranium perchlorate with a medium strongly acidified were revealed: the coordination number 8.7 and R = 0.241 nm [49]. In addition, it was found that three water molecules are located between the first and second coordination spheres at a distance of 0.347 nm. In the same work it was shown that in solutions of uranium sulfate both monodentate and bidentate complexes were formed. Number of the last increases in the system with increasing concentration. In the modern study by the method of molecular dynamics for systems containing one U^{4+} ion per 499 H_2O molecules, the ion U^{4+} has three coordination spheres [56]. The first sphere consists of nine water molecules at a distance of 0.245 nm. The second sphere consists of 19±2 molecules of the solvent and is located at a distance of 0.480 nm from the cation. The number of water molecules in the third sphere is 44, and the distance to them is 0.680 nm. As noted above, the molecular dynamics method often overestimates the distance to the second coordination sphere. By a combination of UV-visible, infrared, and X-ray absorption spectroscopy, as well as by calculations using density functional theory 0.04 M aqueous solutions of U^{4+} acidified with 1 M $HClO_4$ and HNO_3 of the concentration 1.3–9.0 M were examined [57]. It was found that in the uranium perchlorate solution the cation forms the first coordination sphere of 9 or 10 water molecules located at a distance of 0.240 nm. In solutions of uranium nitrate, the water molecules of the coordination sphere of the cation are replaced by oxygen atoms of the nitrate ion resulting in the formation of bidentate complexes with the NO_3^- ion. Number of the anions in the inner sphere of the uranium ion increases from 1.4 to 4.7, and the distance U^{4+}–N in associates, from 0.294 to 0.299 nm with increasing concentration of nitric acid. By *ab initio* calculations it was shown that in aqueous solutions nine water molecules are arranged around the ion U^{4+} in the form of three-cap trigonal prism [52].

Based on the above material we can conclude that the first coordination sphere of the considered cation in aqueous solutions of its salts is composed of nine or ten molecules of water and is located at an average distance of 0.242 nm. The second coordination sphere is also formed, consisting of about nineteen or twenty water molecules. Distance to them should be less than that for Th^{4+} ion, due to reduction of the size of the ion, and less than the same distance for the ion U^{3+}, due to the increase in the charge. We assume that the average distance from the cation is 0.455 nm. Perhaps the third coordination sphere is also formed, but to judge on its quantitative parameters is still too early. The cation can form ion pairs of both contact and noncontact types with the counterions.

Structure of the nearest surrounding of Np^{4+} ion. The structure of aqueous solutions of neptunium(IV) chloride as a function of the concentration of chloride ions was investigated by XAFS [24]. At low concentrations of chloride ions the coordination number of cations was found to equal 11.2, the distance to the coordinated water molecules 0.240 nm. Increasing the anions concentration leads to the formation of contact ion pairs, which, in turn, results in a decrease of the number of water molecules in the nearest surroundings of the cation and in increase in the distance. At the chloride ion concentration 10^{-14} M their number in the cation coordination sphere is equal to two, and the distance to them 0.261 nm. The method of XAFS shows that in the aqueous solution containing 0.05 M Np^{4+}, 0.1 M HNO_3, and 2 M H_2SO_4 the nearest surrounding of Np^{4+} consists of 11 oxygen atoms at a distance of 0.239 nm [58]. The second coordination sphere includes two sulfur atoms at a distance of 0.307 nm. This distance, in our opinion, corresponds to the bidentate coordination of sulfate ion to ion Np^{4+}. A study of association of the Np^{4+} ion with sulfate ions in aqueous solutions of 0.05 M Np^{4+}, containing from 0 to 3.0 M $(NH_4)_2SO_4$ by EXAFS and density functional theory showed that the system includes both mono- and bidentate coordinated sulfate ions [59]. The following set of distances was obtained: Np^{4+}–OH_2 = 0.239 nm, Np^{4+}–S_{mono} = 0.379±0.001 nm, Np^{4+}–S_{bident} = 0.307±0.001 nm. The number of interactions vary with the concentration of sulfate ions: for Np^{4+}–OH_2 from 9.5 to 8.9, for Np^{4+}–S_{mono} from 0 to 1.4, and for Np^{4+}–S_{bident} from 0 to 3.3. In addition, Hennig et al. note that in a series of Th^{4+}– U^{4+}– Np^{4+} the monodentate coordination of the sulfate ion decreases, while the bidentate increases. The results of combined methods EXAFS, density-functional theory, and geometric modeling lead to the conclusion that coordination number of the Np^{4+} ion is either eight or nine with the distance to the coordinated molecules 0.237±0.002 nm [21]. Calculations using density functional theory are consistent with the existence of eight or nine water molecules in the first coordination sphere of the Np^{4+} ion [54]. It was revealed by EXAFS that the Np^{4+} ion in 1 M aqueous $HClO_4$ coordinated ten water molecules at a distance of 0.240 nm [60]. In the solution of neptunium(IV) nitrate the water molecules of the first coordination sphere of the cation are gradually replaced by the coordinated bidentate nitrate ions. In a modern research carried out by treatment of the experimental XANES spectra by *ab initio* calculations it was found that the Np^{4+} ion was coordinated in aqueous solutions with nine water molecules arranged around it in the form of four-cap trigonal prism [52].

We suggest that the structural parameters of hydration of ions U^{4+} and Np^{4+} are similar, so Table 2 includes the coordination number of this ion from recent works. We also suggest that the distance to the first coordination sphere determined in [60] reflects the real parameter most accurately. The Np^{4+} ion should form also the second coordination sphere consisting of about nineteen water molecules located at an average distance of 0.450 nm. The cation can form ion pairs with counterions.

Structure of the nearest surrounding of Pu^{4+} ion. In [22] a theoretical analysis was performed of the results of XANES. The hydrated Pu^{4+} ion is considered as a cube with equal distances Pu^{4+}–OH_2 = 0.239 nm. The plutonium complexes in aqueous solutions of nitric acid were studied by the EXAFS method [61]. When the concentration of nitric acid increases, water molecules in the coordination sphere of the cation are gradually replaced by the nitrate ions. Number of oxygen atoms in the coordination sphere of the ion Pu^{4+} is 11–12. The distance to the oxygen atoms of nitrate ions in this case is equal to 0.249 nm, while to the oxygen atoms of water molecules, 0.238 nm. In more recent studies performed by the same method the distance to 8–9 water molecules of the first sphere was found equal to 0.239 nm [26, 27].

We assume that the coordination number of Pu^{4+} ion should not be higher than that of Np^{4+} ion, and therefore estimate it being in the range 8–9. We suggest that in [27] the average distance to the first coordination shell is estimated more accurately than in other studies. It is safe to assume that the discussed ion, having such a high charge and relatively small size, forms a stable second coordination sphere. However, a quantitative estimate we can make only assuming similarity of the structures of hydrated complexes of four-charged actinide ions. Number of solvent molecules supposedly is equal to eighteen, and the average distance to them is 0.450 nm. Probably, the discussed cation is capable of forming ion pairs with counterions.

Thus, in the series of four-charged actinide ions a trend is seen of a decrease in cation coordination number from 9–10 for Th^{4+} and U^{4+} ions to 8–9 for the Np^{4+} and Pu^{4+} ions. In comparison with the triply charged actinide ions, the decrease in the coordination number begins in the lighter elements. Perhaps this is due to the high ion charge.

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