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Structural Parameters of the Close Environment of Group III Metal Ions in Aqueous Solutions of Their Salts

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Abstract—Published data obtained by various research methods and our own experimental results on the structural characteristics of the nearest environment of aluminum, gallium, indium, thallium, as well as scandium, yttrium and lanthanum ions in aqueous solutions of their salts under ambient conditions are summarized. The structural parameters, like coordination number, interparticle distance, parameters of the second coordination sphere and the types of ion association are discussed. The hydrate complexes of the ions of aluminum and gallium subgroups are compared.

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The present work is a continuation of the studies of structural characteristics of the nearest environment of some ions in aqueous electrolyte solutions under ambient conditions [1–4]. The goal was to summarize the available literature and our own experimental data on such structural parameters of hydrations the aluminum, gallium, indium and thallium(III), as well as scandium, yttrium and lanthanum ions as coordination number the interparticle distance, the parameters of the second coordination sphere, and the characteristics of ion pairs. The second aim was to compare the hydrated complexes of the ions of aluminum and scandium subgroups. The results of structural studies including those of aqueous solutions of salts of the cations under consideration until 1986 have been summarized in [5], and up to 1993, in [6]. It is reasonable to analyze the available literature data in both historical and logical aspects.

Structure of the close environment of the Al^{3+} ion. Aluminum, the third most common element in the crust, plays an important role in the industry, geochemistry, environmental chemistry, and medicine. However, the Al^{3+} ion can show toxic properties, contributing, in particular, to the Alzheimer's disease. [7].

Al^{3+} ion has a small size (0.054 nm) and a large charge, and therefore interacts strongly with the coordinated water molecules forming in aqueous solutions two stable coordination spheres. This may be illustrated by the lifetime of water molecules in the first coordination sphere of the cation [8, 9]. The lifetime is about 1 s, whereas, for example, for Na^+ the order of magnitude of this period is 10^{-12} s and for Mg^{2+} ion, 10^{-6} s. This short-range stability has resulted in a good agreement between the experimentally obtained structural parameters of the close environment of this ion. Numerous structural studies of the Al^{3+} ion hydrate complex showed conclusively that the cation coordinates around itself six octahedrally located water molecules in the first sphere at an average distance of 0.190 nm Also the presence of the second coordination sphere of Al^{3+} ion at an average distance 0.400 nm was established. The formation of ion associates with counterions is not typical for this cation. As actual illustration of these statements the following results of previous works may be regarded.

At an early stage of studying the structure of solutions the coordination number of aluminum ion has been determined by NMR as close or equal to six in 1.5 M aqueous solution of aluminum chloride [10] and aqueous solutions of aluminum perchlorate in the concentration range of 0.96–1.77 mol kg^{-1} [11]. Somewhat later the same values of coordination number were obtained by ^1H NMR solutions of aluminum chloride, bromide, perchlorate, and nitrate [12–14]. In an early study performed by the X-ray diffraction method of 0.5 M aqueous solution of

Parameters of the nearest environment of Al^{3+} ion from the results of the method of molecular dynamics

System	n_I	r_I, nm	n_{II}	r_{II}, nm	References
$AlCl_3$–$200H_2O$	6	0.197	19	0.425	[28]
0.8 M. $AlCl_3$	6	0.192	12	0.409	[29]
Al^{3+}–$512H_2O$ E2	6	0.186	14.6–18.0	0.355	[30][a]
E3	6	0.190	13.6–18.1	0.379	
EPOL	6	0.189	18.7–23.9	0.392	
Al^{3+}–$499H_2O$	6	0.190	16.8	0.420	[31][b]
1sphere QM/MM	6	0.190	13.8	0.420	
2 spheres QM/MM	6	0.180	12.2	0.410	
Al^{3+}–$32H_2O$	6	0.192	11.2	0.421	[32]
Al^{3+}–$64H_2O$	6	0.194	12	0.412	[33]
Al^{3+}–$128H_2O$	6	0.193	12	0.408	
Al^{3+}–$499H_2O$	6	0.188	12.8	0.415	[34]
Al^{3+}–$500H_2O$	6	0.186	12.3	0.390	[35]

[a] Parameters are obtained using different potentials (for the abbreviations, see [30]). [b] The parameters are obtained with different methods of calculation.

aluminum nitrate, the presence of six water molecules in the first coordination sphere of the cation at a distance of 0.190 nm, and twelve water molecules in the second sphere at a distance of 0.410–0.415 nm was established [15]. Six water molecules forming the first sphere of the cation at distances of 0.190 nm (1 M solution) and 0.188 nm (2 M solution), and twelve water molecules in the second sphere at a distance of 0.401 nm were found by small-angle X-ray scattering (SAXS) of 1 M and 2 M aqueous solutions of the aluminum sulfate containing 0.1 M HCl [16]. With the same method it was also confirmed that in the aqueous solution the aluminum nitrate the cation coordinated six water molecules in the first sphere at a distance of 0.190–0.198 nm, which, in turn, at the expense of short direct hydrogen bonds interacted with twelve water molecules of the second coordination sphere located at a distance of 0.410–0.415 nm from the cation [17]. The coordination number of aluminum ion is equal to six as proved by the analysis of the Raman spectra [18]. However, in concentrated solutions (2.9 and 3.7 M) of aluminum chloride the Raman spectroscopy indicated a slight distortion of the ideal octahedral geometry of the first coordination sphere of the cation due to the proximity of the two anions [19].

The nearest environment of this cation was also widely studied by computational methods. In order to study the interaction of aluminum ions with water molecules in its first coordination sphere, a number of *ab initio* calculations was carried out [20–25]. In [26] the following results of *ab initio* calculations were described: $CN = 6$, the Al^{3+}–OH_2 distance is 0.191 nm, the distance to the second coordination sphere is 0.400 nm, and the number of water molecules in it equals 14. A relatively large number of studies on the nearest environment of the cation was performed by the method of molecular dynamics. In [27] it was found by this method that ion Al^{3+} forms a stable complex $Al(H_2O)_6^{3+}$ with water molecules in clusters. Results of other studies are shown in the table.

Raman spectra of aqueous solutions of aluminum chloride, nitrate, and perchlorate in a wide range of concentrations (0.21–3.14 M) showed that the hydrate complex $Al(H_2O)_6^{3+}$ is stable in the studied concentration range. Contact ion pairs in these solutions were not found. In the solution of aluminum sulfate, in contrast, was found the formation of an aluminum–sulfate complex. Ab initio calculations with geometry optimization and calculation of vibration frequencies have also confirmed the presence of the cluster $[Al(OH_2)_1{}^3{}_8{}^+]$ with six water molecules in the first coordination sphere and twelve in the second [36]. The proof of the octahedral geometry of the complex $Al(H_2O)_6^{3+}$ was also obtained using XANES spectroscopy on 20 mM solutions of aluminum chloride, nitrate and sulfate, the electronic structure of this complex was determined as well [37].

However, in a few studies the coordination number of the aluminum ion was found to be other than six.

Early neutron diffraction study of an aqueous solution of aluminum chloride in a wide range of concentrations showed that Al^{3+} ion interacts with eight water molecules in the first sphere and the number of these molecules does not depend on the concentration [38].

The IR spectroscopy have confirmed the presence of the second coordination sphere of aluminum ion in 0.2 M aqueous solution of aluminum perchlorate [39]. Authors note, that the water molecules of the first sphere are tightly bound by hydrogen bonds with water molecules of the second sphere. These, in turn, are connected by hydrogen bonds with the surrounding solvent molecules. The presence around the Al^{3+} ion of the second coordination sphere consisting of 12 water molecules was confirmed also by the calculations using density functional theory [40]. According to the results of SAXS it was concluded that the Al^{3+} ion forms a stable, highly ordered first and second coordination spheres [41]. It was noted that the electron density of the first coordination sphere of the Al^{3+} ion was much higher (by ~71%) than the density of water, the density of the second sphere coincided with that of the water and was not distinguishable from it by this method.

As to the ion association, the following may be stated. The above mentioned studies showed that aluminum ion complex with six water molecules in the first sphere and twelve in the second is stable in nitrate solutions. Hence here the formation of ion pairs was not observed. It was determined by the ^{1}H NMR method that in a 2.1 M solution of aluminum nitrate formed only hydrate-separated ion pairs [14]. From the data of the Raman spectra of 1.3 M solution of aluminum nitrate it was found that NO_3^- ion does not penetrate to the first hydration sphere of the cation [42]. The presence of ionic associates was detected only in aqueous solutions of aluminum sulfate. This fact was experimentally fixed already a long time ago [43, 44]. The study of absorption of ultrasound showed the presence of two relaxation effects in the 0.05, 0.1 and 0.15 M aqueous solution of aluminum sulfate, which, according to Bonsen and Knoch, is due to a stepwise formation of ionic associates dissected first by two and then by one hydration shell [45]. The NMR study revealed that Al^{3+} and SO_4^{2-} ions form an outer-sphere complexes with the sulfate ions in the second coordination sphere of the aluminum ion [46]. By the method of dielectric spectroscopy it was determined that aluminum sulfate solution in the concentration range 0.012–0.65 M contained simultaneously the twice hydrate-separated, once hydrate-separated, and contact ion pairs [47].

Based on the foregoing material, we suggest that the aluminum ion shows a tendency to the formation of ion pairs and more complex associates in aqueous solutions of its sulfate, while it is not prone to the association in solutions of other salts. Probably the coordination spheres of water molecules formed by it are so stable that they prevent the formation of ion pairs with at least singly charged anions. We found no evidence in the literature on the existence of such pairs in an amount sufficient to affect the D-structure of the aluminum salts solutions. This fact points to a similarity of sodium, magnesium, and aluminum ions, which are sufficiently close in size and electronic structure of the outer shell and have a high charge density and also do not show a tendency to ion association. Nevertheless, we assume that the non-contact ion pairs can be formed not only with sulfate ions. It is obvious that the formation of non-contact ion pairs should decrease the number of water molecules in the second coordination sphere of the Al^{3+} ion, which was not mentioned in the cited papers. This prompted us to investigate the aqueous aluminum sulfate solutions with molar ratio of 1:60 and 1:100 (with no shortage of solvent) using a X-ray scattering technique [48]. On the functions of the X-ray scattering intensity a small-angle peak occurred indicating the presence of large sized aggregates in solution. The model analysis confirmed the formation of outer-sphere associates. In addition, it was found that the number of water molecules in the second coordination sphere, which are located at a distance of 0.395 nm, is equal to ten in both systems. It symmetrical distortion of the hydration spheres of sulfate ions consisting of six water molecules was also revealed. The results obtained have led to an assumption on the possible formation of quasi-polymer chains between hydrated Al^{3+} and SO_4^{2-} ions. Probably, these aggregates may contribute to vitrification of aluminum sulfate solutions [49].

The long range ordering in the concentrated solutions of aluminum salts has been also confirmed in the other studies. So at the use of the X-ray scattering, on the intensity curves of X-ray diffraction by the aqueous solutions of aluminum chloride a small-angle peak was found. Gaspar et al. explained its appearance by scattering between the cations located at an average distance of 0.9 nm from each other. They called this ordering the *liquid-type quasy-close packing* [50].

From the above, we can conclude with a considerable degree of confidence that Al^{3+} ion in aqueous solutions of its salts coordinates six water molecules located octahedrally around it in the first coordination sphere at an average distance of 0.190 nm. In addition, it forms a second coordination sphere at a distance of 0.400 nm and can form ion pairs with sulfate ions. Nevertheless, ion association is not typical for it.

Structure of the close environment of Ga^{3+} ion. Interaction of gallium ion in solution can be of both ionic and covalent character. The structure of aqueous solutions of gallium salts has been very poorly studied, and the published information on this matter is rather scarce. A review of all available papers on this subject is given in [51]. More recently only one paper on this topic was published. By EXAFS spectroscopy, the influence of temperature and pressure on the structure of 0.017 and 0.17 M aqueous solutions of gallium bromide was studied [52]. It was shown in this paper that under ambient conditions the Ga^{3+} ions are fully hydrated by about six water molecules at a distance of 0.197 nm. At such low concentrations the ion pairs are not formed.

We have studied by X-ray scattering in a wide temperature range the 1.85 M aqueous solution of gallium perchlorate acidified with 4.1 M $HClO_4$ [51]. The optimal model of the solution at the studied temperatures was found to be the non-contact ion pair $Ga^{3+}(H_2O)_6$–$OClO_3^-$. The average coordination number of Ga^{3+} ion is close to six with the distance to the nearest water molecules 0.194–0.196 nm. The set of main distances in the non-contact ion pairs is: Ga^{3+}–O (to the nearest oxygen atom of the ClO_4^-) 0.403 nm; Ga^{3+}–Cl 0.498 nm, and Ga^{3+}–O (up to two remote oxygen atoms of ClO_4^- ion) 0.480 nm. The fourth oxygen atom of the perchlorate ion in this configuration of the ion pair is located at a distance of approximately 0.600 nm. The cation forms a second coordination sphere at a distance of 0.400–0.403 nm consisting of about 18 water molecules. A large number of water molecules in the second sphere of the cation is probably due to the high charge density of the Ga^{3+} ion. We can assume that each water molecule of the first sphere forms three hydrogen bonds with the water molecules of the second sphere.

A summarization of the available information [51] suggests that the gallium ion forms the first coordination sphere of six water molecules, which are located around the ion octahedrally at a distance of 0.195 nm. It also forms a second coordination sphere, including, probably, twelve water molecules located at an average distance of 0.403 nm from the cation. This cation has a pronounced tendency to form complexes and ionic associates.

Structure of the close environment of In^{3+} ion. The structure of the hydrate complex of indium ion is relatively poorly studied owing to the strong tendency of this cation to hydrolysis and complex formation. In the early X-ray scattering study of aqueous 3 M indium perchlorate solution it was found that the cation is coordinated by six water molecules at an average distance of 0.215±0.003 nm [53]. In subsequent work the X-ray scattering on the 1.7 M aqueous solution of indium sulfate was also undertaken [54]. It was found that In^{3+} ion is surrounded octahedrally by six oxygen atoms belonging to water molecules or sulfate ions, at a distance 0.216 nm. In addition, the cation forms a second coordination sphere of 10.1±0.3 water molecules located at an average distance of 0.419 nm. Also a contact ion pair is formed with sulfate ion. The method of X-ray diffraction was also applied to the study of acidified 3.96 M indium nitrate solution [55]. The distance to six water molecules coordinated in the first sphere is determined equal to 0.217 nm. The presence of the second coordination sphere at a distance of 0.420 nm was also detected. The formation of ion associates with nitrate ions found by the X-ray scattering study of 3.96 M aqueous solution of indium nitrate [56]. The authors examine two models for the possible location of nitrate ions relative to the hydrate complex of the indium ion, the so-called *normal coordination* and a more compact aggregate, the *compact coordination*. Calculations of the functions for these models showed that the preferred one is the *compact configuration*. In a subsequent study the same models were used for the indium nitrate solutions of concentrations 1.30 M and 2.27 M [57]. It is noted that, despite a preference of the *compact configuration* model to reflect the structure of solutions, another model also cannot be excluded.

Structure of hydrated In^{3+} ions in aqueous solutions of indium perchlorate and nitrate was determined by X-ray scattering (solutions of concentration 1.5 M) and EXAFS spectroscopy (in the concentration range (0.005–1.0 M). It was found that the In^{3+} ion coordinates six water molecules in the first coordination sphere at a distance of 0.2131±0.007 nm, each of which interacts through hydrogen bonds with two water molecules of the second coordination sphere at a distance 0.413±0.001 nm from the cation. Electrolyte concentration or various anions were shown not to affect the In^{3+}–O distance in the first sphere [58].

Aqueous solutions of indium perchlorate and nitrate were also investigated by EXAFS spectroscopy at temperatures from 298 K to 623 K [59]. Under ambient conditions the In^{3+} ion coordinates six molecules in the first coordination sphere at a distance of 0.214±0.001 nm. In a solution with the addition of 1.0 M $HClO_4$ the formation of the ion pairs $In(ClO_4)(H_2O)_5^{2+}$ occurs with the In^{3+}–$O(ClO_4^-)$ distance equal to 0.312–0.314 nm. For a system with the addition of 0.10 M HCl at 298 K the formation of complexes $InCl_n(H_2O)_{6-n}^{3-n}$ ($0 \leq \nu \leq 4$) with octahedral coordination is typical. The In^{3+}–Cl and In^{3+}–O distances in these complexes are 0.240 and 0.213 nm, respectively. The existence of the complexes of the halide–In^{3+}–halide type (where halide is Cl^- or Br^-) was determined by Raman spectroscopy in aqueous solutions of indium chloride with concentrations 1.8–5.0 M and indium bromide 1.8–4.0 M) [60]. The study of acidified aqueous solutions of indium perchlorate, nitrate, and sulfate by IR and Raman spectroscopy and by *ab initio* calculations of molecular orbitals [61] showed that in the systems of 1.650 M $In(ClO_4)_3$–0.015 M $HClO_4$, 1.246 M $In(ClO_4)_3$–0.05 M $HClO_4$, and 1.105 M $In(ClO_4)_3$–1.310 M $HClO_4$ the hydrated ion $In(H_2O)_6^{3+}$ was stable, consequently, the contact ion pairs are formed. In 1.117, 0.534 and 0.312 M solutions of indium nitrate both inner-sphere complexes $[In(OH_2)_5 \cdot ONO_2]^{2+}$ and outer-sphere associates $[In(OH_2)_6^{3+}–NO_3^-]$ were formed. The inner-sphere complex is thermodynamically unstable and dissociates upon dilution, thereby increasing the number of outer-sphere associates. In the indium sulfate solutions in the concentration range of 0.0329–1.659 M the stable contact ion associates were registered.

Thus, we can conclude that to the In^{3+} ion a coordination number equal to six is ascribed, the distance to the coordinated water molecules is equal to 0.213 nm. The cation forms a second coordination sphere, which in the solutions without solvent deficiency consists of twelve water molecules located at an average distance of 0.413 nm from the cation. The In^{3+} ion tends to the formation of ion pairs and complexes.

Structure of the close environment of the Tl^{3+} ion. The Tl^{3+} salts of strong acids are most readily soluble in water, but are considerably hydrolyzed. Therefore, the solutions show an acidic reaction. The Tl^{3+} ion rapidly forms complexes with the counterions, especially with halide ions. Study of their structure attracted much attention [62].

To study the structure of the environment of hydrated Tl^{3+} ion the thallium(III) perchlorate solutions are often used, because the perchlorate ion is not prone to complex formation. In crystalline $Tl(ClO_4)_3 \cdot 6H_2O$, the Tl^{3+} ion is surrounded by six water molecules at a distance of 0.223±0.002 nm [63]. The X-ray scattering method revealed that in 1.0 and 2.1 M aqueous solutions of thallium(III) perchlorate the cation coordinates six molecules of water at a distance of 0.2235±0.0005 nm [64]. Methods of EXAFS, X-ray scattering, Raman and IR spectroscopy were used to study the structure of thallium(III) halide complexes in solutions of its chloride, bromide, and cyanide [65]. The distance to six water molecules coordinated by the cation was determined at 0.221±0.002 nm. Using simulations by quantum chemistry and molecular mechanics in combination with molecular dynamics method, for the systems Tl^{3+}–$499H_2O$ similar parameters were obtained: coordination number of the cation was six and the distance Tl^{3+}–O = 0.221 nm [66]. There is a distortion of the first coordination sphere. The presence of the second coordination sphere of the Tl^{3+} ion consisting of 18.1 water molecules located at a distance of 0.439 nm was also established. Vchirawongkwin et al. define this ion as a structure-forming one.

Consequently, the coordination number of ion Tl^{3+} is six, and the distance to the coordinated water molecules is on the average 0.222 nm. The cation forms also the second coordination sphere consisting of eighteen water molecules and located at an average distance of 0.435 nm. We assume that the second sphere is very stable, owing to a relatively small size and high charge of the ion.

The cations of scandium subgroup. The scandium subgroup ions Sc^{3+}, Y^{3+}, and La^{3+} have the electronic configuration of noble gases (d^0), which, in turn, imparts a pronounced electrostatic nature to their interaction with the nearest environment of the water molecules.

The structure of the close environment of Sc^{3+} ion. Recent studies of aqueous solutions of the scandium salts by a combination of Raman spectroscopy and theoretical calculations suggested the value of the cation coordination number equal to six, with the realization of the coordination sphere geometry with the central symmetry [67, 68]. The length of

Sc^{3+}–O bond calculated by the molecular orbital method was estimated at 0.218 nm

It follows from the results of the NMR studies that the cation can form inner-sphere complexes with nitrate and perchlorate ions [69]. Moreover, the type of the associates formed in aqueous solutions strongly affects the medium acidity. The formation of inner-sphere complexes, according to Raman spectroscopy, distinguishes the scandium ion from lanthanum and yttrium ions [70]. It was also found that the Sc^{3+} ion behaves unlike the lanthanide ions at the formation of complexes with nitrate ions. The analysis of the Raman spectra of nitrate solutions of scandium with molar ratio of 1:20 gave hydration number of the cation equal to seven [71].

Studies of 1 M and 3 M aqueous solutions of $Sc(ClO_4)_3$ and 4.6 M solution of $Sc(CF_3SO_3)_3$ under ambient conditions, carried out by X-ray diffraction and EXAFS methods showed that about seven water molecules are coordinated by the Sc^{3+} ion at a distance of 0.218 nm [72]. This result is consistent with the conclusions of [73], where it was shown by Raman spectroscopy of aqueous solutions of $ScCl_3$ and $Sc(ClO_4)_3$ in the glassy state that the spectral patterns of hydrated scandium ions do not correspond to the expected octahedral configuration of complexes as found in the case of $[Al(H_2O)_6]^{3+}$.

The above material should be supplemented by the fact that in [73] almost a linear relationship was found between the ν_1 values of the symmetric stretching vibrations of M^{3+}–H_2O and the inverse square of the M^{3+}–OH_2 distance for the metal ions of the third group with the same coordination numbers. Using the value 0.218 nm of the Sc^{3+}–OH_2 distance obtained by EXAFS spectroscopy and the value of ν_1 for aqueous solutions $ScCl_3$ and $Sc(ClO_4)_3$ in the glassy state [73], Kanno et al. entered into the obtained dependence a similar ratio $1/r^2_{M–O}$ for the Sc^{3+} ion. It turned out that the point corresponding to the Sc^{3+} ion does not lie on a line that combines the ions with coordination numbers equal to eight, or on a line corresponding to ions with coordination numbers equal to nine. Would the hydrated complex of the Sc^{3+} ion be a trigonal prism, as it has been established for the crystal hydrate [74], the value of ν_1 should fall on a line that combines ions with coordination numbers equal to nine. But this does not happen, and in accordance with the proposed relation is assumed that the coordination number of scandium ion is less than eight.

In the structure of crystalline $[Sc(H_2O)_9](CF_3SO_3)_3$, however, the Sc^{3+} ion is surrounded by nine water molecules with six short bonds Sc^{3+}–OH_2 = 0.2171 nm and three long bonds of 0.247 nm in a triangular configuration [74], like those found in crystals of the isomorphous $[Ln(H_2O)_9](CF_3SO_3)_3$ (where Ln corresponds to lanthanide ions).

In a modern study carried out by a combination of XAFS spectroscopy (for 0.98 M solutions of $Sc(ClO_4)_3$ and 0.11 and 0.35 M solutions of $Sc(CF_3SO_3)_3$ with the acidification by the corresponding acids to suppress hydrolysis) and X-ray scattering [for 0.98, 1.05 and 1.77 M solutions of $Sc(ClO_4)_3$] it was found that in a strongly acidified solution of scandium perchlorate the Sc^{3+} ion coordinates eight water molecules surrounding the cation in the form of a trigonal prism with two vertices of 6+1+1 type [75]. The Sc^{3+}–OH_2 distance to six strongly coordinated water molecules is found to be equal to 0.217±0.001 nm The Sc^{3+}–OH_2 distance to one of the molecules located at the top of the geometric figure corresponding to the coordination sphere of the cation is 0.232±0.004 nm, and to the other, 0.250 nm. In addition, the presence of the second coordination sphere of the cation of about twelve water molecules at a distance of 0.427±0.003 nm was found.

We studied by X-ray scattering 1.6 M and 2.8 M aqueous solutions of $ScCl_3$ under ambient conditions [76]. We found that the Sc^{3+} ion coordinated in the first sphere about six water molecules at a distance of 0.218 nm. In solution contact ion pairs of Sc^{3+}–Cl^- type exist with the interparticle distance of 0.263 nm. Thus, the overall coordination number of cation is in the range between seven and eight. The second coordination sphere of the Sc^{3+} ion is formed by 7–9 water molecules at a distance of 0,416 nm. The small number of solvent molecules in the second sphere is explained by the occurrence of chloride ion in the nearest surroundings of the cation. The number of water molecules around the Cl^- ion close to five occurs in many investigated solutions, which is somewhat less than the expected coordination number of the chloride ion equal to six,. This is probably also due to the formation of contact ion pairs. We also investigated 1 M and 3 M aqueous solutions of scandium perchlorate [76]. The optimal model for the 3 M aqueous scandium perchlorate was found to be the model with the average coordination number of the cation close to seven, and the distance from the cation to the first coordination sphere equal to 0.215 nm. The cation also forms the second coordination sphere at a distance of 0.410 nm consisting of water molecules and oxygen atoms of the perchlorate ions. This means that about two water molecules of the second coordination sphere are connected with one water molecule of the first sphere, probably through hydrogen bonds. The system includes the solvent-separated ion pairs characterized by the following set of distances: Sc^{3+}–O(ClO_4^-) 0.410 nm, Sc^{3+}–Cl (ClO_4^-) 0.490–0.510 nm, Sc^{3+}–O (ClO_4^-) 0.535–0.540 nm, where one oxygen atom of the perchlorate ion presumably enters the second coordination sphere of the Sc^{3+} ion, and the other three are oriented to the solvent bulk. The orientation of the perchlorate ion relatively to Sc^{3+} ion was difficult to establish unequivocally. The coordination number of the perchlorate ion is close to five with the Cl(ClO_4^-)–H_2O distance 0.362 nm.

Simulation analysis of the 1 M solution showed that the Sc^{3+} ion coordination number remains almost unchanged upon dilution. The high charge density on the cation can maintain the stability of the coordination sphere, regardless of the concentration. The number of ion pairs in the system decreases, which is explainable by the increase in the fraction of free solvent. The increase in the number of independently hydrated ions leads, in turn, to an increase in the average coordination number of the perchlorate ion and to increase in the number of water molecules in the second coordination sphere of the Sc^{3+} ion.

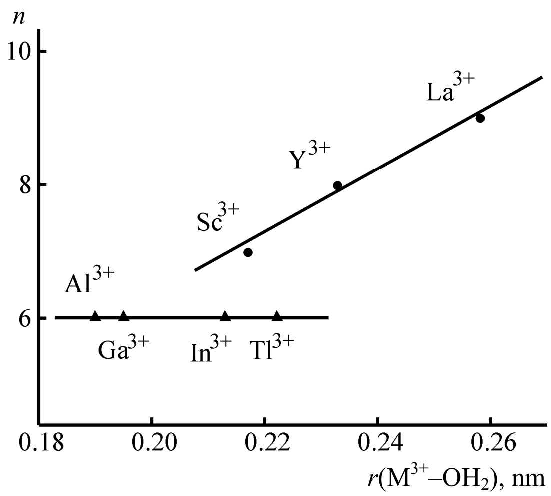
It is clear from the foregoing that the research performed so far does not give yet a clear quantitative description of the near environment of the scandium ion. Its coordination number defined in various studies ranges from six to eight. The distance to the first coordination sphere is within the range of 0.215–0.218 nm. Quantitative parameters of the second sphere are poorly studied. However, based on our own experimental results and conclusions made in [72, 73] we can suggests that the Sc^{3+} ion coordination number in aqueous solutions of its salts equals seven. Regarding the description of the second coordination sphere, we assume that in solutions without solvent deficiency two molecules of water will be connected by hydrogen bonds with each of the seven solvent molecules of the first coordination sphere, forming a second sphere of the fourteen molecules. The discussed cation can form a contact (presumably with halide ions) and non-contact ion pairs.

Structure of the close environment of the Y^{3+} ion. The Y^{3+} ion is known to be prone to hydrolysis, which can only be avoided in aqueous solutions with pH ≤ 3. It was established that in 0.77 M aqueous solution of yttrium selenate and 1.094 and 2.91 M solutions of yttrium perchlorate there are the cation complexes with the number of water molecules, equal to 8±0.3, with the Y^{3+}–O(H_2O) distance equal to 0.233 nm (in selenate solution) and 0.237 nm (in perchlorate solution) [77, 78]. The following parameters are determined for the second coordination spheres: r_{II} = 0.452 nm, n_{II} = 9 for 1.094 M solution of yttrium perchlorate, r_{II} = 0.452 nm, n_{II} = 15 for 2.91 M solution of yttrium perchlorate, and r_{II} = 0.447 nm, n_{II} = 11 for 0.77 M solution yttrium selenate. In addition, the formation of contact ion pairs of cation with selenate ions was established.

The method of anomalous scattering of X-rays was applied to the study of 0.5 M and 1.0 M aqueous solutions of YCl_3 [79]. It was found that the cation had in the near surrounding 8.1±0.3 water molecules at a distance of 0.246±0.002 nm in the first solution and 8.2±0.5 water molecules at a distance of 0.251± 0.002 nm in the second solution.

By EXAFS spectroscopy it was determined that the predominant species in solutions of yttrium chloride and bromide in a concentration range from 2.1 to 0.6 M was the ion Y^{3+}, coordinating eight water molecules [80]. The average distance Y^{3+}–O(H_2O) is estimated at 0.233±0.002 nm for the YBr_3 solution and 0.234±0.002 nm for YCl_3 solution. The absence of contacts between the cation and anion was established, and also was confirmed by Raman spectroscopy. For equimolar 2.67 M aqueous solutions of yttrium chloride and bromide studied by X-ray scattering it was found that the Y^{3+} ion coordinates eight water molecules at a distance of 0.236±0.002 nm [81]. However, there are works in which the determined coordination number of yttrium ions is different from eight. Thus, by EXAFS spectroscopy four solutions were investigated: 0.1 M YCl_3, 0.1 M YCl_3+0.23 M HCl+1.0 M NaCl, 0.1 M YCl_3+0.23 M HCl+2.0 M NaCl, and 0.05 M $Y(NO_3)_3$ [82]. In all the systems the Y^{3+} ion coordination number is found equal to 9 or 10, and the distance to the coordination sphere 0.237± 0.002 nm. Inner-sphere ion pairs with chloride ions were not detected.

By combined methods of X-ray diffraction and EXAFS spectroscopy it was found that in aqueous solutions of yttrium perchlorate (in a concentration range of 0.43–1.71 M) and iodide (1 M) the cation



Dependence of the coordination numbers of ions of aluminum and scandium subgroups on the interparticle distance between the cation and the water molecules in the first coordination sphere.

coordination sphere included eight water molecules arranged as a two-caped trigonal prism with the Y^{3+}–$O(H_2O)$ average distance equal to 0.2368±0.0005 nm [83]. The second coordination sphere of the cation consists of about 16 water molecules at a distance 0.440 nm. No contact ion pairs with chloride ions were found. The presence of contact ion pairs with iodide ions was not observed even in such a concentrated solution as 10 M.

Another confirmation of these results was obtained by EXAFS spectroscopy of the YBr_3 aqueous solutions in the concentration range from 0.005 to 2.0 mol kg^{-1} [84]. It was concluded that yttrium ion coordinated eight water molecules located around the cation as a symmetric square antiprism at a distance of 0.235 nm. This structural configuration remains unchanged over the entire concentration range. The absence of the Y^{3+}–Br^- contact ion pairs was also noted.

The results of the method of anomalous X-ray scattering in 3.5 M aqueous solution of yttrium chloride confirmed the presence of two clearly defined coordination spheres of the cation. The first sphere, located at a distance of 0.230 nm, consists of eight water molecules, and the second, at a distance of 0.477 nm, consists of both water molecules and chloride ions. The Y^{3+}–H distance is 0.295 nm [85]. The method of X-ray scattering showed that in 2.89 M aqueous solution of yttrium nitrate the cation coordinated eight water molecules at a distance of 0.236 nm [86]. Nitrate ions are not included in the first coordination sphere of the cation. The yttrium ion coordination number is equal to eight, as confirmed by molecular dynamics method for the 0.8 M YCl_3 solution, the coordination sphere is a square antiprism [87, 88]. The average Y^{3+}–$O(H_2O)$ distance obtained in the cited work is 0.238 nm. In a modern study by the neutron diffraction method with 0.1 M aqueous solution of yttrium chloride it was also noted that the average coordination number of the cation was eight, and the distance to the coordinated water molecules was 0.233 nm [89].

As can be seen from the above survey, nearly all studies gave the yttrium ion coordination number equal to eight, although the data were obtained using different methods. The resulting distances to the water molecules of the first coordination sphere 0.230–0.238 nm also are well consistent. Consequently, we can conclude that the coordination number of the Y^{3+} ions in aqueous solutions of its salts is equal to eight, with arrangement of water molecules at an average distance of 0.233 nm from the cation. As to the parameters of the second coordination sphere, its structural description was obtained only in three papers [83]. The interval of changes of the experimentally determined distances is 0.440–0.452 nm, and the number of solvent molecules is from 9 to 16. Let us try to evaluate the validity of these characteristics. On the one hand, we can assume that the parameters of the second coordination sphere of the ion Y^{3+} are intermediate between those of the ion Sc^{3+} (N_{II} = 14, r_{II} = 0.425 nm) and ion La^{3+} (N_{II} = 18, r_{II} = 0.465 nm). On the other hand, these parameters should be close to the chemically similar ions Tm^{3+} (N_{II} = 14–16, r_{II} = 0.449 nm) and Er^{3+} (N_{II} = 14–16, r_{II} = 0.448 nm). We assume that the results obtained in more recent work [83] performed by combined precision methods of X-ray scattering and EXAFS spectroscopy more accurately reflect the actual structure of the near environment of the cation and satisfy both conditions. Thus, around the yttrium ions in solution with no solvent deficiency also the second coordination sphere is formed consisting probably of sixteen water molecules located at an average distance equal to 0.440 nm The cation is prone to the formation of ionic associates.

Structure of the nearest environment of the La^{3+} ion. A detailed review on the structural parameters of the nearest environment of lanthanum ion in aqueous solutions we reported in [90]. Finally it may be noted that the La^{3+} ion coordination number is nine, with the three-cap trigonal prism as a the first coordination sphere. The average distance to six nearest water molecules is equal to 0.252 nm, and to three more distant, 0.265 nm. The second coordination sphere is likely to consist of eighteen water molecules (two water molecules of the second sphere interact with one molecule of the first sphere). The distances to the second sphere is in the range of 0.460–0.465 nm The discussed cation forms ionic associates with the counterions, which can be both contact and noncontact ion pairs, depending on the chemical nature and concentration of the anions.

Some generalizations. Analyzing the results of the structural description of the nearest environment of aluminum subgroup ions Al^{3+}, Ga^{3+}, In^{3+}, and Tl^{3+} we can conclude that these cations are very similar to each other in terms of the formation of short-range order in aqueous solutions. They form a stable first coordination sphere of six water molecules, which are located around the cation octahedrally, and the second coordination sphere, whose parameters depend on various factors. In addition, all the discussed cations (except for the ion Al^{3+}) have a strong tendency to form complexes.

Analysis of a series of trivalent cations of the subgroup of scandium Sc^{3+}, Y^{3+} and La^{3+} leads to the conclusion that the coordination number of these ions in aqueous solutions of their salts increases with increasing ionic radius from 7 (Sc^{3+}) to 8 (Y^{3+}) and 9 (La^{3+}). All cations form the second coordination sphere and participate in association with the formation of contact and noncontact ion pairs. The size of the triply charged cations probably does not affect much the parameters of the second coordination sphere and the degree of formation of ion pairs, unlike the case of the singly charged ions. This, of course, is due to the high charge density on these ions and therefore to the formation of sufficiently stable hydrate compounds. It is only presumable that the increase in the radius of the ions leads to increased tendency to form ionic associates of the contact type. As seen, the tendency to form hydrate structures of complexes of trivalent ions in the series Al^{3+}–Ga^{3+}–In^{3+}–Tl^{3+} differs from that of the structure in the series of hydrated ions Sc^{3+}–Y^{3+}–La^{3+}. While the former have octahedral coordination of water molecules, which in fact does not depend on the size of the ion, in the latter case the coordination number of ions increases with their size (see the figure). Such a difference in the structural behavior of the first and second series of the cations with similar charges is due, primarily, to the difference in their electronic structure. Perhaps the electronic configuretion of noble gases and thus a pronounced electrostatic nature of the bonds of the second series makes the size of the coordinating particle so important.

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