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Structure of hydrated complexes formed by metal ions of Groups I—III of the Periodic Table in aqueous electrolyte solutions under ambient conditions

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Published and authors´ experimental data on the structures of aqueous electrolyte solutions under ambient conditions are considered. The hydrated metal complexes formed in aqueous solutions are described systematically depending on the size of the cation, the charge, and the structure of the outer electron shell.

Key words: aqueous solutions, electrolytes, structure, coordination number, interparticle interaction, ion pair.

Introduction

An important aspect in investigations of aqueous solutions of electrolytes is identification and structural characterization of water—electrolyte systems. Numerous monographs and reviews have been devoted to structural description of ionic hydration.[1—8] Of considerable interest is to elucidate the rules that govern the formation of the solution structure. Some of these regularities have already been determined, but this is far from being enough for the understanding of the inner organization of liquids. Therefore, the main goal of this review is to summarize the published data and the experimental results obtained by the authors concerning the structure of liquids and analysis of the structure of electrolyte solutions under ambient conditions in order to create a system of dependences of the structural parameters of solutions on the chemical nature of the ions.

The structure of electrolyte solutions is based on the structure of the solvent, in this particular case, water. Since short-range order parameters for the structure of water under ambient conditions have been mainly determined, a large portion of studies of aqueous electrolyte solutions are currently directed at the structures of the hydrated complexes of ions. The selection of the optimal concentration range is especially important, because the structure of saturated and concentrated solutions can substantially depend on the concentration. However, to elucidate the dependence of solution structurization on the chemical nature of the ions, it is, conversely, expedient to avoid the influence of electrolyte concentration, *i.e.,* to consider the structural parameters of ion hydration in solutions without solvent deficiency.

This review is focused on the analysis of hydrated complexes of cations with the use of some methods of system analysis.[9,10]

To identify the effect of a particular property of particles on the solution structure, a series of particles should be selected in such a way that only one parameter changes over this series, the other parameters remaining constant. On the basis of the Periodic Table of the Elements, we constructed a system of metal cations in which the cations are combined in terms of particular common features. The pattern of this system of relations is shown in Fig. 1. Naturally, these relations are only for classification. The features common to the cations of the given series are presented in brackets, while variable parameters are in parentheses. The fundamentally important properties of the particles include the charge, the radius, and the structure of the outer electron shell. As the structural response of the system to these properties, we analyzed the coordination number (C.N.), the configuration of the hydrated complexes of ions, the presence of second coordination sphere, the ability of ions to form ion pairs, and the type of ion associates. The fragments of the developed pattern for each cation were filled using published data and the experimental results we obtained in our studies of aqueous solutions of electrolytes. These data are discussed below.

It is of interest to follow the effect of the ion radius on the solution structure with an invariable cation charge in the series of alkali metal ions. Detailed analysis of pub-

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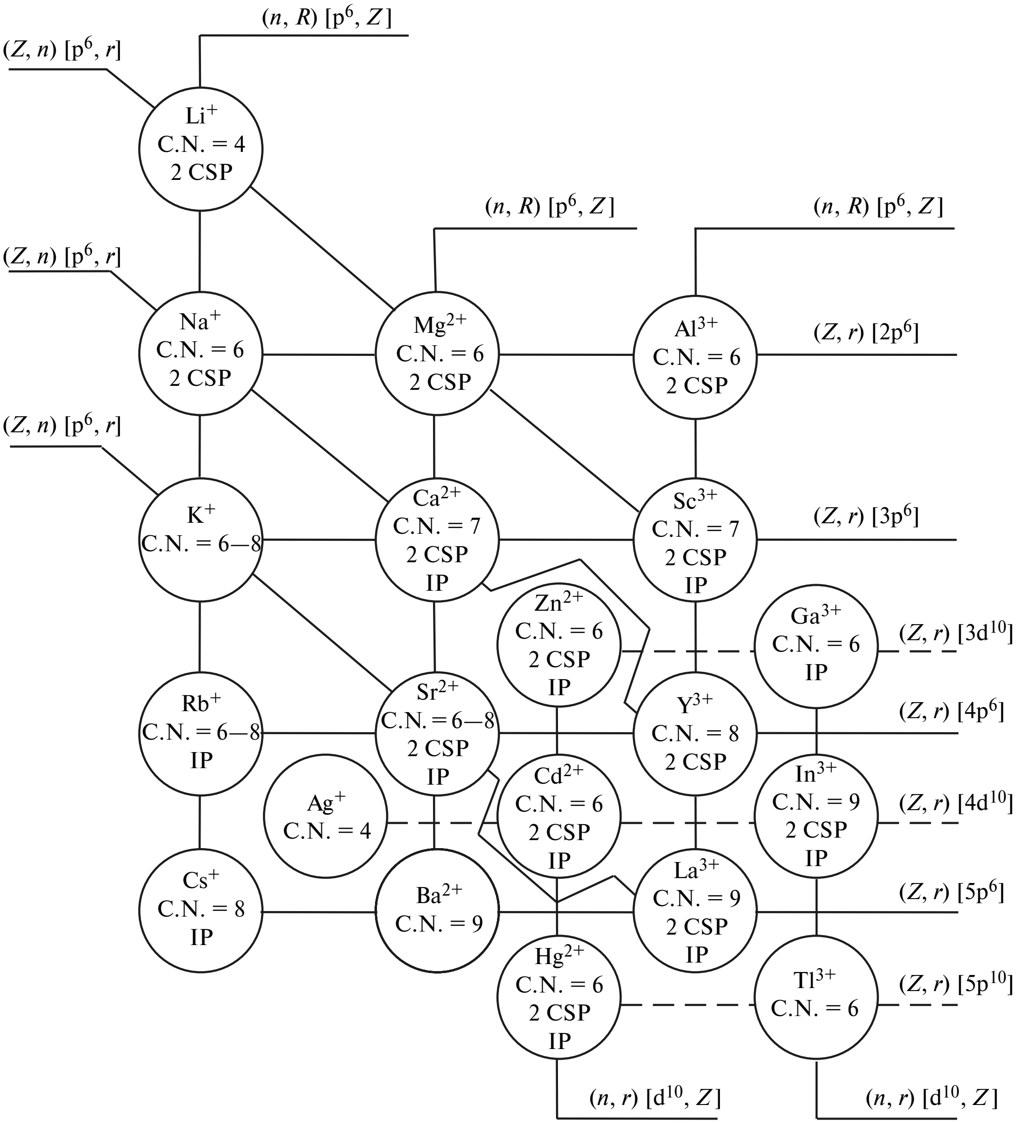

Fig. 1. Relationship of the cations in terms of common features; *r*, *Z* are the ion radius and charge, *n* is the principal quantum number for the outer electron shell, 2 CSP is the presence of a second coordination sphere, IP is the formation of ion pairs.

lished data on each cation needed for this purpose is presented below.

Structures of hydrated complexes formed by Group I metal ions

Hydrated complexes of Li$^+$ ion. The Li$^+$ ion is the smallest one in the series of alkali metal ions and has the highest charge density. Many structural studies of solutions of alkali metal salts are devoted to hydrated complexes of lithium ions.

A large number of works have been undertaken to identify the structure-formimg and structure-breaking properties of ions. Transition from positive hydration, observed for Li$^+$ and Na$^+$ ions, to negative hydration for K$^+$, Rb$^+$, and Cs$^+$ ions was found;[1] later, this has been repeatedly proved by experiments. For example, ^{7}Li, ^{23}Na, and ^{133}Cs NMR measurements for aqueous solutions showed that water molecules adjacent to Li$^+$ and Na$^+$ cations are less mobile and those adjacent to the Cs$^+$ ion are more mobile than those in pure water.[11] It has been assumed[12—15] that structural changes provoked by an ion in the local environment, when this ion is introduced in a solvent, differ appreciably from the changes caused by other similar ions; this is, apparently, responsible for a number of specific physicochemical features of solutions of lithium salts.

Quantitative structural information on the hydration of the Li$^+$ ions under ambient conditions is also rather extensive. A neutron and X-ray diffraction study[16] of the hydrated complex formed by the cations in aqueous solutions of lithium chlorides showed that the ion is surrounded by water molecules with a tetrahedral geometry. Subsequently, many researchers[17—20] confirmed that the C.N. of the lithium ion is four, the $Li^+—OH_2$ distance being 0.19—0.21 nm, and that the molecules surrounding the ion in the first coordination sphere form a regular tetrahedron. Of relatively recent papers, noteworthy are the results of a study of an aqueous solution of lithium bromide (concentration 20 mol.%) by neutron diffraction with isotope substitution.[18] In the ion hydration complex, the $Li^+—O$ distance is 0.196±0.021 nm, the $Li^+—H$ distance is 0.26±0.02 nm, and the angle between the $Li^+—O$ axis and the plane of water molecule is given by $\phi = 27\pm10°$. The average number of water molecules coordinated by the cation was estimated as 3.9±0.5. It was also noted that the number of hydrogen bonds in a solution of LiBr of a similar concentration is much smaller than that in pure water.[18] Analysis of the data on slow neutron scattering by a 2 *M* aqueous solution of LiCl showed that the hydration shell of the cation consists of four water molecules and the time they remain in the hydration shell[21] is given by $i_0 = 25\pm10$ ps.

However, there are also experimental results that predict a coordination number equal to six for the Li^+ ion. X-Ray diffraction and molecular dynamics (MD) studies of solutions of LiI showed that the Li^+ ion has six water molecules in the first coordination sphere and twelve water molecules in the second sphere.[22,23] The presence of six water molecules in the first sphere of Li^+ was also demonstrated in neutron diffraction studies of aqueous solutions of LiCl.[24—26]

A model interpretation of X-ray diffraction data showed that C.N.s of both four and six can be used in models.[27] In the X-ray diffraction studies of aqueous solutions of lithium nitrates, perchlorates, and sulfates carried out by our research group, when analyzing the correspondence between theoretical and experimental structural functions to determine the C.N., we considered in detail not only the major peak but also side contributions of the interactions between water molecules incorporated in the cation coordination sphere and located at the edge of either tetrahedron (C.N. = 4) or octahedron (C.N. = 6).[28] The different distances between water molecules (0.33 nm for C.N. = 4 and 0.28 nm for C.N. = 6) and different numbers of molecules (six in the former case and twelve in the latter case) made essentially distinct contributions to the overall scattering pattern in the model analysis. This allowed us to obtain rather reliable structural parameters for the hydration of this cation and convinced us that the C.N. of lithium ion in concentrated solutions is four.

As regards the results of computer methods, they represent C.N.s equal to four,[29—31] five,[32—34] and six[35] for the Li^+ ion and also confirm[36] the concentration dependence of the C.N.

The concentration dependence of the local environment of the cation was also established[37] by neutron diffraction with $^6Li/^7Li$ isotope substitution. It was found that in a lithium chloride solution with a concentration of 6.7 mol.%, the C.N. is equal to 5.5, whereas an increase in the concentration to 16.7 mol.% entails a decrease in the C.N. to 3.3. An increase of the C.N. from 3.2 in a 14 *M* solution to 6.5 in a 1 *M* solution has also been noted.[38] Neutron diffraction measurements[39] gave average lithium C.N. values equal to six for a lithium bromide solution with a concentration of 10 mol.% and equal to four for a solution with a concentration of 25 mol.%. It was noted[39] that the tetrahedral structure of the hydrated complex of this cation remains invariable up to a concentration of 33 mol.%.

When considering a longer-range order, the problems of investigation of the second coordination sphere, the formation of ion pairs, and determination of their type also cannot be solved unambiguously. The majority of studies admit that Li^+ ions do form the second coordination sphere but neither the number of water molecules involved nor the distance to them were determined reliably. It was found by neutron diffraction that Li^+ ions are surrounded by a second coordination sphere comprising 12 weakly coordinated water molecules located at an average distance of 0.419 nm.[37] According to X-ray diffraction studies of a broad range of solutions of lithium salts with medium concentrations, cations also form a second coordination sphere consisting of 12 water molecules located at a distance of 0.405—0.420 nm.[28] The lability of the second coordination sphere is manifested as a decrease in the number of water molecules following an increase in the concentration of Li^+ ions.

The formation of ion pairs in concentrated solutions of lithium salts has been noted. The Raman spectra of saturated solutions of LiCl and LiBr showed the formation of inner-sphere $LiCl/Br(OH_2)_n{}^+$ complexes (*n* = 3). In more dilute solutions, only the $Li(OH_2)_4{}^+$ hydrated complexes were detected.[40] A correlation between Li^+ and Br^- ions was also found in a solution of lithium bromide at a concentration of 33 mol.%, which was explained by the presence of solvent-separated ion pairs.[39] The contact of each cation with one anion has been established for a 1.791 *M* aqueous solution of LiF by the MD method. This contact results in a noticeable overlap of the hydration shells of the counter-ions and in almost complete destruction of the structure of the surrounding water.[41] Finally, a study of concentrated solutions of lithium bromide $(LiBr)_x(H_2O)_{1-x}$ and $(LiBr)_x(D_2O)_{1-x}$ (x = 0.05—0.25) by Raman spectroscopy showed[42] the presence of both hydrated $Li^+(H_2O)_4$ ions and solvent-separated $Li^+(H_2O)_4...Br^-$ ion pairs.

These results indicate that the Li^+ ion does not tend to form ion pairs with counter-ions in the concentration range under interest. The formation of solvent-separated and contact ion pairs starts only in concentrated or saturated solutions. However, even with this scatter of experimental results, some conclusions can be drawn. The coordination number of the Li^+ ion is equal to four; the coordination sphere is formed by water molecules and is shaped like a regular tetrahedron with Li^+—OH_2 distances of 0.19—0.22 nm. Upon dilution of the solution, the C.N. of the Li^+ ion can increase to six. In addition, the Li^+ ion forms a second coordination sphere with a radius of 0.405—0.415 nm, the number of water molecules in which varies depending on the electrolyte concentration.

Hydrated complexes of Na^+ ion. The Na^+ ion differs from the Li^+ ion by a larger radius and, hence, the lower charge density. This is a reason for the different structural parameters observed in solutions of lithium and sodium salts. In terms of its effect on the structure of water, Na^+ is classified as a positively hydrated ion,[1,11] this effect being feebly defined. The structure of the hydrated complex formed by this ion in aqueous solutions has long remained an object of investigations in chemistry and biology.

Analysis of the structural data available for solutions of sodium salts revealed (as for the Li^+ ion) different results. First of all, the C.N. values were markedly scattered. A model of the solution structure has been proposed[43—45] according to which the Na^+ ion coordinates four water molecules. This hypothesis was confirmed experimentally by an X-ray measurements for a 7 *M* aqueous solution of NaI, which showed that the cation is hydrated by four water molecules, the average Na^+—OH_2 distance being 0.24 nm.[46] Similar results have also been obtained for other solutions of sodium halides.[47,48]

Conversely, several publications attest to a C.N. equal to six for the Na^+ ion. For example, X-ray diffraction analysis of 5 and 7 *M* aqueous solutions of $NaNO_3$ showed that an octahedrally hydrated Na^+ ion involved in interaction with the NO_3^- anion and forming solvent-separated ion pairs is the most appropriate model for describing the experimental data.[49]

There are also data that the C.N. of the Na^+ ion is equal to eight. In a neutron diffraction study of a 1 *M* solution of NaCl in heavy water, the C.N. of this cation was found to be eight and the distance to the nearest water molecules was estimated as 0.25±0.01 nm.[50]

Thus, the C.N. of the Na^+ ion was assumed to be four,[43—47] six,[48] or eight.[49] According to X-ray diffraction studies, the Na^+—OH_2 distances fall in the range of 0.237—0.249 nm.[47—50] These distances obtained by computation techniques are somewhat shorter (0.230—0.236 nm)[51—56] and the C.N. varies between five and six.

The scatter in the description of the structural parameters of the first coordination sphere of the Na^+ ion might be due to the fact that the C.N. of sodium varies depending on the concentration. Previously,[57—59] it has been reported that the Na^+ C.N. equal to six decreases to four only in highly concentrated solutions.

The structure of a nearly saturated aqueous solution of sodium chloride (6.18 *m*) studied by X-ray diffraction at 298 K is as follows. About 30% of ions are involved in ion pairs with a Na^+—Cl^- distance of 0.282 nm. The hydration numbers of Na^+ and Cl^- were found to be 4.6 and 5.3, respectively.[60] An aqueous solution of HCOONa with a concentration of 15 mol.% has been studied by a combination of X-ray and neutron diffraction techniques and Raman spectroscopy. The hydration number of the Na^+ ion was found to be 4.6±0.2, the Na^+...OH_2 distance is 0.237±0.001 nm.[61]

In the case of longer-range hydration, published data attest in favor of the formation of a second coordination sphere around the Na^+ ions.[52,57] X-Ray diffraction studies carried out by our research group for solutions of sodium perchlorates, chromates, and sulfates over a broad concentration range showed the presence of a second coordination sphere around the Na^+ ions at a distance of 0.410—0.420 nm. The number of water molecules involved depends appreciably on the concentration, the greatest value (twelve) being observed at medium concentrations and lower values being found for concentrated solutions.[62—64] The decrease in the number of water molecules in the second coordination sphere of the cation occurs in parallel with the decrease in the hydration number of anions

The problem of ion association in solution of sodiums salts is also still debated. A study of the formation of ion pairs in an aqueous solution of sodium perchlorate by vibrational spectroscopy has shown[65] that up to a 8 *m* concentration, the solution mainly contains independently hydrated ions. In the concentration range $8 < m < 12$, solvent-separated ion pairs are formed, and at higher concentrations, the contact ion pair becomes the major structural unit.

The results of studies on the thermochemistry of salting-out[66] provide evidence for the existence of solvent-separated ion pairs in solutions of sodium sulfate. Examination of the IR spectra of aqueous solutions of $NaClO_4$ showed[67] that these results can be interpreted satisfactorily with the assumption that the solution contains aggregates of the $Na^+(H_2O)_5ClO_4^-$ type. The retention of the symmetric shape of the ν_3 band for the ClO_4^- anion at concentrations up to 6 mol L^{-1} implies that the surrounding of this ion does not change and, hence, the probability of formation of contact ion pairs is very low. For a 2.2 *m* aqueous solution of $NaClO_4$, the Na^+—ClO_4^- pair distribution function, was found[51] to pass through a maximum corresponding to the presence of solvent-separated ion pairs.

According to X-ray diffraction data obtained for aqueous solutions of sodium nitrates, perchlorates, and chromates, the cation has a C.N. of six in any system studied with a $Na^+—OH_2$ distance ranging from 0.231 to 0.248 nm.[62—64] Aqueous solutions of sodium nitrate with molar ratios from 1 : 15 to 1 : 25 are described as containing ion pairs, which disappear on further dilution. In sodium perchlorate solutions, ion pairs, conversely, do not determine the diffusion-average D-structure over the whole concentration range from 1 : 15 to 1 : 100. In a concentrated solution of sodium chromate (1 : 15), contact ion pairs of the $Na^+—OCrO_3^{2-}$ type are formed with a $Na^+—O$ distance of 0.349 nm.

Thus, aqueous solutions of sodium salts starting from molar ratios of 1 : 15 exhibit the tendency for the formation of ion associates. The difference in the type of ion pairs is due to the difference in the spatial configurations and the charge of anions.

The above information can be summarized by concluding that the C.N. of Na^+ is, most likely, six. The water molecules of the first coordination sphere are arranged around the cation according to an octahedral pattern at distances of 0.230—0.245 nm. In addition, the Na^+ ion often forms a second coordination sphere with a radius of 0.410—0.420 nm, in which both the interparticle distances and the number of water molecules (at most, twelve) depend on the sort of counter-ions and the electrolyte concentration. In the concentration range we consider, ion associates do not determine the structure of solutions of sodium salts.

Hydrated complexes of K^+ ion. Structural information concerning hydration of K^+ ions is not often found in the literature. It has been proposed[43—45] that K^+ ions reside in the cavities of the internal structure of water and are surrounded by six solvent molecules, which form a coordination polyhedron shaped like a trigonal prism. This was confirmed in some experimental works,[60,68] according to which the K^+ ion has a first coordination sphere of six water molecules located at distances of 0.28—0.29 nm.

According to a different viewpoint,[51,69] the C.N. of the K^+ ion is equal to eight. This result was obtained for aqueous solutions of potassium sulfate studied by NMR spectroscopy over a broad range of concentrations.[57] A neutron diffraction study of a 1 *M* aqueous solution of KCl in heavy water also showed[46] a C.N. of the cation equal to eight with $K^+—OH_2$ distances equal to 0.270±0.010 nm. A 2.2 *M* aqueous solution of KCl was studied by the molecular dynamics approach. The hydration numbers for the K^+ and Cl^- ions amounted to 7.8 and 7.6, respectively, and the $K^+—OH_2$ and $Cl^-—OH_2$ distances were estimated as 0.280 and 0.313 nm, respectively.[69]

X-ray diffraction studies[28] of solutions of potassium nitrate and sulfate also resulted in different values for the cation C.N. For example, for solutions of potassium nitrate over a wide concentration range, the C.N. of potassium was found to be eight and for solutions of potassium sulfate, it was found to be six. This discrepancy can be due to both the crucial influence of the counter-ion on the K^+ hydration and experimental difficulties arising in determination of this value. A series of X-ray diffraction investigations of aqueous solutions of potassium halides at molar ratios of 1 : 15 and 1 : 25 have shown[70] that the cation coordinates six water molecules located at a distance of 0.283—0.297 nm to form an octahedron around the coordination center. An exception is the solution of KF in which the regular geometry of the first sphere is distorted to form a bipyramid, in the researchers´ opinion, under the action of the anion field.

A study of the possibility of formation of a second coordination sphere by the K^+ ion has shown[71] that among the Li^+, Na^+, and K^+ ions, only K^+ does not form the second hydration shell. Studies of aqueous solutions of potassium nitrates and sulfates over a broad concentration range carried out by our research group[28] also confirmed the lack of the second coordination sphere around the K^+ cations.

The results of studies of the salting-out thermochemistry indicate that the K^+, Rb^+, and Cs^+ ions form contact ion pairs with sulfate ions.[66] The results of X-ray diffraction investigations of concentrated aqueous solutions of KI suggest[72] the formation of $K^+—I^-$ ion pairs. In aqueous solutions of KNO_3, ion pairs were found only in the $KNO_3—15H_2O$ system; moreover, these associates were identified as solvent-separated pairs and they disappeared upon dilution.[28]

The structures of aqueous solutions of potassium chloride (4.56 *m*) and fluoride (16.15 *m*) close to saturation have been studied[60] by X-ray diffraction analysis. It was shown that in a solution of potassium chloride, ~60% of ions form contact ion pairs with a $K^+—Cl^-$ distance of 0.315 nm. The average C.N.s of both K^+ and Cl^- were found to be 5.8. A solution of KF was found to contain ion—ion clusters with $K^+—K^+$ and $F^-—F^-$ distances equal to 0.388 and 0.432 nm. In addition, $K^+—F^-$ ion pairs are formed with an ion—ion distance of 0.269 nm. The n_{KF}, n_{KK}, and n_{FF} numbers of pairs were estimated as 2.3, 1.9, and 1.6, respectively.

Thus, the K^+ ion forms a stable first coordination sphere with a radius of 0.28—0.29 nm. With a high probability, the C.N. of the K^+ ion is considered to be six and with a lower probability, eight. The ambiguity in interpretation of X-ray diffraction data may be due to either the strong masking effect of the solvent, as the K^+ ion is close in size to water molecules, or weak hydration of the ion. The formation of a second coordination sphere is unusual for K^+. In addition, in aqueous solutions of potassium salts, the formation of ion pairs is possible but their number and type depend appreciably on the chemical nature of the counter-ion and on the electrolyte concentration.

Hydrated complexes of Rb^+ ion. The poor knowledge of the hydrated complexes of the Rb^+ ions can be explained by either instability of the structures formed by these ions or a number of experimental difficulties arising in investigations of solutions of rubidium salts. The Rb^+ ion in aqueous solutions is characterized by a negative hydration,[1,73] a C.N. of six[11] or eight,[57] and by the presence of ion pairs.[53,74] Study of the NMR spectrum of an aqueous solution of RbOH has shown[75] that the C.N. of the Rb^+ ion is equal to 3.5. Molecular dynamics calculations[76,77] gave a C.N. value equal to five and a Rb^+—O distance of 0.289 nm. A coordination number of the Rb^+ ion equal to six and a Rb^+—O distance equal to 0.29 nm were determined by EXAFS for a 1 *M* aqueous solution of RbOH,[78] while these values for a rubidium bromide solution were[79] 6.5 and 0.288 nm, respectively.

According to X-ray diffraction data obtained for aqueous solutions of rubidium nitrates and sulfates,[28] the C.N. of this cation is eight and the distance to the coordinated water molecules is 0.280—0.285 nm. No second coordination sphere has been detected for the Rb^+ ion, while the tendency for the formation of ion pairs can be clearly followed.

It appears precocious to make any general conclusions on the basis of these contradictory results. Nevertheless, we present our version of the averaged hydrated complex of Rb^+ ion, which is included in the general pattern (see Fig. 1). The C.N. of the Rb^+ ion in solutions with medium concentrations is assumed to be eight and the distances from the cation to the coordinated water molecules are in the range of 0.280—0.290 nm. The cations do not form a second coordination sphere but form both contact and solvent-separated ion pairs. The type of the latter is determined by the chemical nature of the counterion and the electrolyte concentration.

Hydrated complexes of Cs^+ ion. The data on the structure of the hydrated complexes of Cs^+ ions are fairly extensive but rather ambiguous. The Cs^+ ion has the largest size in the series of alkali metal ions, which may result in a larger number of water molecules in the nearest environment. However, this ion has the lowest (in the same series) charge density, which may entail a decrease in the C.N. Therefore, it is rather difficult to predict the C.N. for the Cs^+ ion. The range of C.N. values established for this ion by different methods is 4—9. It was suggested[1] that the C.N. of the Cs^+ ion in dilute aqueous solutions is close to 3.5. In a series of studies[43—45] using a model of the structure of electrolyte solutions, Cs^+ ions were found to replace water molecules in the ice-like framework, the most probable C.N. being four.

X-ray diffraction studies of aqueous solutions of cesium salts are few. A study of the CsI—H_2O system with a cesium concentration of 2.76 and 5.56 *m* by X-ray diffraction has shown a decrease in the average C.N. of the Cs^+ ion following an increase in the electrolyte concentration.[80] In the researchers´ opinion, this is due to the shortage of water molecules no longer able to form complete independent coordination spheres around the Cs^+ and I^- ions as the solvent deficiency becomes more pronounced. In addition, the formation of Cs^+—I^- contact ion pairs prevents the arrangement of water molecules in the coordination spheres of ions along the Cs^+—I^- bond. It was also noted that the structure of the Cs^+ hydrated complexes is rather sensitive to changes in the concentration or temperature.

The coordination number of the Cs^+ ion equal to eight and the Cs^+—O distances close to 0.31 nm were determined by neutron diffraction for a 1 *M* aqueous solution of CsCl.[17] The same C.N. of Cs^+ with a similar set of interparticle distances have been established[81] by X-ray diffraction for aqueous solutions of CsI at CsI : H_2O molar ratios of 1 : 60 and 1 : 100. In the same study, it has been noted that up to 25% of ions occur in the solutions as ion pairs. Molecular dynamics simulations for a 2.2 *M* aqueous solution of CsF gave a C.N. equal to 7.9 with a distance from the Cs^+ ion to the coordinated water molecules of 0.322 nm,[82] and the C.N. found for a 2.2 *M* aqueous solution of CsI was eight.[83]

Thus, the Cs^+ ion forms the first coordination sphere comprising eight water molecules located, on average, at a distance of 0.305—0.310 nm from this ion, and the parameters of the coordination sphere depend appreciably on a number of factors. A second coordination sphere of the cation is missing from aqueous solutions of cesium salts. The systems under discussion tend to form ion pairs.

The structure of nearly saturated aqueous solutions of cesium fluoride (31.96 *m*) has been studied by X-ray diffraction.[60] The Cs^+—F^- distance was found to be 0.312 nm. The solution was shown to contain clusters consisting of several cations and anions. The interparticle distances are equal to 0.442 and 0.548 nm. The numbers of pairs n_{CsF}, n_{CsCs}, and n_{FF} were estimated to be 3.3, 2.3, and 5.3, respectively. The formation of such associates can be considered as an onset of crystallization.

Hydrated complexes of Ag^+ ion. According to X-ray diffraction data, the C.N. of the Ag^+ ion in 3 and 9 *M* aqueous solutions of silver perchlorate and nitrate is equal to four for a Ag—O distance of 0.240 nm. In solutions of nitrates, the anions are coordinated to the Ag^+ ions as monodentate ligands. Conversely, in perchlorate solutions, the ClO_4^- ion is not contained in the first coordination sphere of the cation.[84] Neutron diffraction measurements for a 3.71 *M* aqueous solution of silver perchlorate have shown[85] that the first hydration shell of the cation contains, on average, 4.1 water molecules, the Ag—O and Ag—D distances are equal to 0.241 and 0.297 nm, respectively, the tilting angle of the water molecules is 45°, and the O—O distances are 0.394 nm.

Analysis of EXAFS data for a 3 *M* aqueous solution of $AgClO_4$ and a 9 *M* solution of $AgNO_3$ also made it possible to determine parameters of the Ag^+ hydrated complex: four water molecules are coordinated to the cation at a distance of 0.231—0.236 nm. In a 9 *M* aqueous solution of $AgNO_3$, 0.384 nm long Ag—Ag contacts have been detected.[86]

Thus, the Ag^+ ion is hydrated in aqueous solutions by four water molecules with an average Ag^+—O distance of 0.231—0.241 nm. The cation does not tend to form a second coordination sphere. In addition, ion pairs, both contact and solvent-separated ones, can be formed in the systems under discussion, their type being mainly determined by the chemical nature of the counter-ion.

General features of the hydrated complexes formed by Group I metals. The survey of the average characteristics of the hydration of alkali metal ions provides the conclusion that an increase in the ion radius entails an increase in the C.N. for single-charged cations (Li^+, 4; Na^+, 6; K^+, 6—8; Rb^+, 8; Cs^+, 8) (Fig. 2). Despite the uncertainty in determining the C.N.s of these ions, it can be noted that, whereas in the case of Li^+ and Na^+, the range of the most probable C.N.s corresponds to values of 4—6, on passing to K^+ and Rb^+ ions, this range shifts to greater values, namely, 6—8. In addition, the first coordination sphere of ions becomes more labile, as indicated by the enhancement of the influence of various factors on structural rearrangements in the local environment of the Rb^+ and Cs^+ ions. Most of the above results point to weakening of hydration on passing from Li^+ to Cs^+, which is attributed to the decrease in the charge density.

The ability to form the second coordination sphere disappears on an increase in the ion size (this was discovered unambiguously only for Li^+ and Na^+ ions), which is also due to the decrease in the charge density on passing from Li^+ to Cs^+. In addition, the tendency of ions for association was found to become more pronounced with an increase in the ion size. This fact may be an illustration for a hypothesis[87,88] according to which cations create areas around themselves with either increased (positive hydration) or decreased (negative hydration) density of arrangement of molecules. Anions are located in solutions mainly in the areas with decreased density of water molecules, *i.e.*, mainly, they are located either in the free solvent if the cations are positively hydrated or near the cations if these are negatively hydrated. An enhancement of the cation hydration results in displacement of the anions from the cation environment. From this standpoint, association with the formation of ion pairs is facilitated on passing to ions with negative hydration.

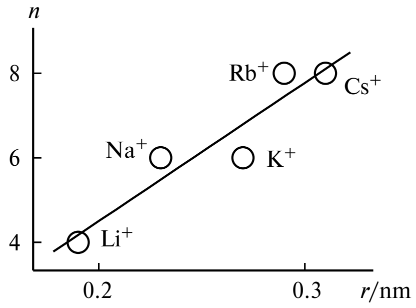

Fig. 2. Dependence of the coordination numbers (*n*) of alkali metal ions on the interparticle distances between the ion and the water molecules of the first coordination sphere (*r*).

Thus, using alkali metal ions as an example, we illustrated the potential of system approach in elucidating the regular features of structure formation in solutions. A similar analysis can be carried out for double- and triple-charged ions.

Structures of hydrated complexes formed by alkaline earth metal ions

Now we consider the structural parameters of hydration in the series of alkaline earth metal ions Be^{2+}—Mg^{2+}—Ca^{2+}—Sr^{2+}—Ba^{2+}. Ions with the charge 2+ have a higher charge density than single-charged ions and, hence, they form more stable hydrated complexes.

Hydrated complexes of Be^{2+} ion. The Be^{2+} ion is the smallest one in the series of alkaline earth metal ions, which determines some specific features of its solvation. In most complex compounds, the C.N. of Be^{2+} ions is equal to four; this provedes grounds for some predictions concerning the structure of its hydrated complexes in solutions. Besides, it can be expected that this ion forms a stable second coordination sphere in aqueous solutions. The following scarce information on the structural parameters of hydration of the Be^+ ion is available. According to X-ray diffraction data, the coordination number of the cation in an aqueous solution of $BeCl_2$ is four and the distance to the nearest water molecules is 0.167 nm.[89] Two computation studies have been reported. For a 1.1 *M* aqueous solution of $BeCl_2$, the MD method showed the presence of a clearly defined first coordination sphere of Be^{2+} comprising four water molecules. The presence of the second coordination sphere around this cation was established.[90] These results were confirmed in a more recent study,[91] which was also performed by the MD approach.

Hydrated complexes of Mg^{2+} ion. The results of numerous studies of the hydration of Mg^{2+} allow one to derive the parameters of its hydrated complexes with a high degree of accuracy. The stability of the coordination sphere of the Mg^{2+} ion might be due to the donor-acceptor nature of the ion—water bond, instead of the ion-dipole nature usual for most other ions.[92]

The majority of structural studies of magnesium-containing aqueous electrolyte systems have been carried out rather long ago; at present, these systems are seldom investigated. By combining X-ray diffraction and neutron diffraction techniques with isomorphous substitution, it has been found that the first coordination sphere of the Mg^{2+} ion is 0.207 nm distand from the ion and consists of six water molecules.[93] An X-ray diffraction study of aqueous solutions of magnesium chloride with concentrations of 1.0, 1.95, and 4.32 mol L^{-1} showed the presence of an octahedral hydration shell of the cation, the $Mg^{2+}—OH_2$ distances being 0.210—0.212 nm.[94] Similar parameters of the first coordination sphere of this cation were also found by X-ray diffraction approach for aqueous solutions of magnesium nitrate.[95] On the basis of a neutron diffraction study of aqueous solutions of magnesium salts, it has been noted[96] that the C.N. values for the Mg^{2+} cation do not depend on the electrolyte concentration or on the type of counter-ions to within the experimental error.

The presence of a second coordination sphere around the Mg^{2+} ion was also established rather reliably. The number of water molecules involved was found to be twelve for solutions of magnesium nitrate or sulfate and the average $Mg^{2+}—OH_2$ distance is 0.420 nm.[93,97] By analysis of the IR spectra of a 0.4 *M* aqueous solution of magnesium perchlorate, the distance between the water molecules of the first and second hydration shells was determined to be 0.276 nm.[98]

The systems we discuss contain only small amounts of ion pairs. A Raman spectroscopy study showed that even concentrated solutions of magnesium perchlorate contain predominantly independently hydrated ions.[99] Analysis of the dependence of osmotic activity coefficients of the Mg^{2+} and ClO_4^- ions in aqueous solutions on the electrolyte concentration provided the conclusion that perchlorate ions enter the second coordination sphere of the cation.[100] For aqueous solutions of magnesium sulfate, the proportion of $Mg^{2+}—SO_4^{2-}$ ion pairs was estimated to be 8—15% of the amount of the dissolved salt (isothermal compressibility study[101]) or 10% for the concentration range from 0.1 to 2.5 mol L^{-1} (Raman spectroscopy data).[102] It has also been noted[103] that the formation of $Mg^{2+}—SO_4^{2-}$ ion pairs is not accompanied by ion dehydration. Examination of the Raman spectra of aqueous solutions of $Mg(AcO)_2$ in the concentration range from 0.65 to 3.24 mol L^{-1} showed the presence of complexes formed by the cation with one anion, which are transformed into compounds with two anions in saturated solutions.[104] The presence of both 1 : 1 and 1 : 2 complexes has been demonstrated[105] by Raman spectroscopy for solutions of magnesium thiocyanate in the concentration range from 3.4 to 7.5 mol L^{-1}.

X-ray diffraction study of aqueous solutions of magnesium nitrate, perchlorate, and sulfate over a broad concentration range[106,107] showed that the cations have the first coordination sphere consisting of six water molecules arranged according to an octahedral pattern at a 0.210—0.220 nm distance from the cation and the second sphere at a distance of 0.410—0.420 nm. As the electrolyte concentration increases, the number of water molecules in the second sphere decreases and on dilution, it increases to twelve.

Thus, it can be regarded as proven that in solutions without solvent deficiency, Mg^{2+} ions coordinate six water molecules arranged according to an octahedral geometry 0.205—0.215 nm away from the cation. The cation also forms a stable second coordination sphere consisting of twelve water molecules situated at an average distance of 0.410 nm. The ion pairs do not determine the *D*-structure of aqueous solutions of magnesium salts.

Hydrated complexes of Ca^{2+} ion. Characteristic features of hydration of the Ca^{2+} ion are the flexibility of coordination geometry and high mobility of water molecules in the local environment. The unstable coordination sphere around this ion is susceptible to the influence of the second hydration sphere. Owing to these properties, the Ca^{2+} ion is useful for monitoring the conformational changes in biological processes in the human body (in the control of metabolism, nerve impulses, muscle contraction, blood clotting, or cell division).[108] Due to the high biochemical importance of the hydrated Ca^{2+} ion, numerous structural studies of its salts in aqueous solutions have been performed. However, the above-mentioned lability of the first coordination sphere markedly complicates the interpretation of experimental data, which, in turn, results in pronounced discrepancies of the obtained results.

Concentrated solutions of calcium chloride $CaCl_2 \cdot RH_2O$ with the molar ratios $R = 4.0$ and $T = 393$ K; $R = 5.6$ and $T = 345$ K; $R = 6.0$ and $T = 306$ K; and $R = 8.6$ and $T = 298$ K have been studied by X-ray diffraction analysis.[109] The results were interpreted in the following way. The coordination number of the Ca^{2+} cation is equal to six at $Ca^{2+}—H_2O$ distances of 0.244—0.246 nm. For $R = 6$, one Cl^- ion is bound to Ca^{2+} cation, whereas for $R = 4$, two Cl^- anions are coordinated to the Ca^{2+} cation. Solutions of calcium chloride and nitrate have been studied[110] by neutron diffraction with isomorphous substitution (^{44}Ca, ^{NAT}Ca). The number of water molecules in the first coordination sphere of the calcium ion decreases from ten to six as *R* increases from 1 to 4.5. X-Ray diffraction data were used to calculate[111] the radial distribution functions (RDF) for 1.2 and 4.5 *M* aqueous solutions of calcium bromide. It was shown that the $Ca^{2+}—OH_2$ interaction is reflected in the RDF as a peak at 0.250 nm and that experimental functions are adequately described by models for the local environment of the cation both comprising six and eight water molecules. The same research group has studied[112] aqueous solutions of calcium chloride in the 1—4 mol L^{-1} concentration range, the hydration number for this ion being determined to be six with a $Ca^{2+}—OH_2$ distance of 0.242 nm. It was shown that this system contains neither ion associates nor second coordination sphere of the cation. According to MD computations, the hydration number of the Ca^{2+} ion for aqueous solutions of calcium chloride[113,114] occurs in the 9.2—10 range; according to another version, it is equal[115] to 8.2. A concentrated aqueous solution with the composition $Ca(NO_3)_2 \cdot 3.5H_2O$ has been studied by X-ray diffraction.[116] It was found that the Ca^{2+} ion binds nine O atoms that belong to three or four water molecules and nitrate ions, by analogy with the structures of the $Ca(NO_3)_2 \cdot 4H_2O$ and $Ca(NO_3)_2 \cdot 3.5H_2O$ crystal hydrates. For the aqueous solutions $Ca(NO_3)_2 \cdot 25H_2O$ and $Ca(NO_3)_2 \cdot 40H_2O$, which have also been studied by X-ray diffraction, the C.N. of the Ca^{2+} ion and the Ca^{2+}—OH_2 distance were found[117,118] to decrease from six to five and from 0.255 to 0.239 nm, respectively, with an increase in the electrolyte concentration.

The use of EXAFS, X-ray diffraction, and MD techniques for investigating the structure of calcium halide solutions showed that the C.N. of Ca^{2+} is eight and the Ca^{2+}—OH_2 distance is equal to 0.246 nm. A second coordination sphere of the cation was detected at a distance of 0.458 nm.[119]

Analysis of the results obtained by computations also shows a substantial scatter.[120—122] The final C.N. values appear to be higher with the use of pair potentials (9.0—9.3) calculated by *ab initio* techniques than in the case where calculations involved the potentials that take into account many-particle effects either directly or as effective pair potentials (7.0—8.6). The Ca^{2+}—OH_2 distances lie in the range of 0.239—0.254 nm in the former case and 0.240—0.250 nm in the latter case.

Thus, the C.N. values obtained for the Ca^{2+} ion vary from six to nine. The reasons for these discrepancies may be in the nature of interaction of the Ca^{2+} ion with the coordinated water molecules.[123]

In the solid state, calcium nitrate crystallizes as $Ca(NO_3)_2 \cdot RH_2O$ ($R = 2, 3, 4$). When $R = 2$, the Ca^{2+} ion coordinates ten O atoms belonging to nitrate ions.[124] When $R = 3$, the local environment of the cation contains nine O atoms, three from three H_2O molecules and six from three NO_3^- ions.[125] When $R = 4$, the Ca^{2+} ion coordinates nine O atoms, four from H_2O molecules and five from NO_3^- ions.[126]

As regards association between the Ca^{2+} and NO_3^- ions, analysis of the Raman spectra showed the presence of both contact and solvent-separated ion pairs,[126—130] the extent of their formation being markedly dependent on the electrolyte concentration.[131] Recent studies of supercooled and vitrified solutions of calcium nitrate by IR and Raman spectroscopy demonstrated[132,133] that the proportion of the contact ion pairs increases upon vitrification. Based on the results of ultrasound and hypersound velocity and adiabatic compressibility measurements for aqueous solutions of calcium nitrate over a broad concentration range, it was established that the bond between Ca^{2+} and NO_3^- is mainly of the ion-dipole nature.[134]

According to our investigations,[135] the C.N. of the Ca^{2+} ion is equal to 7.7 in a saturated solution (6 mol L^{-1}) of calcium nitrate and is close to seven in a more dilute solution (3 mol L^{-1}). A slight increase in the C.N. in a saturated solution can be due to the higher degree of system structuring under conditions close to crystallization. Contact ion pairs are present in both solutions studied. The Ca^{2+} ion has a second coordination sphere with a radius of 0.425—0.435 nm.

Hydrated complexes of Sr^{2+} ion. Published data on the structure of aqueous solutions of strontium salts are scarce. Early X-ray measurements[136] for an aqueous solution of strontium chloride with a molar ratio of 1 : 21 resulted in an average cation C.N. equal to 7.9 and a distance to water molecules in the coordination sphere equal to 0.260 nm. A similar value has been obtained[137] by the same method for 1.53 and 2.00 *M* aqueous solutions of $SrCl_2$. The peak at 0.265 nm on correlation functions was interpreted as the Sr^{2+}—OH_2 distance. Further model interpretation of the data showed that Sr^{2+} ions have both a first coordination sphere comprising eight water molecules at a distance of 0.265 nm and a second sphere whose composition depends appreciably on the concentration.

The structure of the hydrated Sr^{2+} ion in aqueous solutions has been studied using X-ray diffraction and EXAFS techniques. Both approaches resulted in a C.N. value of 8.1(3) and a Sr^{2+}—O bond length of 0.263(2) nm. The second coordination sphere of the cation consisting of approximately 13 water molecules distant by 0.480 nm from the cation appears "highly smeared"; presumably,[138] two water molecules of the second sphere are located at a shorter distance. The presence at 298 K of the first coordination sphere containing eight water molecules at a distance of 0.257 nm was also confirmed[139] by the EXAFS method for an aqueous solution containing 0.10 *m* of the Sr^{2+} ion.

The data of Raman spectroscopy for aqueous solutions of strontium nitrate demonstrate[140] the presence of $Sr(NO_3)^+$ and $Sr(NO_3)_2$ species. This was also confirmed[141] by the results of an X-ray diffraction study of an aqueous solution of strontium nitrate at a Sr^{2+} : H_2O molar ratio of 1 : 25; NO_3^-—Sr^{2+}—NO_3^- ionic triads were identified.

Thus, it can be concluded that the Sr^{2+} ion coordinates eight water molecules at an average distance of 0.260 nm. The second coordination sphere is formed at a distance of 0.480 nm, the number of water molecules it involves depending on various parameters. In addition, the tendency for the formation of ion pairs is clearly defined.

Hydrated complexes of Ba^{2+} ion. The pronounced absorption of X-rays by the Ba^{2+} ion accounts for substantial experimental difficulties encountered in X-ray diffraction studies of this ion. The results of the sparse works dealing with the structural aspects of hydration of the Ba^{2+} ion are as follows. X-Ray diffraction study of an aqueous solution of barium chloride with a $Ba^{2+} : H_2O$ molar ratio of 1 : 36 gave**[136]** a cation C.N. equal to 9.5 and a distance to coordinated water molecules of 0.290 nm. By combining X-ray diffraction and EXAFS methods, the C.N. of the Ba^{2+} ion was found to be 8.1(3) and the Ba^{2+}—O bond length, 0.281(2) nm. The second coordination sphere of the Ba^{2+} cation, as in the case of Sr^{2+}, is not clearly defined and numbers about 13 water molecules located at a distance of 0.480 nm; two water molecules are, apparently, situated closer to the cation.**[138]**

Thus, it can be inferred that the hydration sphere of the Ba^{2+} ion contains eight or nine water molecules separated by 0.280—0.290 nm from the cation. Probably, the Ba^{2+} ion forms the second coordination sphere spaced by a distance of 0.480 nm and comprising, in solutions without solvent deficiency, 12—13 water molecules. The ability of these cations to form ion pairs is a matter of conjectures.

Structural features of formation of hydration shells in the series of alkaline earth metal ions. To summarize the foregoing, it can be concluded that the obvious increase in the ion—water interparticle distance with an increase in the ion radius entails an increase in the C.N. from four (Be^{2+}) to six (Mg^{2+}), seven (Ca^{2+}), and eight (Sr^{2+}, Ba^{2+}) (Fig. 3). This is accompanied by some decrease in the ability of the cation to form the second hydration sphere and by an increase in the proportion of ion pairs in the solution. The last-mentioned conclusion is in line with the results of a study,**[142]** which demonstrates the increase in the role of ion association in the sequence $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$ for aqueous solutions of nitrates and perchlorates using IR, Raman, and NMR spectroscopy.

Structures of hydrated complexes of double-charged d-element cations

Hydrated complexes of Zn^{2+} ion. The coordination number of the hydrated Zn^{2+} ion in aqueous solutions has been established rather accurately. It is accepted that Zn^{2+} ions coordinate six water molecules according to an octahedral geometry in the first sphere. Most publications confirm also the ability of the Zn^{2+} ion to form a second coordination sphere. The question of the presence and type of ion pairs in solutions of zinc salts remains moot. In view of the pronounced tendency of Zn^{2+} ions for complexation, some researchers report the structural characteristics of Zn^{2+} complexes with various anions.

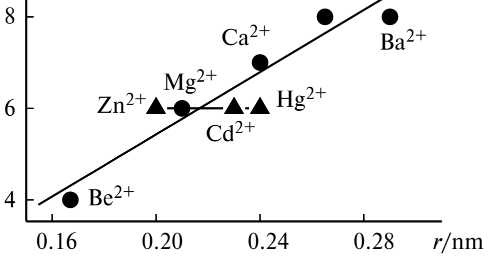

Fig. 3. Dependence of the coordination numbers (*n*) of double-charged metal ions on the interparticle distances between the ion and the water molecules of the first coordination sphere (*r*).

Aqueous solutions of zinc perchlorate and sulfate have been studied by X-ray diffraction.**[143]** For both solutions, it was found that Zn^{2+} is hydrated according to an octahedral geometry, the Zn^{2+}—OH_2 distance being 0.208 nm. In solutions of zinc sulfate, no contact ion pairs were detected. In another publication,**[144]** X-ray diffraction measurements for aqueous solutions of zinc sulfate showed not only the presence of octahedrally hydrated cations but also the presence of a second coordination sphere consisting of twelve water molecules and the existence of $Zn(H_2O)_5{}^{2+}$—$SO_4{}^{2-}$ contact ion pairs. The presence of up to 40% of ion pairs in solutions of zinc sulfate has been confirmed in another publication**[145]** where these solutions were studied by X-ray diffraction over a broad concentration range.

Raman spectroscopy data obtained for aqueous solutions of zinc perchlorate over a broad concentration range (0.5—3.54 mol L^{-1}) attest to stability of octahedrally hydrated Zn^{2+} ions in the systems under study. The water molecules of the first coordination sphere of the cation form strong hydrogen bonds with the water molecules of the second hydration sphere. No ion pairs have been detected.**[146,147]** However, other studies**[148,149]** using the same method showed the presence of contact ion pairs in aqueous solutions of zinc sulfate.

The structure of aqueous solutions of $Zn(NO_3)_2$ in the concentration range of 2.7—0.005 *m* has been studied by EXAFS.**[150]** Neither the distance from the cation to the first coordination sphere ($Zn—O_I = 0.205$ nm) nor the C.N., equal to six, change noticeably upon variation of the salt concentration. The second coordination sphere consists of 11.6±1.6 water molecules located at a distance of 0.410 nm. The most concentrated solution (2.7 *m*) is an exception: the number of water molecules in the second sphere diminishes to 6.8±1.5.

The formation of ion pairs in solutions of zinc salts depends on the concentration. Analysis of the Raman spectra of aqueous solutions of $Zn(NO_3)_2$ showed that solutions with concentrations of <3.5 mol L^{-1} contain predominanly hydrated $Zn(H_2O)_6{}^{2+}$ and $NO_3{}^-$ ions not bound to one another. The contact ion pairs, $Zn(H_2O)_5{}^{2+}$—$NO_3{}^-$, are formed only in solutions with high salt concentrations.**[151]** The results of X-ray diffraction measurements for these solutions showed**[152]** that ion pairs are not formed up to concentrations of 4.72 mol L^{-1}. According to Raman spectroscopy, the following equilibria exist in aqueous solutions of zinc nitrate over a broad concentration range:[153]

$$Zn(H_2O)_6^{2+} + NO_3^- \rightleftharpoons Zn(H_2O)_6NO_3^+ \rightleftharpoons$$
$$\rightleftharpoons Zn(NO_3)(H_2O)_5^+ \rightleftharpoons Zn(H_2O)_4(NO_3^-)_2 \rightleftharpoons$$
$$\rightleftharpoons [Zn(NO_3)_2](H_2O)_x.$$

Finally, it can be concluded that in dilute aqueous solutions at medium concentrations, the Zn^{2+} ion forms the first coordination sphere in which six water molecules are located around the cation at average distances of 0.208—0.215 nm to form an octahedron and the second sphere consisting of approximately 12 water molecules located at 0.410 nm distance from the cation. As the concentration increases, the Zn^{2+} ions form initially solvent-separated ion pairs and then contact ion pairs with polyatomic oxygen-containing or other anions.

Hydrated complexes of Cd^{2+} ion. The Cd^{2+} ion is a strong complexing agent; this fact determines its behavior in solutions. This ion also tends to form ion pairs with counter-ions. Only the quantitative parameters of these structures are debatable.

The results of sound velocity measurements in aqueous solutions of transition metal sulfates showed that the formation of ion pairs with the anions is accompanied by detachment of about three water molecules from the cation hydration shell. The proportion of inner-sphere ion pairs was estimated[154] to be 20%. In our opinion, this interpretation of experimental data appears doubtful, as it was shown by X-ray diffraction that during the formation of ion pairs, an O atom of the SO_4^{2-} ion replaces one water molecule in the Cd^{2+} coordination sphere and, hence, the octahedral geometry of the first sphere is retained.[155,156]

Measurements of the density, viscosity, and electrical conductivity for aqueous solutions of cadmium sulfate and the diffusion coefficients of the Cd^{2+} and SO_4^{2-} ions at $SO_4^{2-} : Cd^{2+}$ molar ratios from 1 to 3 (concentration range 1.2—3.0 mol L^{-1}) demonstrated that cadmium(II) mono- and bisulfate complexes are formed in concentrated solutions. The former predominate in stoichiometric solutions, while the latter, in those with component ratios of ≥2.[157] The solutions: 3 *M* $CdSO_4$, 1 *M* $CdSO_4$ + + 2 *M* $(NH_4)_2SO_4$, 1 *M* $CdSO_4$ + 2 *M* H_2SO_4, and 1 *M* $Cd(ClO_4)_2$ + 1 *M* $HClO_4$ have been studied by X-ray diffraction.[158] It was found that in each of these solutions, the Cd^{2+} ion has an octahedral environment; in the first three systems, the Cd^{2+} ions coordinate the SO_4^{2-} ions in the monodentate mode. The Cd^{2+}—O bond length is 0.228 nm and the Cd^{2+}—O—S angle is 134°. The average number of SO_4^{2-} groups coordinated by each Cd^{2+} ion is equal to 0.8, 1.6, and 1.2, respectively. The ClO_4^- ions are not involved in coordination. The presence of $Cd^{2+}—OSO_3^{2-}$ contact ion pairs in aqueous solutions of cadmium sulfate over a broad concentration range was confirmed by IR and Raman spectroscopy; the content of associates increases with an increase in the salt concentration up to saturation of the solutions.[159]

A similar tendency of the cation for independent hydration in dilute systems and formation of ion pairs of various sorts in concentrated solutions can be noted for cadmium nitrate. Study of a 4.54 *M* aqueous solution of $Cd(NO_3)_2$ by X-ray diffraction and Raman spectroscopy revealed the presence of a second coordination sphere in addition to the Cd^{2+}ions hydrated independently by six water molecules. The solution contains also inner-sphere $Cd(H_2O)_5ONO_2^+$ complexes with an Cd^{2+}—O—N angle of 118°.[160] Analysis of the Raman spectra of aqueous solutions of cadmium nitrate with Cd : H_2O molar ratios of 1 : 15 and 1 : 40 attest that the C.N. of Cd^{2+} does not depend on the salt concentration.[161] In a previous publication[153] using the same method, the following reaction pattern was proposed:

$$Cd^{2+} + NO_3^- \rightleftharpoons Cd(H_2O)_6NO_3^+ \rightleftharpoons$$
$$\rightleftharpoons Cd(NO_3)(H_2O)_5^+ \rightleftharpoons Cd(NO_3)_2(H_2O) \rightleftharpoons$$
$$\rightleftharpoons [Cd(NO_3)_2]_x(H_2O)_y.$$

The results of X-ray diffraction data for aqueous solutions of cadmium nitrate over a broad concentration range can be formulated as follows.[162] In a melt of the $Cd(NO_3)_2 \cdot 4H_2O$ crystal hydrate (T = 332 K), the local environment of the cation contains two NO_3^- ions located in mutually perpendicular planes. Each nitrate ion is surrounded by four water molecules with N—OH_2 distances of 0.340 nm. The contributions of the $Cd^{2+}—OH_2$ distances were not detected on the RDF.

On passing to the $Cd(NO_3)_2—10H_2O$ system, the positions of the nitrate ions (whose number is still two) near the cation change, and two water molecules enter the local environment of the Cd^{2+} ion, being arranged at a distance of 0.235 nm. The Cd^{2+}—N distance increases from 0.330 to 0.361 nm. Further dilution of the solution (to a molar ratio of 1 : 25) does not influence the type of the associate. The Cd^{2+}—N distance slightly increases (to 0.375 nm) and a second shell comprising six water molecules is formed at a distance of 0.420 nm. For solutions with molar ratios of 1 : 40 and 1 : 60, the optimal models proved to be similar: they contain isolated hydrated Cd^{2+} and NO_3^- ions. Each cation coordinates six water molecules in the first coordination sphere and eight molecules in the second sphere.

X-ray diffraction data for aqueous solutions of cadmium phosphate showed the presence of inner-sphere $Cd(H_2O)_{6-x}(OPO_3H_2)^{2-x}$ complexes where the phosphate O atoms have replaced the water molecules in the hydrated $Cd(H_2O)_6^{2+}$ ions. The PO_4^{2-} anion is located near the cation, the Cd^{2+}—O—P angle being equal to 130°.[163]

The results obtained by Raman spectroscopy suggest that the Cd^{2+} ion in an aqueous solution of cadmium perchlorate forms a stable first coordination sphere comprising six water molecules and a second sphere of twelve water molecules, while ion pairs with perchlorate anions are totally missing at any concentration. Due to the polarization effect of the Cd^{2+} ion, the water molecules located closer to it form strong hydrogen bonds with the water molecules of the second sphere.[164] This is in good agreement with X-ray diffraction data for aqueous solutions of cadmium perchlorate where the Cd^{2+}—OH_2 bond length was also determined to be 0.231±0.002 nm.[165]

Thus, the Cd^{2+} ion coordinates six water molecules in the first coordination sphere at a distance of 0.225—0.230 nm, forms a second coordination sphere at an average distance of 0.450 nm, and exhibits a clear-cut tendency for the formation of ion pairs.

Hydrated complexes of Hg^{2+} ion. Only a few studies dealing with the structure of aqueous solutions of mercury salts have been published. Solutions of mercury(II) perchlorate in aqueous $HClO_4$ with an Hg^{2+} concentration ranging from 2 to 4.6 mol L^{-1} have been investigated by X-ray diffraction.[166] It was found that Hg^{2+} ions have both the first coordination sphere consisting of six water molecules at a distance of 0.240 nm and the second sphere separated from the cation by 0.420 nm. Hydrolysis of Hg^{2+} perchlorate changes the Hg^{2+}—O distances in the first sphere, two bonds being shortened to 0.20—0.21 nm and the other four bonds being elongated to 0.250 nm. Binuclear complexes with an Hg^{2+}—Hg^{2+} distance equal to 0.364 nm were also found in the solutions.

Aqueous solutions of $HgCl_2$, $HgBr_2$, and $Hg(CN)_2$ have been studied by EXAFS.[167] The cation—anion distances for mercury chloride and bromide were found to be 0.229(2) and 0.242(2) nm, respectively, while the Hg—C and Hg—N distances for $Hg(CN)_2$ amounted to 0.204(2) and 0.318(3) nm. Low intensity of the EXAFS signal was explained by distortion of the first coordination sphere of the cation, which is due to the second-order Jahn—Teller effect.

Study of the IR spectra of aqueous solutions of mercury(II) nitrate revealed the formation of inner-sphere complexes and distortion of the nitrate ion geometry caused by the formation of ion pairs.[168] The solutions contain not only coordinated but also free nitrate ions; the metal—oxygen interactions were found to involve a significant contribution of covalent binding.

Aqueous solutions of mercury(II) nitrate with molar ratios of 1 : 25 and 1 : 40 have been studied by X-ray diffraction analysis.[169,170] The model describing most adequately the structure of a more concentrated solution is an ionic triad with Hg^{2+}—N distances of 0.375 nm and an Hg^{2+}—O—N bond angle of 125°. On dilution of the solution, this angle increases to 139°. Besides two O atoms of the nitrate ion, the local environment of the cation includes two water molecules at 0.250 nm distance from the metal and four water molecules forming the second coordination sphere at a distance of 0.405 nm.

Structural features of the hydrated complexes of double-charged d-element cations. The foregoing data indicate that Zn^{2+}, Cd^{2+}, and Hg^{2+} d-element ions exhibit fairly similar structural properties, namely, an octahedral coordination sphere, the trend for the formation of both contact and solvent-separated ion pairs, and the presence of a second coordination sphere. The increase in the ion size in this series does not entail any significant changes in the nature of hydrated complexes, other than the regular increase in the distance between the cation and the coordinated water molecules (see Fig. 3).

Structures of hydrated complexes formed by Group III metal ions

Hydrated complexes of Al^{3+} ion. Numerous structural studies of the hydrated complex of the Al^{3+} ion have shown rather convincingly a coordination sphere of six water molecules at an average distance of 0.190 nm, the presence of a second coordination sphere at a distance of 0.400 nm, and the possible formation of ion associates. These conclusions are illustrated by the publications discussed below.

It has been shown by X-ray diffraction that in an aqueous solution of aluminum nitrate, the Al^{3+} ion coordinates six water molecules in the first sphere distant by 0.190—0.198 nm from the ion. In turn, these molecules are bound by short straight hydrogen bonds to 12 water molecules of the second coordination sphere separated from the cation by 0.410—0.415 nm.[171] Similar results have been obtained for solutions of aluminum nitrate in a publication,[172] according to which the NO_3^- ion is not incorporated in the first hydration shell of the cation. An identical structural environment of the cation was found by X-ray diffraction for 1 and 2 *M* aqueous solutions of aluminum sulfate containing 0.1 *M* HCl.[173] According to NMR data, the Al^{3+} and SO_4^{2-} ions interact with each other to give an outer-sphere complex with the SO_4^{2-} ion being a part of the second coordination sphere of the cation.[174] Ultrasound absorption measurements for 0.05, 0.1, and 0.15 *M* aqueous solutions of aluminum sulfate showed the presence of two relaxation effects, which are related in the researchers´ opinion, to the stepwise formation of ion pairs separated by one and two hydration shells.[175]

Examination of the Raman spectra of aqueous solutions of aluminum chloride, nitrate, and perchlorate provided evidence for the stability of the $Al(H_2O)_6^{3+}$ ion and for the absence of contact ion pairs in a concentration range of 0.21—3.14 mol L^{-1}. Conversely, a solution of aluminum sulfate was found to contain an aluminum—sulfate complex. The *ab initio* geometry optimization and frequency calculations also confirmed the presence of the $[Al(OH_2)_{18}]^{3+}$ cluster with six water molecules in the first sphere and twelve water molecules in the second sphere.[176]

The above data provide the conclusion that the Al^{3+} ion tends to form ion pairs and more complex associates in aqueous solutions of aluminum sulfate, but this tendency is lost for salts with other anions.

Hydrated complexes of scandium group ions in aqueous solutions. Scandium group ions, Sc^{3+}, Y^{3+}, and La^{3+}, have the electron configuration of inert gases (d^0); this makes their interactions clearly electrostatic.

Hydrated complexes of Sc^{3+} ion. The Sc^{3+} ion has the smallest ion radius ($r = 0.075$ nm) in this group, which is intermediate between the radii of the Al^{3+} ion (0.054 nm) with a C.N. of six and the Y^{3+} ion (0.90 nm) with a C.N. of eight.[8] It has been considered for a long period that the Sc^{3+} ion coordinates six water molecules, by analogy with the structure of a large number of studied crystal hydrates with oxygen-containing ligands.[177] However, recent publications[178,179] showed that the C.N. of the Sc^{3+} ion varies over a broad range from three to nine in complexes with oxygen-donor ligands. The coordination sphere of the Sc^{3+} ion in crystal hydrates can have different parameters and its configurations can differ only slightly in energy. Based on the chemical properties of Sc^{3+}, one should expect lability of this ion in ligand exchange reactions in aqueous solutions.

Recent investigations of aqueous solutions of scandium salts carried out by Raman spectroscopy and model calculations led to the conclusion that the C.N. of Sc^{3+} is six and the coordination sphere is centrally symmetric.[180] The Sc^{3+}—O bond length calculated by the molecular orbital approach is 0.218 nm.

The clearly pronounced susceptibility of the hydrated Sc^{3+} ion for hydrolysis has been established rather long ago.[181] Both polynuclear ($Sc_2(OH)_2{}^{4+}$, $Sc_3(OH)_4{}^{5+}$, and $Sc_4(OH)_6{}^{6+}$) and mononuclear ($ScOH^{2+}$ и $Sc(OH)_2{}^{+}$) ions have been found in solutions of scandium salts.[182]

As shown by Raman spectroscopy, the formation of inner-sphere complexes distinguishes the Sc^{3+} ion from Y^{3+} and La^{3+} ions.[183] It was also found that the behavior of the Sc^{3+} ion in complexation with nitrate anions differs from that of lanthanide ions. Using Raman spectroscopy data for solutions of scandium nitrate, the hydration number of the cation was found to be seven.[184]

X-ray diffraction and EXAFS studies of aqueous solutions of $Sc(ClO_4)_3$ and $Sc(CF_3SO_3)_3$ under ambient conditions also indicate that the Sc^{3+} ion coordinates about seven water molecules located at 0.218 nm distance.[185] This result is in good agreement with the conclusions of a publication[186] in which aqueous solutions of $ScCl_3$ and $Sc(ClO_4)_3$ in the glassy state were studied by Raman spectroscopy and it was found that the structures of hydrated scandium ions do not correspond to the expected octahedral configuration existing in the case of $[Al(H_2O)_6]^{3+}$.

Note that a nearly linear correlation was found[186] between the ν_1 value for the symmetric stretching vibration of the $M—OH_2$ bond and the reciprocal squared $M—OH_2$ distance for Group III metal ions with identical C.N. Using the $Sc^{3+}—OH_2$ distance obtained by EXAFS (0.218 nm) and the ν_1 value for aqueous solutions of $ScCl_3$ and $Sc(ClO_4)_3$ in the glassy state, the analogous $1/r^2{}_{M—O}$ ratio for the considered ion was introduced into this dependence.[186] The point corresponding to the Sc^{3+} ion lies neither on the line for ions with C.N. = 8 nor on the line for ions with C.N. = 9. If the hydrated complex of the Sc^{3+} ion were a trigonal prism, as has been found for the crystal,[187] the ν_1 value would fit in the line for C.N. = 9. However, this does not the case; in conformity with the proposed correlation, the C.N. of this ion is assumed to be lower than eight.

However, in the structure of the $[Sc(H_2O)_9](CF_3SO_3)_3$ crystal, the Sc^{3+} ion is surrounded by nine water molecules with six short $Sc^{3+}—OH_2$ bonds (0.2171 nm) and three long bonds (0.247 nm) in a trigonal configuration,[187] as was found for the isomorphous $[Ln(H_2O)_9](CF_3SO_3)_3$ complex (Ln is a lanthanide ion) in the crystalline state.

According to X-ray diffraction data, in an aqueous solution of scandium chloride, the Sc^{3+} ion coordinates six water molecules located 0.218 nm away from the cation.[188] The solution also contains $Sc^{3+}—Cl^-$ contact ion pairs with an interatomic distance of 0.263 nm, which is indicative of a number of the closest neighbors of the cation equal to seven. The second coordination sphere of the Sc^{3+} ion is formed at a distance of 0.416 nm. The number of water molecules around the Cl^- ion is about five; this is somewhat below the usual value and has been explained by the formation of ion pairs.

A model that implies a cation C.N. close to seven and a distance to the first coordination sphere equal to 0.215 nm was obtained as the most adequate one for 1 and 3 *M* aqueous solutions of scandium perchlorate.[188] The cation also forms a second coordination sphere involving water molecules and perchlorate O atoms and located 0.410 nm away from the cation. This means that approximately two water molecules of the second coordination sphere are linked to one water molecule of the first sphere. Solvent-separated ion pairs formed by Sc^{3+} and $ClO_4{}^-$ are characterized by Sc^{3+}—Cl distances of 0.490—0.510 nm and Sc^{3+}—O distances of 0.410 and 0.535—0.540 nm; one perchlorate O atom is assumed to be a part of the second coordination sphere of Sc^{3+} and the other three atoms are directed toward the solvent. It was difficult to establish unequivocally the orientation of the perchlorate ion toward Sc^{3+}.

As the solution is diluted to a concentration of 1 mol L^{-1}, the Sc^{3+} C.N. remains the same as for a 3 *M* solution, but the amount of ion pairs in the system decreases. An increase in the proportion of free solvent entails an increase in both the hydration number of the perchlorate ion and the number of water molecules in the second coordination sphere of the cation.

Hydrated complexes of Y^{3+} ion. The Y^{3+} ion is rather similar to heavy lanthanide ions in size and chemical behavior. The similarity of the ion radii has been employed[189,190] in X-ray diffraction experiments dealing with the structure of hydrated lanthanide ions in aqueous solutions for isomorphous substitution.

It has been established by EXAFS[191] that the Y^{3+} ion coordinating eight water molecules is the predominant species in solutions of yttrium chloride and bromide in the concentration range from 2.1 to 0.6 mol L^{-1}. The average Y^{3+}—OH_2 distances were determined to be 0.233±0.002 nm for a YBr_3 solution and 0.234±0.002 nm for a YCl_3 solution.

An X-ray diffraction study of equimolar concentrated aqueous solutions of yttrium chloride and bromide has shown[192] that the cation coordinates eight water molecules at a distance of 0.236 nm. A similar result was derived by combining the X-ray diffraction and EXAFS approaches.[193] The Y^{3+}—OH_2 distance determined more precisely from the EXAFS data amounts to 0.2365 nm. The presence of a second coordination sphere distant by 0.440 nm from this cation and consisting of ~16 water molecules was noted. One more validation of these results was obtained by EXAFS for aqueous solutions of YBr_3 in a concentration range from 0.005 to 2.0 *m*.[194] It was concluded that the Y^{3+} ion coordinates eight water molecules, arranged around the cation as a symmetric square antiprism at a distance of 0.235 nm. The lack of contact ion pairs of the Y^{3+}—Br^- type was also noted.

Recent results obtained by anomalous X-ray diffraction for a 3.5 *m* aqueous solution of yttrium chloride confirmed the presence of two clearly definable coordination spheres around the cation. The first sphere located at a distance of 0.230 nm involves eight water molecules, while the second sphere spaced by 0.477 nm contains both water molecules and chloride ions.[195]

Thus, one can conclude with a high degree of reliability that the Y^{3+} ion in aqueous solutions has a C.N. equal to eight but the water molecules are located at a distance of 0.233 nm from the coordinating center. A second coordination sphere is also formed at a ~0.440 nm distance from the cation.

Hydrated complexes of La^{3+} ion. The assumption that the C.N. of lanthanide ions in aqueous solutions changes from nine to eight for ions from the middle of the lanthanide row, which was called the "gadolinium effect", has now been generally recognized.[196—198] This review gives structural parameters for solutions containing salts of one member of this row, namely, the La^{3+} ion.

The results of X-ray diffraction study with isomorphous substitution of an aqueous solution of lanthanum selenate with a molar ratio of 1 : 70 provided a C.N. value equal to eight and a distance to the coordinated water molecules equal to 0.256 nm. The presence of contact ion pairs with a La^{3+}—O—Se bond angle of 140° was also noted; in the researchers´ opinion,[199] this attests to a monodentate mode of binding. No outer-sphere complexes were found. More recent studies testify in favor of a lanthanum C.N. equal to nine. X-ray diffraction data for a concentrated aqueous solution of $LaCl_3$ indicate[200] that the $[La(H_2O)_9Cl_2]^+$ complex surrounded by water molecules of the second coordination sphere is the key structural unit of this solution.

X-ray diffraction and EXAFS studies of the structure of the hydrated La^{3+} ion in a lanthanum perchlorate solution showed that this cation coordinates nine water molecules arranged at different distances. The distances to the nearest water molecules of the hydration sphere were 0.252(2) nm, those to more remote molecules were 0.265(3) nm. X-Ray diffraction data point to the presence of a second coordination sphere comprising eighteen water molecules located 0.463(2) nm away from the cation.[201]

Thus, the La^{3+} ion has a C.N. of nine, forms a second coordination sphere, and can form contact ion pairs with counter-ions.

Structural features of the hydrated complexes of scandium group ions. Thus, analysis of the structural aspects of hydration in the series of triple-charged cations (Sc^{3+}, Y^{3+}, and La^{3+}) reveals an increase in the C.N. following an increase in the ion radius from seven (Sc^{3+}) to eight (Y^{3+}) and to nine (La^{3+}) (Fig. 4). All the cations form a second coordination sphere and are involved in association to give both contact and solvent-separated ion pairs. The effect of the size of triple-charged cations on the parameters of the second coordination sphere and on the degree of formation of ion pairs is difficult to estimate due to the high charge density on the ions and formation of rather stable hydrated complexes.

Hydrated complexes of gallium group ions in aqueous solutions. *Hydrated complexes of Ga^{3+} ion*. The Ga^{3+} ion is situated in Group III of the Periodic Table and is capable of both ionic and covalent interactions in solutions. The

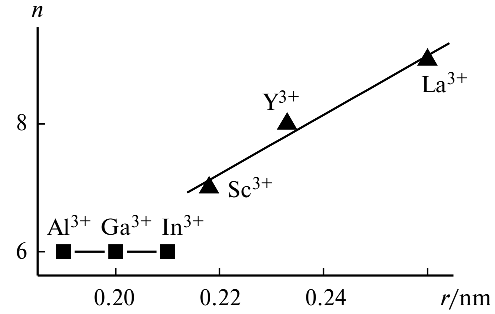

Fig. 4. Dependence of the coordination numbers (*n*) of triple-charged metal ions on the interparticle distances between the ion and the water molecules of the first coordination sphere (*r*).

structure of aqueous solutions of gallium salts is rather poorly studied and published information dealing with the relevant subjects is scarce.

A 1.5 *M* solution of gallium perchlorate has been studied by X-ray diffraction technique in a known work;[202] in the same publication, more dilute solutions (0.005—1.0 mol L^{-1}) were investigated by EXAFS. It was shown that Ga^{3+} ion coordinates six water molecules in the first sphere at a distance of 0.1955 nm and twelve molecules in the second sphere at 0.405 nm. According to the drawn conclusions,[202] neither the concentration, nor the type of counter-ion (solutions of nitrates were also considered) influence the structural parameters of the cation hydration.

When looking for some other information concerning the systems under interest, we turned to studies dealing with the influence of a temperature decrease on the structure of solutions of gallium halides. Raman spectroscopy showed that under usual conditions, solutions of gallium halides contain both octahedrally hydrated Ga^{3+} ions and tetrahedral $[GaX_4]^-$ complexes ($X = Cl^-, Br^-$).[203,204] Hence, an equilibrium between these complexes and hydrated Ga^{3+} ions occurs in the system, the equilibrium position depending probably on the molar ratio of cations and anions.

Study of a 3 *M* solution of gallium perchlorate, a 2 *M* solution of gallium bromide, and a 1.69 *M* $GaBr_3$—4.05 *M* LiBr system with a high $Ga^{3+} : Br^-$ molar ratio using Raman spectroscopy, EXAFS, and X-ray diffraction provided the following information.[205] Only hydrated Ga^{3+} ions were found in the gallium perchlorate solution, while both $Ga(H_2O)_6{}^{3+}$ ions and $[GaBr_4]^-$ complexes with Ga^{3+}—OH_2 distances of 0.196 nm and Ga^{3+}—Br^- distances of 0.233 nm were detected in the $GaBr_3$ solution. In addition, the Ga^{3+} forms a second coordination sphere at 0.403 nm distance, and the hydration shell of the Br^- ion occurs at a distance of 0.335 nm. The content of gallium bromide complexes in a 2.01 *M* solution of $GaBr_3$ is relatively low, but it markedly increases in the 1.69 *M* $GaBr_3$—4.05 *M* LiBr solution. The methods used did not show any significant amounts of intermediate species between the $Ga(H_2O)_6{}^{3+}$ and $[GaBr_4]^-$ ions.

Hydrated complexes of In^{3+} ion. The data obtained for aqueous solutions of indium bromide (3.06 mol L^{-1}) and chloride (3.22 mol L^{-1}) indicate[206] that the associates formed in the system consist of two anions coordinated around the In^{3+} ion, which is hydrated by five water molecules.

The structure of the hydrated In^{3+} ion in aqueous solutions of indium perchlorate and nitrate was determined by X-ray diffraction (solutions with a concentration of 1.5 mol L^{-1}) and EXAFS (0.005—1.0 mol L^{-1}). The cation coordinates six water molecules in the first coordination sphere at a distance of 0.2131(7) nm. Each of these molecules is linked by hydrogen bonds to two water molecules in the second coordination sphere, which are 0.413(1) nm distant from the cation. Neither electrolyte concentration nor the nature of the counter-ion affect the In^{3+}—O distance for the first coordination sphere.[202]

Aqueous solutions of indium perchlorate and nitrate have been studied[207] by EXAFS in the temperature range from 25 to 350 °C. It was shown that the In^{3+} ion coordinates six water molecules in the first coordination sphere at a 0.214±0.001 nm distance. Upon the addition of 1.0 *m* $HClO_4$, the $In(ClO_4)(H_2O)_5{}^{2+}$ ion pairs are formed in which the In^{3+}—$O(ClO_4{}^-)$ bond length is 0.312—0.314 nm. In the $InCl_n(H_2O)_{6-n}{}^{3-n}$ complex ($0 \le n \le 4$), having an octahedral geometry, the In^{3+}—Cl and In^{3+}—O distances are 0.240 and 0.213 nm, respectively.

Thus, the C.N. usual for the In^{3+} ion is six and the distances to the coordinated water molecules are 0.231 nm. The second coordination sphere spaced by 0.413 nm and the tendency of the In^{3+} ion for the formation of ion pairs largely determine the structure of aqueous solutions of its salts.

Hydrated complexes of Tl^{3+} ion. In solutions of thallium perchlorate, the cation coordinates six water molecules in the first coordination sphere and forms a second coordination sphere 0.430 nm distant from the cation.[208,209]

Structural features of the hydrated complexes of Group III metal ions. To summarize the results of the structural description of the hydration of the Al^{3+} ions and gallium group metal cations (Ga^{3+}, In^{3+}, and Tl^{3+}), it can be concluded that these cations are rather similar to each other as regards structure formation in solutions (see Fig. 4). All these ions form both a first coordination sphere including six water molecules and a second coordination sphere whose parameters depend on a number of factors. In addition, all these cations exhibit a clear-cut tendency for complexation.

The hydrated complexes of gallium group ions differ from those found for scandium group ions. Whereas in the former case, cations have an octahedral coordination of water molecules, which virtually does not depend on the ion size, in the latter case, the C.N. of the ions depends on their size and increases from seven (Sc^{3+}) to eight (Y^{3+}) and nine (La^{3+}). This difference in the structural behaviors of the former and latter groups of cations with the same charge is mainly due to the difference in their electron configurations.

* * *

The results presented here allow one to interpret the dependence of the structural parameters of cation hydration in aqueous solutions without solvent deficiency on the cation size under ambient conditions.

For Group I—III of the Periodic Table, the C.N.s of metal ions in aqueous solutions increase along the groups with an increase in the cation—water distance. The correlations are regular; in the case of double-charged cations, the correlation is nearly linear.

Conversely, the cations of d-elements behave in a similar way in the formation of hydrated complexes irrespective of the ion size or even on the charge. They tend to form a first coordination sphere consisting of six water molecules, a second coordination sphere, and ion pairs and they are also prone to complex formation.

Having this scheme of structurization in solutions at hand, one can attempt to predict characteristics of some ions poorly accessible for investigation. Let us consider, for example, the K^+ ion. This ion falls out of the monotonic pattern of variation of the C.N. of single-charged ions *vs.* the cation—water interparticle distance, if the C.N. of K^+ is taken to be six or eight. However, after an analysis, the following assumptions can be made. The K^+ ion resembles the Ca^{2+} and Sc^{3+} ions (see Fig. 1) regarding a common feature, namely, the $3p^6$ electron configuration. For another series of ions with the same common feature, Na^+, Mg^{2+}, and Al^{3+}, this circumstance results in identical C.N. values equal to six. It can be expected that the hydrated complex of the K^+ ion would also bear a similarity with the ions that belong to the same group in terms of this feature, *i.e.*, Ca^{2+} and Sc^{3+}, in particular, its C.N. is expected to be close to seven. In this case, the uncertainty in the experimental results may be due both to the difficulty in investigating the hydration of the K^+ ion and to the instability of the coordination sphere; as a consequence, the C.N. values of both six and eight have been found.

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