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Comparative Analysis of Structural Parameters of the Nearest Surrounding of Nitrate and Perchlorate Ions in Aqueous Solutions of Electrolytes

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Abstract—Data on structural parameters of the nearest surrounding of nitrate and perchlorate ions in aqueous solutions under standard conditions have been generalized. Hydration numbers, interparticle distances, and ionic association types have been discussed and compared. The major difference between the ions is that nitrate ion tends to form ion pairs, whereas perchlorate ion does not.

Keywords: electrolyte solution, nitrate ion, perchlorate ion, structure, hydration number, interparticle distance, ionic association

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Discussion of structural parameters of the nearest surrounding of ions in aqueous solutions presumes generalization of a huge amount of experimental and simulation data. In a series of earlier papers data on hydrate complexes of monoatomic cations [1–3] and halide ions [4] have been reviewed. Determination of structure of hydrate complexes of anions (even monoatomic ones) is a challenge because their interaction with solvent is weaker than in the case of cations. Study of hydration and structuring of multiatomic anions (in particular, single-charged oxygen-containing NO_3^- and ClO_4^-) is even more complex, and the reported results are often contradictory.

This work aimed to generalize and critically compare the available data on structural parameters of the nearest surrounding of nitrate and perchlorate ions in aqueous solutions. The following parameters were considered: number of water molecules strongly interacting with the anion, distance between the central atom of the anion and the bound water molecules, ability of the anions to form ion pairs, and type of the ion pairs (if any formed). Furthermore, changes of the anion structure upon interaction with the solvent and cations were analyzed.

Structure of the Nearest Surrounding of NO_3^-

To date, a number of papers have been published describing the short-range ordering by nitrate ions in aqueous solutions. The presented results are contradictory; therefore, for clearer understanding, below we will analyze the different structural parameters reported in the literature in an individual manner.

Structure of nitrate ion. When in the gas phase, nitrate ion is planar with the O–N–O bond angles of 120° and the N–O and O–O bond lengths of 0.126 and 0.219 nm, respectively [5] (D_{3h} symmetry [6]). In polar solvents, the medium effects change electronic and geometry structure of the anion, including the symmetry change. For example, neutron diffraction study demonstrated that in certain alkali metal melt the N–O distance was of 0.1251 nm [7]. According to resonance Raman spectroscopy data for aqueous solutions of metal nitrates, the gas-phase symmetry of nitrate anion was distorted [8, 9]. Waterland et al. supposed that localization of negative charge at one of oxygen atoms of nitrate anion was energetically favorable, causing the stronger hydrogen bonds formation and polarization of surrounding solvent molecules. On the contrary, simulation of nitrate ion

Table 1. Structural parameters of the nearest surrounding of nitrate ion in aqueous solutions

System	Method[a]	N–O(H_2O) distance, nm	Coordination number of the anion	References
8 M NH_4NO_3	XRD	0.350	9	[17]
$AgNO_3$–$28H_2O$	″	0.317	43	[18]
2.53 M $Al(NO_3)_3$	″	0.339	6	[19]
4.72 M $Zn(NO_3)_2$	″	0.344	9	[20]
4.4 M $Mn(NO_3)_2$	″	0.344	9	[21]
4.54 M $Cd(NO_3)_2$	″	0.349	8.8	[22]
3 M $AgNO_3$	″	0.35	11	[23]
9 M $AgNO_3$	″	0.34	7.2	[23]
HNO_3–$25H_2O$	″	0.325	9	[24]
0.386 M $Ni(NO_3)_2$	IR	–	3.7	[25]
1 M KNO_3	MD	0.36	10–11	[26]
NO_3^-–$496H_2O$	″	0.351	7.9	[27]

[a] XRD is X-ray diffraction, IR is infrared spectroscopy, MD is molecular dymanics.

structure in the aqueous solution revealed that its symmetry remained intact, and the anion was planar [10].

Influence of nitrate ions on the solvent structure. Early papers investigating the structural changes of nitrate solutions dealt majorly with the ions influence on the solvent structure. IR spectroscopy data showed that nitrate ion disrupted the solvent structure [11, 12]; however, the effect was less pronounced than in the case of perchlorate ion.

Parameters of the nearest surrounding of nitrate ions. Early attempts to determine quantitative parameters of the nearest surrounding of nitrate ion failed. For instance, the X-ray diffraction analysis of aqueous solution of $Cr(NO_3)_3$ (2 mol/L) revealed that nitrate ion did not form any stable coordination sphere of the solvent molecules [13]. Similar studies did not detect any stable coordination sphere of nitrate ion in solutions of $Mg(NO_3)_2$ (2 and 4 mol/L) [14] and $Fe(NO_3)_3$ (0.776–2.482 mol/L) [15]. Presumably, the relatively weak interaction of nitrate ions with water was not observed in the presence of strongly hydrated multi-charged cations. NMR studies estimated the hydration number of nitrate ion equal to 0.5 [16].

In other X-ray diffraction studies it was shown that at developing models, describing experimental radial distribution functions, it was necessary to include discrete interaction of nitrate ion with water molecules. Some of the quantitative parameters of hydration sphere of nitrate ions are listed in Table 1.

As seen in Table 1, the distance between oxygen atoms of nitrate ion and those of water $O(NO_3^-)$–OH_2 was 0.288–0.300 nm, practically equal to the spacing between water molecules in the pure solvent (≈ 0.290 nm). Hence, that parameter could not be used to estimate the strength of hydrogen bonds between nitrate ions and water.

Besides those mentioned in Table 1, there were other papers dealing with structuring of nitrate solutions worth detailed discussion; their results are commented on hereinafter. In particular, X-ray diffraction study of aqueous solutions of sodium nitrate (5 and 7 mol/L) revealed the relatively strong interaction of the anion with three to six solvent molecules [28]. Moreover, ions associates were observed, with the hydrated cation interacting with more than a single nitrate ion. Neutron scattering studies demonstrated that five water molecules were located at the N–OH_2 distance of 0.340 nm in aqueous solutions of $NaNO_3$ (7.8 mol/L [29] and 10 mol % [30]). At the same time, similar investigation of solutions of ND_4NO_3 (12 and 18 mol/L) did not reveal the presence of any stable hydration sphere of the anion [31].

Study of some solutions of the group I metals, and zinc and cobalt nitrates [32] led to a conclusion that in dilute aqueous solutions nitrate ion was hydrated with nine water molecules located at an average distance N–OH_2 of 0.340–0.350 nm. Increasing the solution con-centration induced the formation of solvent-separated and contact ion pairs, those processes being accom-panied by dehydration of the anion. Further increase of the salts concentration led to the formation of more complex ion associates.

Nitrate ion clusters with variable number of water molecules were explored in simulation studies. It was shown that addition of one water molecule at the oxygen atom of nitrate ion extended the N–O bond with that atom, whereas the other N–O bonds became shorter [33]. Photoionization and theoretical simulation studies stated that the NO_3^-–nH_2O (n = 1–6) cluster in the gas phase was planar and three water molecules formed the first hydration sphere of the anion [34]. Three more water molecules constituted the second coordination sphere with no direct contact with the anion. Wang et al. [34] presumed that such cluster was extremely stable, and its structure would be preserved in the aqueous solutions. In the case of the NO_3^-–nH_2O (n = 1–8) system, three different types of the structure were observed, corresponding to the double symmetric bonds, single hydrogen bond, and to hydrogen bonds between the water molecules [35]. It was found that the anion location on the cluster surface was preferential over the corresponding structures with the inner anion location at $3 \leq n \leq 8$ [36]. Noteworthily, the surface location of nitrate anion with respect to the solvent molecules aggregate was considered favorable in the case of spatially constrained nitrate ion (in the cluster or at the interface boundary) [37]. IR spectroscopy studies revealed that the double hydrogen bond-ing was favorable in the cases of the clusters with $n \leq 4$ [38]. At $n = 4$, the planar symmetry was distorted, and hydrogen bonds between water molecules were formed. Up to $n = 6$ all water molecules in the cluster were bound to the nitrate ion to form its inner coordination sphere.

Molecular dynamics study revealed that in the case of the $4AgNO_3$–$248H_2O$ system the N–OH_2 distance was 0.35 nm, the number of oxygen atoms at that distance being equal to eight [39]; whereas in the case of the K^+–NO_3^-–$341H_2O$ system the N–OH_2 and O(NO_3^-)–OH_2 distances were 0.377 and 0.292 nm, respectively [40]. It was concluded in the latter study that water molecules were coordinated at oxygen atoms of nitrate ion rather than at the nitrogen atom, being located above and below the planar anion.

Analysis of NMR relaxation data showed that coordination number of nitrate ion equaled six [41]. The QM/MM molecular mechanics simulation of the NO_3^-–$199H_2O$ system confirmed that nitrate ion was surrounded with a clearly observed yet weakly bound first coordination sphere [42]. The coordinated molecules lability (fast exchange of the coordinated molecules) led to disruption of the solvent structure by nitrate ions.

As nitrate ions are found to weakly interact with water molecules, structural parameters of their hydration depends on a number of factors; that is the main reason of large scatter of the reported structural data. According to the set of above-reported data, the number of water molecules coordinated by nitrate ion is a function of the system concentration. Indeed, in most cases in the concentrated solutions the coordination number of nitrate ion equaled five, whereas in the cases of dilute solutions it was close to nine. Such trend was reliably confirmed by systematic studies of the similar solutions over a range of concentration. For example, for aqueous solutions of potassium nitrate at 333 K the anion coordination number decreased from 4.7 down to 3.5 as the concentration increased from 0.3 to 7.0 mol/L (Monte Carlo simulation and molecular dynamics) [43–45]. The increase in the concentration of the same salt aqueous solution from 1.9 to 7.5 mol/L was accompanied with decreasing number of water molecules in the nearest surrounding of the anion (the N–O distance of 0.370 nm) from 11.2 to 10.2 (X-ray diffraction analysis, neutron diffraction, and molecular dynamics) [46].

Ion association. Nitrate ions are known to form ion pairs, but the reports on the type of their coordination with cations are ambiguous. For example, Raman spectroscopy studies of solutions of various metal nitrates revealed that nitrate ion was deformed upon formation of the ion pairs (the anion symmetry was changed from D_{3h} to C_{2v}) [47]; that confirmed the cation coordination via oxygen atom of nitrate ions. At the same time, vibration spectroscopy demonstrated that Ag^+ and nitrate ions formed the ion pair with significant contribution of covalent interaction, the cation being located above the plane of nitrate ion [48].

The papers studying the structuring of aqueous solutions of metal nitrates can be roughly divided into two groups: those demonstrating formation of the contact-ion pairs and those revealing the solvent-separated associates (Table 2).

Several studies not mentioned in Table 2 are worth detailed comments. For example, luminescent spectroscopy of europium nitrate solutions revealed the formation of the inner-sphere ion pair with the cation hydration sphere containing 6.9 water molecules [69].

Type of the associates to be formed was found to be dependent on the cation nature. For instance, the $[Eu(NO_3)]^{2+}$ contact ion pairs and the $[Eu(NO_3)_2]^+$ triplets were detected in europium nitrate solutions, whereas in solutions of erbium nitrate (Er being chemically alike Eu) only the complexes with a single nitrate ion were exclusively stable [70]. An interesting example of influence of the cation nature was reported in [71] (Raman spectroscopy). At the molar ratio of 1 : 20, in the scandium nitrate solution the formation of ion associates with preferential type of the $[Sc(NO_3)]^{2+}$ and bidentate coordinated nitrate ion was observed; at the same time, no ion associates were found in the solutions of aluminum and gallium nitrates at the same molar ratio of the components.

X-ray diffraction studies allowed determination of interparticle distances in the formed associates. For example, contact ion pairs with the Er^{3+}–$N(NO_3^-)$ distance of 0.286 nm were found in erbium nitrate solutions (0.99 and 2.89 mol/L) [72]. Contact ion pairs with the Th^{4+}–$N(NO_3^-)$ distance of 0.31 nm were detected in solutions of thorium nitrate (0.99, 1.06, and 2.52 mol/L) [73]. In both cases nitrate ions interacted with the cation as bidentate ligands. Those results in combination with the data summarized in Table 2 demonstrated that the bidentate coordination for nitrate ion was typical of multi-charged cations or for highly concentrated systems.

X-ray diffraction analysis and Raman spectroscopy studies confirmed the formation of contact ion pairs with the Ca^{2+}–$N(NO_3^-)$ distance of 0.300–0.310 nm in aqueous solutions of calcium nitrate (3.6 and 6.0 mol/L) [74, 75]. Similarly, contact ion pairs were observed in solutions of manganese nitrate (4.4 mol/L) [21] and cadmium nitrate (4.54 mol/L) [22]. In those ion pairs nitrate ion acted as monodentate ligand, and the cation was located in the nitrate ion plane, the M^{2+}–O–N bond angles being of 125° (M = Mn) and 118° (M = Cd). Similar type of ion pairs was found in aqueous solutions of silver nitrate (3 and 9 mol/L) [23, 76]. The Ag^+–N distance was 0.315 nm (3 mol/L) and 0.326 nm (9 mol/L), whereas the Ag^+–$O(NO_3^-)$ distance was 0.309 nm independently of the concentration. Contact ion pairs with the Cu^{2+}–N distance of 0.303 nm (1.5 mol/L) and 0.307 nm (3.0 mol/L) were revealed by X-ray diffraction analysis in solutions of copper nitrate [77]. EXAFS spectroscopy showed that nitrate ions formed contact ion pairs with lanthanide cations (Nd^{3+}–Lu^{3+}, 1 mol/L) at relatively low anion concentration (2 mol/L HNO_3) [78]. The Ln^{3+}–$O(NO_3^-)$ distance was 0.24 to 0.26 nm depending on the cation nature. As nitrate ion was located 0.01 nm farther from the cation than did water molecule, the cation was bound to nitrate ion somewhat weaker than to the solvent molecule.

Raman spectroscopy study of magnesium nitrate solutions showed that the hydrated ions were isolated in dilute solution, and the contact ion pairs appeared at the salt to water molar ratio of 1 : 6 or higher [79]. Similar behavior was confirmed in [80] (IR and Raman): the non-contact ion pairs were detected at magnesium nitrate concentration above 2.5 mol/L, further increase of the salt concentration yielded to the formation of contact ion pairs with monodentate coordination of nitrate ion to the cation. At higher concentration part of the anions showed bidentate coordination. X-ray diffraction detected the $Cd^{2+}(H_2O)$–ONO_2^- non-contact ion pairs in aqueous solution of $Cd(NO_3)_2$ (4.54 mol/L) [22]. Analysis of Raman spectra of aqueous solutions of sodium nitrate (1–8 mol/L) showed that independently hydrated ions, solvent-separated ion pairs, contact ion pairs, or ion aggregates existed in the solution depending on its concentration [81]. The transition between independently hydrated ions and non-contact ion pairs was found in aqueous zinc nitrate solutions with increasing the concentration above 3.5 mol/L by means of IR spectroscopy [82].

There were several reports on co-existence of various types of the associates in the solution. For example, ultrasound absorption studies demonstrated that both inner- and outer-sphere ion pairs were present in aqueous solutions of lanthanide nitrates [83–85]. According to analysis of vibration spectra of a solution of indium nitrate (1.117 mol/L), both the

Table 2. Types of ion associates of nitrate ions

Salt	Concentration	Associate type[a]	Method	References
$In(NO_3)_3$	4.2 mol/L	CIP	Raman spectroscopy	[49]
$Ca(NO_3)_2$	2.08–13.15 mol/kg	″	″	[50]
$Ln(NO_3)_3$	0–0.33 mol/L	nCIP	Solvent extraction	[51]
$Zn(NO_3)_2$	Saturated solution	CIP	IR and Raman spectroscopy	[52]
$Zn(NO_3)_2$ and NH_4NO_3	$3Zn(NO_3)_2–2NH_4NO_3–15H_2O$	″	″	[52]
$Nd(NO_3)_3$	0.1 mol/L	″	Differential absorption spectroscopy (visible)	[53]
$Ca(NO_3)_2$	0.5–7.2 mol/L	nCIP	Raman spectroscopy	[54]
$K_2Ce(NO_3)_4$	1 mol/L	CIP	IR and Raman spectroscopy	[55]
$Ce(OH)_4+HNO_3$	$[NO_3^-]/[Ce^{4+}] = 3$	bi	″	[55]
$Er(NO_3)_3$	0.6–1.6 mol/L	CIP	Dilatometry, electron microscopy, NMR	[56]
$Cd(NO_3)_2$	4.55 mol/L	CIP (mono)	IR and Raman spectroscopy	[57]
$Hg(NO_3)_2$	4.6 mol/L	″	″	[58]
$Bi(NO_3)_3$	(1) $[Bi^{3+}] = 0.98$ mol/L, $[NO_3^-] = 1.47$ mol/L (2) $[Bi^{3+}] = 0.55$ mol/L, $[NO_3^-] = 1.90$ mol/L	CIP (bi)	″	[59]
$Dy(NO_3)_3$	up to 2.4 mol/L	″	NMR	[60]
$Gd(NO_3)_3$	1.12 mol/L 3.06 mol/L	CIP (mono+bi)	IR and Raman spectroscopy	[61]
$Ce(NO_3)_3$	0.5–3.0 mol/L	″	″	[62]
$Sr(NO_3)_2$	0.25–2.70 mol/L	CIP (triplets)	Raman spectroscopy	[63]
$Mg(NO_3)_2$	≥2 mol/L	CIP	″	[64]
$Ca(NO_3)_2$	0.9 mol/L	″	″	[65]
$La(NO_3)_3$	$La(NO_3)_3–20H_2O$	CIP (mono+bi)	″	[66]
$LiNO_3$	≥1 mol/L	CIP	″	[67]
$Cd(NO_3)_2$	≥0.2 mol/L	″	″	[67]
$Mg(NO_3)_2$	0.015–5.28 mol/kg	nCIP	″	[68]

[a] (CIP) is contact ion pair, (nCIP) is non-contact ion pair, (mono) is monodentate coordination of nitrate ion, (bi) is bidentate coordination of nitrate ion, (mono+bi) is of mono- and bidentate coordinations of nitrate ions.

$[In(OH_2)_5(NO_3)]^{2+}$ inner-sphere and the $[In(OH_2)_6]^{3+}\cdot NO_3^-$ outer-sphere complexes co-existed [86]. After dilution to 0.534 mol/L, the inner-sphere complexes decomposed, and the number of the outer-sphere ones increased. In the even more dilute solution (0.312 mol/L), the ions were independently hydrated. Various types of ion associates, including dimers, triplets, solvent-separated ion pairs, and more complex clusters were present in aqueous solutions of potassium nitrate (Monte Carlo simulation, 333 K, 0.302–6.994 mol/L) [45].

To summarize, in dilute aqueous solutions, when the number of the solvent molecules is enough to level off the effect of the cation nature, each oxygen atom of nitrate ion formed three hydrogen bonds with the nearest water molecules. The anion hydration sphere consisting of nine water molecules located at the $N–OH_2$ distance of 0.340–0.350 nm was thus formed. Increasing the solution concentration induced dehydration of the anion to form consequently the solvent-separated and the contact ion pairs. When in the contact ion pair, nitrate ion can act either as mono- or as bidentate ligand, the latter coordination being typical of the associates with multi-charged cations. Further increase of the solution concentration can be accompanied with the formation of more complex associates. The types of formed ion associates and the concentration ranges of their stability depend on the cation nature.

Structure of the Nearest Surrounding of ClO_4^-

Structure of perchlorate ion. Perchlorate ion is a single-charged anion, larger than nitrate one. According to X-ray diffraction analysis, perchlorate ion in aqueous solution is a regular tetrahedron with the Cl–O distance of 0.143 nm and the O–O one of 0.234 nm [87, 88].

Influence of perchlorate ions on the solvent structure. Perchlorate ion is known to interact with water molecules via weak hydrogen bonds [89] and to disrupt the solvent structure [90–95]. The interaction weakness is a key reason of the complications that arise when analyzing the data on perchlorate nearest surrounding, in particular, that obtained by X-ray diffraction [96].

Parameters of the nearest surrounding of perchlorate ions. Studies of structural parameters of the nearest surrounding of perchlorate ion are scarcer than those in the case of nitrate ion. Neutron scattering study of aqueous solution of sodium perchlorate (3.25 mol/L) detected 4–5 water molecules in the nearest surrounding of the anion located at 0.37 nm from the chlorine atom [97]. Parameters of the nearest surrounding of the anion were estimated by X-ray analysis as well. For example, the $Cl–OH_2$ distance was 0.357 nm in solution of silver perchlorate at the molar ratio of 1 : 20 (the number of coordinated water molecules, 25.6, was highly overestimated) [18]. In the solutions of the same salt (3 and 9 mol/L) the $Cl–OH_2$ distance to approximately eight water molecules was 0.370 nm [23]. Coordination number of perchlorate ion was found equal to eight, the $Cl–OH_2$ distance being 0.380 nm in solutions of lanthanide perchlorates (1–3 mol/L) [98].

Molecular dynamics simulation of structure of sodium perchlorate solution (2.2 mol/L) showed that the anion hydration shell consisted of eight water molecules located at the $Cl–O(H_2O)$ distance of 0.368 nm [99]. Water molecules distribution around the anion was uniform, pointing at its low hydration ability. IR spectroscopy studies of aqueous solutions of nickel perchlorate allowed determination of the anion coordination number of 4.6 ± 0.8 (0.20–0.96 mol/L) [100] and 3.8 ± 0.3 (0.384 mol/L) [25]. In the latter case, the $O(ClO_4^-)–OH_2$ distance was 0.307 ± 0.001 nm [25].

X-ray diffraction analysis of aqueous solutions of perchloric acid as well as lithium, sodium, and magnesium perchlorates showed that coordination number of the anion was a function of both the electrolyte concentration and the counterion nature [32, 101–103]. In particular, dilution of the solutions led to the increase in the perchlorate ion coordination number from four to ten ($HClO_4$), from eight to twelve ($LiClO_4$), and from six to ten [$NaClO_4$ and $Mg(ClO_4)_2$]. Hence, perchlorate ion can coordinate up to twelve water molecules; however, such hydration state is not always attained. In the cases of all studied systems except $NaClO_4–5H_2O$, independent hydration of ClO_4^- was observed, confirming the weak tendency of the ions towards association. The formation of contract ion pairs in the said exceptional case was due to the solvent deficit and was in good agreement with the abnormal electrical conductivity of concentrated sodium perchlorate solutions [104].

X-ray diffraction analysis and EXAFS spectroscopy were applied to structural study of aqueous solutions of gallium, indium, and chromium(III) perchlorates at 1.5 mol/L; the coordination number was 4.5 ± 0.7, the $Cl–OH_2$ and $O(ClO_4^-)–OH_2$ distances being 0.368 ± 0.003 nm and 0.305 ± 0.002 nm, respectively [105].

Ion association. Perchlorate ion is known for its low ability to form associates with cations. For example, Raman spectroscopy study of solutions of 17 perchlorates revealed possibility of the associates formation in three cases only (Tl^+, Mn^{2+}, and La^{3+}) [106]. The same method applied to the study of lithium (1–4 mol/L) and sodium (1–5 mol/L) perchlorates [107] revealed no associates formation. Perchlorate solutions are often used to study cations hydrations, as such choice of the anion allows for keeping hydration sphere of cation intact.

However, several papers reported on formation of contact ion pairs involving perchlorate ions. In particular, X-ray diffraction analysis of aqueous solutions of silver perchlorate (3 and 9 mol/L) revealed the formation of contact ion pairs, the ClO_4^- ion acting as monodentate ligand [23]. Further, ion pairs formation was detected in solutions of americium(III) perchlorate [108].

IR spectroscopy studies confirmed the presence of water-separated ion pairs in sodium perchlorate solutions (below 6 mol/L), the ion pairs turned into the contact ones as the salt concentration was up to 8 and 10 mol/L [109]. Formation of contact ion pairs in solutions of sodium perchlorate was additionally confirmed by conductometry [110], NMR [111–113], Raman [114], and vibration spectroscopy [115] studies; however, the reported concentration ranges of the contact ion pairs existence reported in the listed papers were contradictory. Outer-sphere ion pairs were detected in solutions of europium perchlorate by means of fluorescence spectroscopy [116, 117]. The non-contact ion associates of ClO_4^- ion were reported in the case of aqueous solution of iron(III) perchlorate as well [118].

The effect of the cation nature on ionic association of perchlorate anion was investigated in [119] using a combination of spectroscopy methods (IR, Raman, and NMR). It was demonstrated that contact and non-contact ion pairs were present in solutions of strontium and calcium perchlorates; the threshold concentration of the association being lower in the case of the calcium salt. For magnesium perchlorate, no ion association was observed up to a concentration of the saturated solution.

Molecular dynamics simulation of structure of sodium perchlorate solution (2.2 mol/L) confirmed formation of non-contact ion pairs [99]. The non-contact ion pairs were observed in aqueous solutions of copper perchlorate by EXAFS spectroscopy, the higher salt concentration enhancing the association [120]. X-ray diffraction analysis showed the formation of contact iron pairs at very high concentration of erbium perchlorate [121], whereas no contact pairs were found in solutions of thorium perchlorate at all [122]. Even the non-contact ion pairs did not exist in solution of $Th(ClO_4)_4$ (0.99 mol/L); perchlorate ion entering the second coordination sphere of the cation at the salt concentration of 2.5 mol/L (perchlorate ion acted as bidentate ligand). Ab initio simulation demonstrated that bidentate coordination of the anion was preferential over mono- or tridentate one in the course of the $Li^+–ClO_4^-$ ion pair formation [123].

Formation of the $M\cdots(H_2O)_n\cdots ClO_4^-$ non-contact ion pairs was detected by means of spectroscopy in aqueous solutions of lithium, sodium, and magnesium perchlorate at concentrations below 3 mol/L [124]. Raman spectroscopy studies confirmed the absence of contact ion pairs in aqueous solutions of calcium [75], zinc [125], scandium [126], and manganese [127] perchlorates over a wide concentration range.

Generalizing the above-discussed studies, it should be noted that perchlorate ion weakly coordinates water molecules and practically does not form contact ion associates in aqueous solutions. The hydrating water molecules are located at 0.365–0.370 nm from the chlorine atom; in dilute aqueous solutions, perchlorate ion can coordinate up to twelve water molecules with weak hydrogen bonds (three water molecule per each oxygen atom of the anion).

The common feature of nitrates and perchlorates behavior in aqueous solution is that they form labile hydration sphere, the number of coordinated water molecules depending on the concentration and the cation nature. The hydration sphere is formed via weak hydrogen bonds. Each oxygen atom of the anions can coordinate up to three water molecules in dilute solutions. The distance between oxygen atoms of the anions and the coordinated water molecules is nearly the same as that between water molecules in bulk solvent.

The main structural difference between solutions of nitrates and perchlorates is that the former tend to readily form contact ion pairs. The difference was directly observed in studies of solutions of nitrates and perchlorates under identical conditions, for example, in NMR studies of lanthanum salts by NMR [128] and of indium salts by vibration spectroscopy [86]. Likely, the difference in association behavior of nitrates and perchlorates is partially caused by steric factors.

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