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Structural Parameters of the Nearest Surrounding of Halide Ions in the Aqueous Electrolyte Solutions

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Abstract—Literature data and own experimental results on structural characteristics of the halide ions nearest surrounding in the aqueous electrolyte solutions under standard conditions has been summarized. Structural parameters like coordination number, interparticle distance, and ion association type have been discussed. It has been shown that in the halide ions series, from fluoride to iodide, the coordination number gradually increases from 6 to 8. In the same row, the coordination sphere stability decreases, this is reflected in more asymmetrical arrangement of water molecules of the nearest surrounding.

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Various properties of electrolyte solutions are significantly affected by anions nature, however, for many of them the structural parameters of the nearest surrounding have not been unambiguously determined. In the case of halide ions, these parameters are more certain, yet their interpretation is not completely clear. This is partially due to the fact that the interaction of anions with water is in general weaker than that of cations. On the other hand, their strength is comparable with that of water–water interaction in the bulk solvent. It should be noted that the orientation of water molecule comprising the halide ions coordination sphere is different from that of water molecules solvating cations. The hydrogen atom (or atoms) of the solvent are oriented towards the anion, this makes the anion nearest surrounding somewhat special. Aqueous metal halides solutions have been thoroughly studied with structural methods, but the major attention has been paid to the hydration structural parameters of cations. In some cases halides have been chosen as study objects in order to simplify the results interpretation; it has been assumed that the impact of halide aquatic complex into the experimental functions is either negligible or well known.

Hereinafter, the information available regarding each halide anion will be summarized and analyzed.

Structure of the F^- ion nearest surrounding. As far as the structure formation in aqueous solutions is concerned, the fluoride ion F^- is different from other halide ions. Being of the smallest size and thus of the highest charge density, the fluoride ion induces the strongest interactions with water molecules. This was experimentally proved by the determination of the water molecule residence time in the coordination sphere that was longer in the case of fluoride ion than in the cases of the other halide ions [1, 2]. Fluoride ion, having the ionic radius of 0.133 nm, close to oxygen atomic radius, could occupy the nodes or voids in the tetrahedral water network structure [3]. It should be noted that fluoride ion, unlike the other halide ions, was a structuremaking one, according to its effect on the solvent structure [4, 5]. However, even concerning that property there were some discrepancies. For instance, basing on results of Raman spectroscopy it was stated that all halide ions disrupted the tetrahedral water structure [6]; halide ions were arranged in the following series according to their disruptive effect: $F^- < Cl^- < Br^- < I^-$. Another Raman study revealed strong hydrogen bonding of fluoride ion with water molecules in aqueous KF and CsF solutions [7].

There were quite a few experimental studies on the local order in the nearest surrounding of fluoride ion. In an early X-ray diffraction study of 2.31 and 5.05 mol l^{-1} aqueous ammonium fluoride and 2.06, 3.03 and 4.17 mol l^{-1} aqueous potassium fluoride, the coordination number of the fluoride ion was determined

Table 1. Coordination numbers of F^- ion and F^-–H_2O distances in aqueous solutions as determined by computational methods

System	F^-–H_2O distance, nm	Coordination number	Method	References
LiF :200H_2O	0.230	4	Monte Carlo	[13]
LiF, NaF, KF:200H_2O	0.30±0.05	4.5±0.7	Monte Carlo	[14]
F^-:215H_2O	0.260	4.09±0.1	Monte Carlo	[15]
2.2 M CsF	0.264	6.8	Molecular dynamics	[16]
F^-:125H_2O	0.267	5.8	Molecular dynamics	[1]
F^-:79H_2O	0.288	6	Molecular dynamics	[17]
F^-:125H_2O	0.260	6.2	Monte Carlo	[18]
NaF, KF	0.275	7	Integral equations	[19]
F^-:125H_2O	0.262	6.6	Molecular dynamics	[20]
F^-:124H_2O	0.254	3.7	Monte Carlo	[21]
F^-:150H_2O	0.261	6.0	Molecular dynamics	[22]
F^-:124H_2O	0.253	6.0	Monte Carlo	[23]
F^-:215H_2O	0.260	6.3	Molecular dynamics	[24]
F^-:196H_2O	0.257	6.7	Monte Carlo	[25]
F^-:225H_2O	0.266	6.1	Molecular dynamics	[26]
F^-:120, 215, and 511H_2O	0.265	5.1	Monte Carlo	[27]
F^-:64H_2O	0.266	5	Density functional theory	[28]
F^-:215H_2O	0.260	4.1	Molecular dynamics	[29]
F^-:1000H_2O	0.278	6.7	Molecular dynamics	[30]

to be 4.5 [8]. The X-ray diffraction study of aqueous potassium fluoride (molar ratio of 1:15) gave the coordination number of fluoride ion equal four, and the fluoride–water distance of 0.268 nm [9]. The formation of K^+–F^- contact ion pairs in the system was proved. The more recent study of aqueous potassium fluoride solution by means of neutron diffraction revealed that the coordination number of F^- ion decreased with the increase in the concentration. At the salt-to-water molar ratio of 1.2:100 the coordination number was determined to be 6.9, at the molar ratio of 2.4:100 the coordination number was 6.0, and at the molar ratio of 4.8:100 the coordination number was 5.2 [10]. Furthermore, according to Soper et al., the anion formed the second coordination sphere.

On the contrary, there were many computational works on the aquatic complex structure of the fluoride ion. In the chronologically first study, a theoretical investigation of the energy characteristics dependence on the hydrated ions coordination number, the latter of fluoride ion was found to be eight [11]. By means of molecular dynamics, the coordination number of anion in cesium fluoride solution was determined to be 6.3±0.1 [12]. Results of further studies are collected in Table 1.

From the data in Table 1 it is clear that the most frequent result of simulation was fluoride ion coordination number close to four and six. The interparticle F^-–H_2O distances determined from diffraction results were in the range of 0.262–0.270 nm, while those deduced from computer simulation were of 0.254–0.288 nm (the smallest and the largest value being excluded).

When ions interact with clusters of water, in case of cations the interactions are so strong that they may penetrate inside the cluster, while for halide anions the interaction energy with water is comparable with the energy of water–water interaction. Thus, there is a competition between the anions and water for hydrogen bonding sites of the other water molecules. It is generally assumed that water clusters are too stable to be disrupted by the neighboring single-charged anion. Thus, anions are located at the surface of such clusters, being not fully hydrated. However, the fluoride anion may be an exception due to its high charge density, and may be located within the water cluster.

Further the papers are discussed on the location of fluoride ions with respect to the solvent molecules. In an early work, by Monte Carlo method the fluoride ion was found fully hydrated in case of four-molecule water cluster [31]. Molecular dynamics study of the $F^-(H_2O)_n$ (n = 3–6) complex structure [32] led to the anion coordination number of 5.8 and the F^-–OH_2 distance of 0.270 nm [32]. Another work also by Dang [33] gave the coordination number of 6.2, the interparticle distance being the same. Similarly, molecular dynamics study of the $F^-(H_2O)_n$ (n = 2, 3, … 15) clusters [34] revealed that fluoride ion was fully hydrated, being located inside the cluster. This conclusion was confirmed in the later molecular dynamics study of the $F^-(H_2O)_n$ (n = 1–10) clusters and of the F^-:215 H_2O system [35]. In [35], the coordination number of fluoride ion of 6, and the distances to coordinated water molecules, F^-–O and F^-–H, of 0.27 and 0.17 nm, respectively, were reported. However, later [36] it was shown by *ab initio* computation that the fluoride ion interacted with only three water molecules, whereas the forth water molecule was expelled to the second coordination sphere of the anion and thus interacted efficiently with the other water molecules. In the molecular dynamics study of the temperature effect on the $F^-(H_2O)_{11}$ cluster it was found that at low temperature (0 K) fluoride ion was located at the cluster surface, and upon heating (to 200 K and above) it got more and more hydrated [37]. Experimental and theoretical investigation of the $F^-(H_2O)_{3–5}$ system showed that F^- was located inside the water cluster [38]. Monte Carlo studies of the $F^-(H_2O)_4$ complex [39] led to the conclusion that the fluoride ion was hydrated by four water molecules. Computational study of the electronic structure of the $F^-(H_2O)_n$ (n = 4, 8, 12, 16) clusters showed that tetrahedral coordination of four water molecules to fluoride ion was the most stable arrangement in aqueous solution [40].

By using the quantum-chemical and statistical mechanics methods in combination, fluoride ion coordination number was determined as 4.68 [41]. In [42] the structural parameters of fluoride ion hydration were studied by *ab initio* calculations of the $F^-(H_2O)_n$ (n = 1–10) complexes in order to interpret the experimental Raman spectra. When averaging over a prolonged time interval, the most stable geometry of the coordination sphere was that corresponding to coordination number of six. According to molecular dynamics simulation with taking into account the classical pair potential of the F^-:199 H_2O system [43], the anion coordination number was 5.8, and the distance between the anion and coordinated water molecule was 0.253 nm. The same system simulation by means of quantum and molecular mechanics (QM/MM) gave the coordination number of 4.6 and the F^-–H_2O distance of 0.268 nm. Tongraar et al. commented that the classical simulation methods could only give limited information on the coordination geometry as far as weak anion–water hydration complexes were concerned. In the further work by the same authors [5], the orientation of water molecules in the anion coordination sphere was deduced by means of the QM/MM method; in each of the water molecules only a single hydrogen atom participated in the hydrogen bonding with fluoride anion, whereas in the case of chloride anion part of water molecules was bound to the anion via both hydrogen atoms. In the modern molecular dynamics study the 12NaF:2352H_2O system was examined; both number of oxygen atoms and number of hydrogen atoms in the nearest anion surrounding were found to be equal to 6.3 [44].

The molecular dynamics study of the 1.791 mol l^{-1} LiF aqueous solution showed the formation of contact ion pairs, with strong overlap of the cation and anion hydration spheres [45]. The formation of contact ion pairs of fluoride anion with +4-charged cations was confirmed by EXAFS spectroscopy of diluted aqueous solutions [46].

From the above discussed it follows that the coordination number of F^- anion as determined by variety of methods and under different conditions is in the range of 3.85 to 8. As fluoride ion forms relatively weak coordination sphere, its coordination number is likely to be dependent on the concentration (this was confirmed in [10]) and on the cation nature. Thus, the coordination number of 4 determined in some works may be due to high electrolyte concentration in the system. Coordination number of 8 has been determined in a single work, and thus is not trustworthy. Fluoride ion size is similar to that of potassium ion (K^+ coordination number is 6–8), but the charge of F^- is negative. By analogy with potassium ion, coordination number of six, but not four, is the most probable in the case of fluoride ion. It is likely that in the excess of solvent the coordination number of F^- ion is six, the average distance to the coordinated water molecules being equal to 0.265 nm. Basing on the majority of published results and on the physical characteristics of fluoride anion (size, charge), the second coordination sphere is unlikely to exist in the case of fluoride anion, whereas the tendency to form contact ion pairs is expected.

Structure of the Cl^- ion nearest surrounding. Cl^- ion is of great biological importance, firstly in the biochemical signal conductance, as a counter-ion of H^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} during their transport across the cell membrane [47].

When placed in an aqueous medium, chloride ion disrupts the water structure [4]. Cl^- size is 0.181 nm, consequently, the average distance to coordinated water molecules should be close to 0.321 nm. In the early X-ray diffraction studies the distance between the anion and the coordination water molecules was determined approximately at 0.320 nm [48, 49]. Coordination number of the anion in the concentrated aqueous solution of lithium chloride was 8–9 [50]. In further study, again by X-ray diffraction, the 7.48, 10.08, and 12.28 mol l^{-1} aqueous hydrochloric acid solutions were studied; it was determined that the first coordination sphere of chlorine anion consisted of eight water molecules and was located at a distance of 0.325 nm from the anion [51]. According to Wertz, the coordination sphere of chloride ion in hydrochloric acid solutions was more ordered than that in the aqueous solutions of alkali metal chlorides. This study also revealed the existence of O–O contacts at relatively short distances of 0.25–0.26 nm, thus the existence of the second coordination sphere was presumed to be located at a distance of 0.62±0.01 nm. However, the formation of the second coordination sphere at such a distance appears questionable; even if it was formed, it should be located closer to the anion.

Hydrochloric acid aqueous solutions in a wide concentration range were studied by means of neutron and X-ray diffraction in an early work [52]. The coordination number of Cl^- was determined to be four, and a distance to coordinated water molecules was 0.313 nm. Distinct Cl^-–$D(D_2O)$ distance was not established, which, as Triolo et al. believed, meant that the oriented coordination sphere was not formed around the chloride anion. The instability of the chloride ion coordination sphere was also reflected in that the anion nearest surrounding (six water molecules) in the $MgCl_2{:}12H_2O$ crystal hydrate was highly disordered, and the distances to those molecules varied within the range of 0.311 to 0.326 nm [53]. In [54], by means of neutron diffraction with isotope substitution, the 5.32 mol l^{-1} aqueous solution of sodium chloride was studied; it was found that the anion had a single coordination sphere consisting of 5.5±0.2 water molecules at the average distance of 0.32 nm. Later the same method was applied to the study of 3 mol l^{-1} nickel chloride and 10 mol l^{-1} lithium chloride solutions at varied pressure [55]. Under standard conditions, it was found that the number of water molecules in the nearest anion surrounding was 5.5±0.5 (with the Cl^-–OH_2 distance of 0.325±0.006 nm) in the case of nickel chloride and 5.8±0.5 (Cl^-–OH_2 distance being the same) in the case of lithium chloride.

In the X-ray diffraction studies of 1 and 2 mol l^{-1} aluminum chloride solutions, the anion coordination number was determined to be six [56]. Six water molecules at 0.310–0.320 nm from the anion were found in the first coordination sphere of chloride ion in other studies as well [53, 57–61]. In [62], by means of neutron diffraction, the average of 6.4 water molecules in the anion coordination sphere were found in 2 mol l^{-1} solution of nickel chloride, the Cl–H^1, Cl–O, and Cl–H^2 distances being 0.228, 0.310, and 0.370 nm, respectively. The Cl^-–O–H bond angle was 12° [63]. In another study carried out by the same method [64] the coordination number of the anion in 1.7, 5.8, and 8.6 mol l^{-1} aqueous lithium chloride was found to be 5.8±0.5, the Cl^-–O distance being 0.324 nm. X-ray diffraction was applied to the study of 2 mol l^{-1} aqueous ammonium chloride in [65]. It was found that the anion coordination number was 6±1, and the distance to coordinated water molecules was 0.314±0.002 nm. Much later, the same X-ray diffraction method was used in the study of aqueous potassium chloride (molar ratio of 1:15); the anion coordination number was six, and the distance to coordinated water molecules was 0.325 nm [9]. In [66], the neutron diffraction with isotope substitution was applied to study of water molecules coordination around the chloride ion in the solutions containing different cations. Basing on the results, Cummings et al. concluded that the chloride ion hydration was not much sensitive to cations nature and the solution ionic strength, with the only possible exception of the transition metal ion Ni^{2+}. Later the same method was applied to the study of some electrolyte solutions in deuterated water (mainly, of zinc chloride of varied

Table 2. Coordination numbers of Cl^- ion and $Cl^-–H_2O$ distances in aqueous solutions as determined by computational methods

System	$Cl^-–H_2O$ distance, nm	Coordination number	Method	References
$Cl^-:200H_2O$	0.34	5.6	Monte Carlo	[75]
$Cl^-:215H_2O$	0.325	8.36	Monte Carlo	[15]
$Cl^-:125H_2O$	0.329	7.2	Molecular dynamics	[1]
$Cl^-:79H_2O$	0.328	7	Molecular dynamics	[17]
$Cl^-:125H_2O$	0.321	7.4	Monte Carlo	[18]
NaCl, KCl	0.345	11.73	Integral equations	[19]
$Cl^-:150H_2O$	0.319	7.0	Molecular dynamics	[22]
$Cl^-:124H_2O$	0.316	6.0	Monte Carlo	[23]
$Cl^-:215H_2O$	0.320	7.2	Molecular dynamics	[24]
$Cl^-:196H_2O$	0.3225	7.5	Monte Carlo	[25]
$Cl^-:255H_2O$	0.336	6.4	Molecular dynamics	[26]
$Cl^-:64H_2O$	0.318	5.4	Molecular dynamics	[76]
$Cl^-:1000H_2O$	0.315	7.0	Molecular dynamics	[30]
1.32–6.61 M NaCl	0.340	6.89–7.19	Molecular dynamics	[77]

concentration) [67]. Powell et al. concluded that $Cl^-–D$ distance was within the 0.22–0.23 nm range, the $Cl^-–D–O$ group was almost linear, and the number of water molecules in the first coordination sphere of the chloride ion was six or less, being dependent on the solution ionic strength as well as on the cation type.

In a series of computer modeling works [68–71] the chloride coordination number range was estimated at 1 to 8. The range was that wide due to the fact that the result was affected by a number of computational parameters. For example, in [72] it was shown that accounting for the anion polarizability strongly influenced the result. The molecular dynamics simulation of $Cl^-(H_2O)_n$ (n = 2, 3, … 15) clusters demonstrated that chloride ion was not fully hydrated in an aqueous solution, but was located at the surface of water molecules cluster [34, 73]. Such surface location of the anion was confirmed in another study by means of *ab initio* simulation using polarizable potentials for water molecules [74]. It was specified that the chloride ion location with respect to water molecules cluster depended on whether polarizable model of water was used in computation, or not. Furthermore, after having studied the clusters containing 100 and 255 water molecules, Stuart et al. noted that with larger clusters chloride ion was more hydrated (changed its location to that inside the cluster). The study of temperature effect on the $Cl^-(H_2O)_{11}$ cluster by means of molecular dynamics showed that both at low temperature (0 K) and upon heating (up to above 200 K) the chloride ion was only located at the cluster surface [37].

Some computer modeling results are listed in Table 2, in the chronological order.

By means of the density functional method it was found that the average chloride ion coordination number was 5.6, five of the hydrogen atoms being located closer to the anion [78]. Combined quantum-chemical and statistical mechanics computations led to chloride coordination number of 6.25 [41].

In the following studies the effects of nature and concentration of the counter-ions were examined. A wide range of lithium chloride and sodium chloride solutions were studied by Monte Carlo method in [79]. The distance to the solvent molecules was 0.321 nm for all systems. Unexpectedly, the coordination number of chloride ion as determined in that work increased with increase of the solute concentration: with LiCl concentration increasing from 1.32 to 12.92 mol l^{-1}, the chloride coordination number increased from 8.0 to 8.7; with NaCl concentration increasing from 1.1 to 5.12 mol l^{-1}, the chloride coordination number increased from 7.9 to 8.6; the effect of the cation on chloride coordination sphere was also commented. In one of the recent studies of cesium chloride aqueous solutions (1.5, 7.5, and 15 mol %) the results of X-ray and neutron scattering were combined with molecular dynamics and Monte Carlo simulations [80]. With increasing salt concentration the average coordination number of chloride ion decreased from 7 to 5, and contact ion pairs appeared. In another study of magnesium and calcium chlorides (molar ratios of 1:17, 1:40, and 1:83) by means of neutron scattering and Monte Carlo simulation it was found that in the presence of Mg^{2+} the anion coordination sphere was less stable than in the presence of Ca^{2+} [81]. The distance from the anion to water molecules was 0.321 nm.

The nearest order formed by the chloride ions in aqueous solutions was studied by means of molecular dynamics method and EXAFS spectroscopy, in order to reproduce the experimental spectrum by simulation [82]. The results of the experiment were as follows: $r(Cl^{-}–O) = 0.3110$ nm, coordination number = 6.4; computer simulation results were slightly different: $r(Cl^{-}–O) = 0.322$ nm, coordination number = 6.2. In another study of potassium chloride aqueous solutions the anion coordination number was determined as a function of concentration: in the solution of 1.2:100 molar ratio the coordination number was 7.1, at molar ratio of 2.4:100 the coordination number was 6.2, and at molar ratio of 4.8:100 the coordination number was 6.4 [10]. In the cases of sodium chloride aqueous solutions the anion coordination number was determined by neutron scattering: the coordination number was 7.4±0.8 and 7.3±0.8 at the salt concentration of 4 and 2 mol kg^{-1}, respectively, the distance between the anion and water molecules being equal 0.320 nm [83]. Interesting results of molecular dynamics study were reported in [84]: with increasing concentration of lithium chloride aqueous solution from 0.22 to 2.88 mol l^{-1}, the chloride ion hydration number slightly increased from 7.2 to 7.8, and then decreased to 7.3 as the salt concentration further increased to 3.97 mol l^{-1}. In the case of rubidium chloride aqueous solution, the anion hydration number decreased from 7.2 to 5.6. According to Du et al., this was an evidence of the cation size effect on the structural parameters of the anion nearest surrounding in the concentrated aqueous solutions; in particular, in the case of lithium chloride solutions with increasing concentration the formation of ion pairs was enhanced. When an ion pair in lithium chloride solution was formed, the water molecules from the stable coordination sphere of the cation entered the hydration sphere of the anion as well. In the case of rubidium chloride solutions the coordination sphere of the cation was less stable, and when the ion pair was formed, the water molecule hydrating the cation was merely substituted by the anion. According to X-ray diffraction and molecular dynamics studies of lithium chloride solutions (the salt concentration in the range of 0.5–14 mol kg^{-1}), the chloride ion coordination number did not change with concentration being equal to 7–7.5 [85, 86]. The $Cl^{-}–O$ and $Cl^{-}–H$ distances were 0.322 and 0.227 nm, respectively. This is quite a strange result, because at the same time Bouazizi et al. observed the decrease in the lithium coordination sphere, more stable due to higher charge density. In the neutron diffraction study of aqueous hydrochloric acid solution (molar ratio of 1:17 and 1:83) it was determined that in both cases there were 6.5 to 7 water molecules in the nearest surrounding of chloride ion [87]. In another study the same method of neutron diffraction was applied to aqueous solutions of lithium chloride (3.02 mol l^{-1}) and cesium chloride (3.0 mol l^{-1}); in both cases the anion coordination number was 5.5±0.5, and the distance to water molecules equaled approximately 0.32 nm [88]. Molecular dynamics study of the $Cl^{-}:215H_2O$ system lead to the $Cl^{-}–OH_2$ distance of 0.320 nm, average coordination number being six [89]. According to Zhao et al., the coordination sphere structure was not isotropic, the interactions were stronger at one side of the anion and relatively weak at the opposite side; this led to the formation of some void near the anion. This conclusion was in good agreement with the results of another study (by the same method of neutron diffraction) of the system $Cl^{-}:550\ H_2O$, in that study a small void was observed in a region opposite to the direction of induced dipoles [90]. In the combined study (XAFS spectroscopy of 2 mol l^{-1} aqueous calcium chloride and QM/MM molecular dynamics simulation of $Cl^{-}:199\ H_2O$ system), the simulation led to the anion coordination number of 5.1±1.3 with the distance to water molecules of 0.3200±0.0034 nm, whereas experimental data gave the coordination number of 6.0±1.7, and $r = 0.3047±0.0040$ nm [91]. In another molecular dynamics study, the number of oxygen atoms in the anion nearest surrounding was found equal to 7.4 for the $12NaCl:2352H_2O$ system [44], the number of hydrogen atoms equaled 6.8. By neutron diffraction method it was determined that there were 6.0±1.3 water molecules at the $Cl^{-}–O$ distance of 0.315 nm in the chloride anion nearest surrounding in the $LiCl:40H_2O$ system [92].

It should be noted that being a spherical atomic ion, chloride ion tended to form ion pairs and complexes. It was capable of forming the ion pairs with majority of the above-mentioned cations.

In some works the probability of direct contact between the anions was discussed. For example, the formation of ion pairs of the Cl^-–Cl^- type was found by molecular dynamic study of the 2 ions:125 water molecules system [93]. In another study of 1 mol l^{-1} aqueous sodium chloride, also by means of molecular dynamics, the contact between anions was shown to exist due to interaction with three shared water molecules, this was described as follows: $[2Cl^-(H_2O)_3]$ [94]. This was also confirmed by experimental studies. For instance, by neutron diffraction with isotopic substitution, the pair distribution functions $g_{ClCl}(r)$ were obtained for 8.6 mol l^{-1} aqueous lithium chloride in heavy water [60]. The number of direct contacts between chloride anions was estimated at 1.2±0.5. However, in [95], basing on Monte Carlo method and molecular dynamics data for 5 mol l^{-1} NaCl, the formation of ion pairs between anions was denied.

From the above mentioned results it follows that the most frequently reported coordination numbers of chloride ions are six and seven, the recent works giving most often the latter value. Thus, in diluted aqueous solutions chloride ion can coordinate six to seven water molecules, this number seemingly decreasing with growing concentration. The distance between the anion and coordinated water is 0.310–0.320 nm. The anion does not form the second coordination sphere. The chloride ion tends to form ion pairs primarily of the contact type.

Structure of the Br^- ion nearest surrounding. According to calculation of hydration entropic parameters [4], the bromide ion disrupts water structure. The first coordination sphere consisting of six solvent molecules was found by X-ray diffraction [96–99] and neutron diffraction [100] studies. The Br^-–H_2O distance was observed in the range of 0.330–0.340 nm. Such characteristics were obtained in the cases of the following studied systems: 2.1, 4.5, and 5.6 mol l^{-1} LiBr [$r(Br^-–O) = 0.330$ nm] [96], 1.2 and 2.0 mol l^{-1} $CaBr_2$ ($r = 0.330$ nm) [97], 2 mol l^{-1} $NiBr_2$ ($r = 0.312$ nm) [98], and 4 mol l^{-1} $NiBr_2$ ($r = 0.335$ nm) [101]. It should be noted that the ionic radius of Br^- ion equals 0.196 nm, thus the average distance to the coordinated water molecules should be close to 0.336 nm. In the early computational study [102], the geometry and the electronic structure of the $Br(H_2O)_n^-$, $n = 1–8$ complex was determined. It was noted that despite the large size of the bromide ion, the preferred coordination number of it was six, due to weak interactions with water molecules. By means of IR spectroscopy, the coordination number of bromide was estimated at 6.3 in 0.377 mol l^{-1} aqueous nickel bromide solution, the distance to coordinated water molecules being equal 0.343±0.002 nm [103]. However, shorter distance between the anion and the nearest surrounding water molecules was reported as well. For example, by EXAFS spectroscopy this distance in aqueous copper bromide solution was determined at 0.314 nm [104], and in the case of 0.1 mol l^{-1} aqueous potassium bromide solution it was 0.319 nm, coordination number of the bromide solution being fixed at six during the spectra manipulation [105, 106]. By using the same method, the Br^-–O distance for a series of proton-containing solvents was found to be in the 0.31–0.32 nm range [107]. EXAFS study of the diluted RbBr solutions lead to the coordination number of 6.6 and the mean distance between the anion and coordinated water molecule 0.323 nm [108]. The increase in the concentration to above 4 mol kg^{-1} led to the decrease in the number of water molecules coordinated by bromide ion and to the formation of ion pairs with the cation.

Molecular dynamics study of the $Br^-(H_2O)_n$, $n = 1, 2, \ldots 15$ cluster suggested the anion was located at the surface of water molecules cluster [109].

In some studies the coordination number other than six was determined for bromide anion. For example, EXAFS spectroscopy study of diluted rubidium bromide solutions led to the coordination number of 6.9 [110]. However, D'Angelo et al. made a strange conclusion: They assumed that besides the first coordination sphere existed also the second and the third ones. By combination of EXAFS spectroscopy and molecular dynamics methods, the coordination number of bromide was determined at 7.2±0.4 in 0.2 and 1.5 mol l^{-1} aqueous rubidium bromide solutions, the distance to coordinated water molecules being equal to 0.336 nm [111]. Results of some computer simulation studies are collected in Table 3.

By anomalous X-ray scattering of 6 mol l^{-1} aqueous rubidium bromide solution [115] it was shown that there might be 6 to 7.5 water molecules on the average in the anion coordination sphere located at 0.340 nm from the anion. It was specified that there was no reason to assume the existence of longer range

Table 3. Coordination numbers of Br^- ion and $Br^-–H_2O$ distances in aqueous solutions as determined by computational methods

System	$Br^-–H_2O$ distance, nm	Coordination number	Method	References
3.57 M LiBr	0.335	9.3	Monte Carlo	[79]
$Br^-:216H_2O$			Monte Carlo	[112]
quantum approach	0.345	7.7		
classical approach	0.332	7.8		
$Br^-:150H_2O$	0.337	7.3	Molecular dynamics	[22]
$Br^-:215H_2O$	0.330	7.5	Molecular dynamics	[24]
Br^-:116, 211, and $507H_2O$	0.343	7	Monte Carlo	[27]
$Br^-:819H_2O$	0.333	6.5	Molecular dynamics	[113]
0.9 mol % CsBr		6.5	Monte Carlo	[114]
7.6 mol % CsBr		5.6		
$Br^-:1000H_2O$	0.336	7.6	Molecular dynamics	[30]

ordering near bromide ion. The X-ray diffraction of aqueous potas-sium bromide (molar ratio of 1:15) revealed the antiprism shape of Br^- ion coordination sphere [9]. The molecular dynamics study of 1.6 mol l^{-1} aqueous HBr solution showed that the most stable inner coordination sphere had the [4 + 2] type structure with the mean distance to water molecules of 0.337 nm. The four nearest water molecules were arranged in the shape of a pyramid, while the other two were located at the other side of the apex [116]. The study of 0.3 mol l^{-1} YBr_3 aqueous solution by combination of EXAFS spectroscopy and Monte Carlo method gave the anion coordination number of 6±0.5 with the distance to coordinated water molecules of 0.344±0.007 nm. In the study on refinement of the anion–water interaction potential, for the $1Br^-:211H_2O$ system the anion coordination number was estimated at ~7. Furthermore, approxi-mately six hydrogen atoms were located at a distance of 0.240–0.255 nm, thus showing that the water molecules were coordinated to the anion only by a single hydrogen atom [118].

In the following series of studies the concentration effect on the nearest surrounding structure of the bromide ion was assessed. The analysis of X-ray absorption spectra (EXAFS and XANES) of aqueous zinc bromide solution showed that upon increase in the concentration from 0.1 mol kg^{-1} to 1 mol kg^{-1} the coordination number of the anion decreased from 6.3±0.09 (r = 0.331±0.007 nm) to 4.5±0.08 (r = 0.330±0.003 nm) [119]. Simultaneously, the Br^- ion entered the cation coordination sphere, being located at the distance of 0.2380±0.0019 nm from the cation. The averaged number of the anions in the nearest surrounding of the cation was 0.5. In the modern study by neutron diffraction and computer simulation the coordination number of bromide ion was determined in potassium bromide aqueous solutions: 6.7 for the molar ratio of 1.2:100, 6.4 for the molar ratio on 2.4:100, and 6.4 for the molar ratio of 4.8:100 [10]. In another study by means of molecular dynamics and Monte Carlo methods it was demonstrated that in 2 mol l^{-1} rubidium bromide solution the anion coordination sphere was much diffused [120]. The estimated coordination number of bromide anion was in the range of five to seven. The undefined structure of bromide ion coordination sphere and its asymmetry were also commented on in [113].

EXAFS spectroscopy of 0.017 and 0.17 mol l^{-1} aqueous gallium bromide solution demonstrated that bromide ions were hydrated by eight water molecules located at a distance of 0.337 nm. In such diluted solutions, ion pairs were not formed [121]. In a modern molecular dynamics study [44] the number of oxygen atoms of water molecules in the nearest surrounding of the anion was found at 7.8 (the hydrogen atoms number was 6.6) in the case of $12NaBr:2352H_2O$ system.

Similarly to chloride ion, bromide ion tended to form ion pairs and complexes [122]. The type of the associates depended of a number of conditions, like the chemical nature of the cation, electrolyte concentration, molar ratio of the cations and bromide ions, etc. By means of X-ray diffraction of the concentrated aqueous solutions of $FeBr_2$ (2.7 and 4.5 mol l^{-1}) and

Table 4. Coordination numbers of I^- ion and I^-–H_2O distances in aqueous solutions as determined by computational methods

System	I^-–H_2O distance, nm	Coordination number	Method	References
2.03 M LiI	0.368	7.3	Molecular dynamics	[138]
LiI:25H_2O	0.364	7.7	Molecular dynamics	[139]
CsI:20H_2O	0.364	9.8	Molecular dynamics	[140]
3.95 M NaI	0.356	10.5	Monte Carlo	[79]
I^-:150H_2O	0.371	9.7	Molecular dynamics	[22]
I^-:30H_2O	–	6.6	Molecular dynamics	[141]
I^-:115, 210, and 506H_2O	0.364	8.3	Monte Carlo	[27]
I^-:64 H_2O	0.355	6.6	Density functional theory	[142]
I^-:199H_2O	0.375	8	Molecular dynamics	[143]

$CoBr_2$ (2.8 and 4.3 mol l^{-1}), the average number of the anions in contact with a single metal ion was determined at 0.325 and 0.747 (iron bromide solutions of respective concentration) and at 0.280 and 0.595 (cobalt bromide solutions of respective concentration) [123]. It was concluded that in the concentrated aqueous solutions the prevailing complex type was octahedral $[MBr(H_2O)_5]^+$ and $[M(H_2O)_6]$, with M being Fe or Co. The combination of EXAFS spectroscopy and molecular dynamics was used in the study of wide range of lithium bromide solutions with addition of K^+ and Ca^{2+} ions [124], it was confirmed that the nearest surrounding of bromide ion depended on the counter-ion type and concentration. When the ion pair was formed, the number of water molecules coordinated by the anion might decrease, as water molecules could not be located along the cation–anion bond [125].

To conclude, in diluted aqueous electrolyte solutions the hydration shell of bromide ion consists of approximately seven water molecules located at an average distance of 0.330–0.340 nm. The bromide coordination sphere is likely to be somewhat asymmetric. The increase in the concentration leads to decrease in the the water molecules number in the anion hydration sphere. The second coordination sphere is not observed in the case of bromide anion, whereas ion associates are formed.

Structure of the I^- ion nearest surrounding. The I^- ion is known to disrupt water structure [4]. Iodide ion hydration is the weakest of all halide ions due to its largest size [126], this has lead to certain complications in the determination of its coordination number. The smallest iodide ion coordination number reported in the literature was 0.8 (aqueous zinc iodide solution at the molar ratio of 1:55) [127], while the highest coordination number was 9.6 (aqueous lithium iodide solution at molar ratio of 1:25) [128]. I^- ionic radius equals 0.220 nm, thus the average distance to the coordinated water molecules should be close to 0.360 nm. The I^-–OH_2 bond length was in the range of 0.355–0.370 nm, as determined by diffraction methods. In an early study of 7 mol l^{-1} aqueous sodium iodide solution by X-ray diffraction, the iodide ion coordination number was estimated at six, the distance to coordinated water molecules being equal to 0.360 nm [129]. In the sodium iodide aqueous solutions X-ray and neutron diffraction methods detected the anion coordination number of eight, with water molecules located at 0.360 nm from the anion [130]. IR spectroscopy gave the anion coordination number of 9.1±0.3 and the distance to coordinated water molecules of 0.364±0.002 nm in 0.386 mol l^{-1} aqueous solution of nickel iodide aqueous solutions [103]. X-ray diffraction study of sodium iodide found eight water molecules in the anion coordination sphere, at an average distance of 0.350 nm (in the case of independent hydration) as well as contact ion pairs formation accompanied by the decrease in the number of water molecules in the ions hydration spheres [131, 132]. A photoelectron spectroscopy study of the $I^-(H_2O)_n$, n = 1–15 cluster showed that there were six water molecules in the nearest surrounding of I^- ion [133]. The coordination sphere consisting of six solvent molecules arranged in the shape of a prism with a dense particles packing (at a distance of 0.355 nm from the anion) was observed by X-ray diffraction studies of potassium iodide aqueous solution [9]. Molecular dynamics simulation of the photoelectron spectra of the $I^-(H_2O)_n$ (n = 1–15) clusters led to the coordination number of iodide equal to 4 or 5 [134]. However, Dang et al. noted that such low coordination number was due to asymmetry of the anion hydration sphere. The asymmetry of water molecules arrangement around the anion was earlier confirmed by theoretical calculations [135, 136]. Furthermore, it was stated that at $n > 6$, the equilibrium symmetrical and asymmetrical arrangements of water molecules in the $I^-(H_2O)_n$, cluster were isoenergetic [137]. Results of some computer modeling studies are collected in Table 4.

Anomalous X-ray diffraction study of 6 mol l^{-1} aqueous sodium iodide and 3 mol l^{-1} aqueous cesium iodide solutions estimated the I^-–O distance at 0.379±0.005 nm, with the coordination number of 8.8 [144]. The ion pairs were found in the solutions, with the distance Na^+–I^- of 0.317±0.005 nm and Cs^+–I^- of 0.384±0.005 nm; the number of contacts being 1.6 and 2.7, respec-tively. In a modern study by combined method of neutron scattering and computer modeling of potas-sium iodide aqueous solution, the I^- coordination number of 6.7 (molar ratio of 1.2:100), 6.6 (molar ratio of 2.4:100), and 7.1 (molar ratio of 4.8:100) was determined [10]. However, Soper et al. commented on the uncertainty of this parameter determination. Moreover, in a series of photoelectron spectroscopy studies of the $I^-(H_2O)_n$ (n = 1–60) system it was stated that the anion was located at the surface of the water molecules clusters [145, 146]. The analysis of experimental and theoretical data [147] led to the conclusion that iodide ion location depended on the water cluster size, and the transition to the inner location of the anion occurred at 60 water molecules in the cluster. Further, Monte Carlo method indicated that in the cases of clusters of 12, 20 [148], or 32 [149] water molecules I^- ion was located at the cluster surface, whereas complete hydration was preferable in the case of 64 water molecules cluster [149].

Significant disordering of the iodide ion coordination sphere was noticed in a modern study of the $1I^-:1192H_2O$ system by means of EXAFS spectroscopy, quantum and molecular mechanics, and molecular dynamics [150]. As has been noticed above, this is one of the reasons of the uncertainty in the anion coordination number determination. In the study of 0.4 mol l^{-1} aqueous sodium iodide solution by means of EXAFS spectroscopy and molecular dynamics it was determined that the anion coordinated approximately 6.3 water molecules with the I^-–O and I^-–H distances of 0.350 and 0.265 nm, respectively [151]. In another modern molecular dynamics study the number of oxygen atoms from water molecules in the nearest anion surrounding was found to be 8.2 in the case of the $12NaI:2352H_2O$ system; the number of hydrogen atoms equaled 7.1 [44].

The molecular dynamics study of aqueous cesium iodide showed that the increase in its concentration from 0.22 to 3.97 mol led to the decrease in the iodide ion hydration number from 7.6 to 5.3 [84].

Thus, keeping in mind relatively significant uncertainty, it can be concluded that iodide ion coordinates eight water molecules located at the average distance of 0.360 nm. The coordination sphere is somewhat disordered and is not of regular shape. The anion does not form the second coordination sphere and tends to form ion associates.

To conclude, in the series of halide ions, F^- – Cl^- – Br^- – I^-, the distance to the nearest coordinated water molecules evidently increases; simultaneously, the coordination number steadily increases from six to eight (similar effect has been observed in the row of alkali metal ions). In the same series, the stability of coordination sphere likely decreases due to lower ion charge density; the destabilization is reflected in enhancement of asymmetry of the nearest water molecules arrangement.

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