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# Comparative Review of Structural Parameters of the Nearest Surrounding of Monoatomic Cations in Water and Methanol Media

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**Abstract**—Literature data on structure of coordination sphere of selected monoatomic cations in aqueous and methanol solutions have been reviewed and compared. The following structural parameters have been considered: coordination number, interparticle distances, the second coordination sphere features, and ionic association type. It has been revealed that for doubly charged ions the parameters of the first coordination sphere are similar in the both solvents. The second coordination sphere of the same cation consists of fewer solvating molecules located farther from the ion in the case of methanol as compared to water.

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The structures of the nearest surrounding of most hydrated monoatomic ions have been studied in detail both theoretically and experimentally. However, knowledge of the ions solvation in non-aqueous solutions is limited. For example, the available information is scanty in the case of solutions in methanol, the simplest alcohol. The presence of hydrophobic methyl group leads to changes of the bulk solvent structure as compared to water, in particular, to disappearance of the quasi-tetrahedral spacial organization of hydrogen bonds [1]. In contrast to water, in the case of methanol solutions the association of the solvent leads to chains, rings, and small clusters of the hydrogen-bonded alcohol molecules [2–4]. It is natural that the nearest surrounding of the solvated ions in water and in methanol solutions can be different.

This work aimed to collect the available data on solvation of monoatomic cations in methanol solution and to compare the coordination sphere structures with those in aqueous solution. As the information on the ions coordination in methanol solutions was limited, only selected cations were considered; however, the review was supposed to predict the structural parameters of the solvation spheres of some cations not studied so far. The data on aqueous solutions to be used for comparison was extracted from the reviews on the corresponding cations.

In general, the structure of the nearest surrounding of an ion in solution is determined by the interplay of ion–ion, ion–solvent, and solvent–solvent interactions; consequently, the changes of the pure solvent structure will induce changes of the ion solvation sphere. As a reasonable simplification, two effects may be responsible for the differences to be observed between methanol and water. First, water molecules form stronger hydrogen bonds than do methanol molecules; thus, methanol coordination to an ion is energetically more favorable, and the ion coordination number in methanol solution may be higher than in water. On the other hand, methanol molecules are larger; this may sterically limit the coordination number of the ion in methanol solution.

As the interaction between metal ions and methanol carbon is relatively weak, and the carbon position is usually not fixed, the interparticle distances discussed below are related to the $M^{n+}$–$O(CH_3OH)$ distance, if not stated otherwise.

Among alkali metal ions, the charge density of $Li^+$ and $Na^+$ is the highest, they likely completely realize the coordination ability in diluted aqueous solutions, and they can hardly coordinate more of solvent molecules in methanol solution than they do in the excess of water. On the contrary, the charge density of $Rb^+$ and $Cs^+$ may be insufficient to coordinate all the geometrically available water molecules in the solution; possibly, in methanol solutions their coordination number will increase.

**$Li^+$ solvation sphere.** The coordination number of $Li^+$ in methanol was assumed to be four from the IR and NMR data [5, 6]. That was later confirmed directly from MS study of LiI clusters: it was found that in the most stable clusters methanol molecules were aligned symmetrically around the cation. When the number of methanol molecules reached four, the $Li^+$–$I^-$ distance increased sharply, and the ion pair separated [7].

The concentrated solutions of LiBr (25 mol %) and LiI (33 mol %) in methanol were studied by neutron diffraction [8]. The following parameters were extracted: $r(Li^+–O)$ = 0.197±0.005 nm and $N$ (coordination number) = 3.0±0.5 (LiBr), $r(Li^+–O)$ = 0.193±0.005 nm and $N$ = 1.8±0.5 (LiI). It was assumed that one or two sites in the cation coordination sphere could be occupied by the anions. The ab initio calculations also revealed that in the case of $Li^+(CH_3OH)_n$ ($n$ = 1–5) clusters in the gas phase the first coordination sphere of the cation included only four methanol molecules [9], while the fifth molecule was expelled to the second coordination sphere. However, the above-mentioned findings contradicted with X-ray diffraction data [10]: for lithium salt solution in methanol it was determined that with increasing the salt concentration from 1 to 6 mol/L, the number of $Li^+$–O coordinations was decreased from 5.9±0.1 to 1.5±0.1 (LiCl) and from 6.2±0.1 to 4.8±0.1 (LiI). Thus, the coordination number of $Li^+$ in diluted methanol solutions was concluded to be six. The interatomic distances in the studied solutions were as follows: $r(Li^+–O)$ = 0.206 nm and $r(Li^+–C)$ = 0.270 nm in the case of LiCl, $r(Li^+–O)$ = 0.197 nm and $r(Li^+–C)$ = 0.290 nm in the case of LiI. The ion associates were formed in more concentrated solutions. The results of some other studies of lithium salts in methanol are summarized in Table 1.

The ion association effect was also examined in other studies [11, 12]. By means of MS, it was found that the number of methanol molecules coordinated to $Li^+$ was higher in the case of LiI than in the case of LiCl; that was explained by weaker interaction between $Li^+$ and $I^-$ that made the solvation with methanol more favorable. Furthermore, the coordination number up to six was confirmed in those reports.

Thus, from the reference data it followed that $Li^+$ could coordinate four to six molecules of methanol in the first coordination sphere, the distances being in the range of $r(Li^+–O)$ = 0.190–0.207 nm. The second coordination sphere was observed as well, consisting of four methanol molecules located at $r(Li^+–O_{II})$ = 0.420 nm. It could be assumed that in the diluted solutions the number of methanol molecules in the second coordination sphere could be up to six. The ion association was typical for the lithium salts solution in methanol.

In the aqueous solutions [13], $Li^+$ coordinated four water molecules located at $r$ = 0.195–0.22 nm in the first coordination sphere; $N(Li^+)$ could be increased to six in diluted solutions. Even in the concentrated solutions, the second coordination sphere was formed around $Li^+$ at the distance of 0.405–0.415 nm. The number of water molecules was increasing upon dilution, finally reaching 12. $Li^+$ ions did not form ion associates in dilute solutions; however, depending on the counterion nature, the solvent separated or contact ion pairs could be formed in the concentrated solutions.

The following conclusions were made from the comparison of $Li^+$ solvation in aqueous and methanol solutions.

The coordination number of the cation was the same in aqueous or methanol media. Noteworthily, this was also stated basing on the chemical shift analysis [14].

The distance to the molecules of the first coordination sphere $r(Li^+–O)$ was slightly shorter in the case of methanol, however, the difference was within the accuracy of the reported data.

The second coordination sphere consisted of fewer solvent molecules in the case of methanol as compared to water. This was in line with the number of hydrogen bonds formed by methanol molecule (2) as compared to that in the case of water (4). The solvent molecules forming the second coordination sphere were located farther from the cation in the case of methanol solutions, due to larger volume of methanol.

The ion pairs formation was favorable in methanol, due to about twice smaller dielectric constant of it as compared to water.

**$Na^+$ solvation sphere.** The Monte Carlo simulation of the 1 $Na^+$ – 127 $CH_3OH$ system revealed six alcohol molecules in the nearest surrounding of the ion at the distance of 0.235 nm [15]. It was assumed that the second coordination sphere consisted of six methanol molecules as well. The solvation number of six was confirmed by IR spectroscopy [6] and by the Monte

**Table 1.** Structural parameters of the nearest surrounding of alkali metal ions in methanol

| System | Method | Coordination number *N* | $r(M^+–O)$, nm | References |
|---|---|---|---|---|
| $Li^+–127CH_3OH^a$ | Molecular dynamics | 4 | 0.190 | [16] |
| $Li^+–25CH_3OH$ | Molecular dynamics | 4 | 0.200 | [17] |
| $Li^+–225CH_3OH$ | Molecular dynamics | 4.2 | | [18] |
| $Na^+–127CH_3OH^b$ | Monte Carlo | 6 | 0.235 | [19] |
| 0.6 mol/L NaCl | Molecular dynamics | 6 | | [20] |
| $Na^+–215CH_3OH$ | Monte Carlo | 5.6 | | [21, 22] |
| $Na^+–255CH_3OH$ | Monte Carlo | 6 | 0.25 | [23] |
| $16NaCl–400CH_3OH$ | Molecular dynamics | 6 | 0.245 nm | [24] |
| $Na^+–225CH_3OH$ | Molecular dynamics | 5.66 | | [18] |
| $Na^+–25CH_3OH$ | Molecular dynamics | 5 | 0.240 | [25] |
| $K^+–255CH_3OH$ | Monte Carlo | 6.1 | 0.27 | [23] |
| $K^+–225CH_3OH$ | Molecular dynamics | 6.09 | | [18] |
| $K^+–25CH_3OH$ | Molecular dynamics | 5.41 | 0.270 | [25] |

[a] $N_{II} = 4$, $r(M^+–O_{II}) = 0.420$ nm; [b] $N_{II} = 6$, $r(M^+–O_{II}) = 0.450$ nm.

Carlo simulation of the $Na^+(CH_3OH)_n$ ($n$ = 3–25) clusters in the gas phase [26]. No hydrogen bonding was found between methanol molecules in the first coordination sphere. Theoretical study gave the coordination number of $Na^+$ in methanol of 5.5, the distance to coordinated molecules being of 0.255 nm [27]. From molecular dynamics study [28], the coordination number of $Na^+$ equaled 6, and the distance to the coordination sphere equaled 0.232 nm in the case of the system 8 $Na^+$ – 8 $Cl^-$ – 400 solvent molecules, the solvent being a mixture of water and methanol. As commented in [29], the introduction of chloride only influenced the ions solvation state but had no effect on the bulky solvent structure. Six molecules of methanol was found to be the limiting coordination number of sodium ion in the study of the $Na^+(CH_3OH)_n$ clusters [30]. Molecular dynamics simulation of the 1 $Na^+$ – 25 $CH_3OH$ system showed that the average coordination number of the cation was of 4.4 with $r(Na^+–O) = 0.237$ nm [31], the decrease of the coordination number being assigned to larger volume of methanol. The peak corresponding to the second coordination sphere was observed at $r$ = 0.450 nm; however, its discussion was missing in the paper. Some other results are summarized in Table 1.

Thus, basing on the above-mentioned results, the nearest surrounding of $Na^+$ in methanol consisted of 4.4–6 coordinated solvent molecules at a distance of $r(Na^+–O_I) = 0.232–0.255$ nm. The second coordination sphere included 6 methanol molecules located at a distance of $r(Na^+–O_{II}) = 0.450$ nm.

According to [32], in the concentrated aqueous solutions the coordination number of $Na^+$ equaled four, and the dilution increased *N* to six. The distance to the coordinated water molecules was practically independent of dilution, $r = 0.230–0.245$ nm. The second coordination sphere of $Na^+$ ion was revealed in the diluted solutions, at a distance of $r = 0.410–0.420$ nm. The number of water molecules (up to 12) depended on the dilution and on the counterion type. The ion pairs were only formed in the concentrated solutions.

Thus, from the comparison of water and methanol solutions of sodium salts it followed: (1) the first coordination spheres were similar; (2) the second coordination sphere consisted of less molecules in the case of methanol, and the number of alcohol molecules in the second coordination sphere did not exceed that in the first sphere; (3) the distance to the second coordination sphere was longer in the case of methanol due to steric factor.

**$K^+$ solvation sphere.** In the theoretical study [27] the coordination sphere of $K^+$ in methanol was found to consist of 6.0 solvent molecules located at a distance of 0.295 nm. In the study of the M($CH_3OH$)$_7$ clusters (M = $Li^+$, $Na^+$, or $K^+$) it was confirmed that $Na^+$ and $K^+$ accommodated more of methanol molecules than did $Li^+$, and that the second coordination sphere was absent in the case of $K^+$ [33]. From acoustic and synchrotron annihilation studies of KI solutions in methanol, the coordination number of $K^+$ equaled five [34]. Results of other studies are collected in Table 1.

In the aqueous solution, the relatively unstable first coordination sphere was formed by $K^+$ at a distance of 0.28–0.29 nm [35]. The cation coordination number likely equaled 8 or 6. The second sphere formation was not typical for $K^+$, whereas both contact and solvent separated ion pairs were likely formed in potassium salts aqueous solutions.

Evidently, at that point the clear comparison of $K^+$ behavior in aqueous and methanol solutions could not be made due to lack of information about methanol solutions. It seemed that the distance to the coordination sphere in water was somewhat longer; the second coordination sphere was not formed in the both solvents.

**$Cs^+$ solvation sphere.** IR studies of the $Cs(CH_3OH)_n^+$, $n$ = 4–25 clusters in gas phase revealed ten methanol molecules in the coordination sphere of $Cs^+$ [36, 37]. The Monte Carlo simulation of the same clusters confirmed the coordination number of ten, and the distance to the coordination sphere was of 0.310 nm [37]. In the molecular dynamics study of the 1 $Cs^+$ – 225$CH_3OH$ system the cation coordination number was of 6.82 [18].

In the aqueous solutions, the relatively unstable first coordination sphere of $Cs^+$ likely consisted of eight water molecules at a distance of 0.300–0.320 nm [35]. The coordination parameters were highly condition-dependent; in particular, the number of solvating water molecules was decreasing with increasing salt concentration. The second coordination sphere was absent in the case of $Cs^+$. On the contrary, formation of ion pairs with the counterions was characteristic of $Cs^+$, the type and quantity of the pairs being dependent on the salt concentration and the counterion nature. Although not well supported, it seemed that $Cs^+$ coordination number towards methanol was higher than that in the case of water.

**$Ag^+$ solvation sphere.** The solvation of $Ag^+$ with methanol was studied in the gas phase, the most stable complexes included three [38] or four [39] methanol molecules. However, the information on such complexes was very limited; moreover, even the hydration of $Ag^+$ was not studied in detail. Thus, the comparison of coordination spheres of $Ag^+$ in water and methanol solutions was hardly possible at that point.

**$Cu^{2+}$ solvation sphere.** EXAFS spectroscopy study revealed that $Cu^{2+}$ coordinated 3.8 methanol molecules in the solution, they were located at equatorial positions with $r$ = 0.197 nm [40]. The distance to the axial methanol molecules could not be determined. By means of EXAFS and XANES spectroscopy it was found that in 0.1 mol/L solution, $Cu^{2+}$ ion was surrounded by five methanol molecules forming a square pyramid with $r(Cu^{2+}–O_{eq})$ = 0.195 nm and $r(Cu^{2+}–O_{ax})$ = 0.223 nm [41].

In the diluted water solutions, $Cu^{2+}$ coordinated six molecules of water: four at the equatorial positions with $r$ = 0.196±0.004 nm and two at the axial positions with $r$ = 0.240±0.010 nm [42]. Ion pairs could be formed in the copper(II) salt solutions as well, they were in the equilibrium with isolated hydrated cations. The second coordination sphere was observed at $r$ = 0.415±0.010 nm. Likely, no more than eight water molecules could enter the second coordination sphere, meaning that two water molecules were bound to each of the equatorial water molecules of the first sphere.

Similar to the previously reported case of $Ag^+$, comparison of $Cu^{2+}$ coordination in the aqueous and methanol solutions could hardly be made at that point, due to limited information available. However, the distance to equatorial molecules was seemingly quite similar in the both solvents cases.

As the charge density of the alkali earth metal ions was higher than that of the alkali metal ions, the first coordination spheres should be similar in water and in methanol, the second sphere should accommodate less of methanol molecules as compared to water, the second sphere should be larger in methanol, and the ion pairs should be readily formed in methanol solutions.

**$Mg^{2+}$ solvation sphere.** X-ray diffraction studies showed that six methanol molecules at 0.207 nm formed a relatively rigid octahedron around $Mg^{2+}$ [43]. Some other related results are collected in Table 2. From the data presented, $Mg^{2+}$ coordinated six molecules of methanol in the solutions; the distance to the coordinated solvent was of 0.200–0.215 nm. The formation of the second coordination sphere was demonstrated in a single work: $N = 7$, $r = 0.400$ nm [47].

The conductivity of $MgCl_2$ in methanol [44] and ultrasound absorption by 0.2 mol/L $Mg(ClO_4)_2$ in aqueous methanol [45] studies revealed formation of the solvated ion pairs in those solutions.

In the aqueous solutions, $Mg^{2+}$ coordinated six water molecules located at the average distance of 0.209–0.215 nm [46]. In diluted solutions, the second coordination sphere was formed of 12 water molecules located at $r = 0.410$ nm. Formation of solvent separated ion pairs was possible in concentrated solutions.

Thus, the parameters of the first coordination sphere of $Mg^{2+}$ were similar in aqueous and methanol solutions. The second coordination sphere was formed as well; however, its size in the case of methanol solution [47] seemed underestimated, as it was hardly possible that larger methanol molecules were located closer to the central ion than the smaller water molecules. The ions association was possible in the both solvents, being more favorable in the case of methanol.

**$Ca^{2+}$ solvation sphere.** From the measurements of sound velocity and viscosity of $CaCl_2$ in methanol, the cation coordination number equaled 5.5 [48]. According to the molecular dynamics simulation of EXAFS spectrum, $Ca^{2+}$ coordination number was of six, $r(Ca^{2+}–O) = 0.240$ nm [49]. X-ray diffraction studies of $CaCl_2$ solutions in methanol [50] gave following results. $N$ decreased from 6 to 5.1 as the salt concentration increased from 1 mol/L to 2 mol/L. It was commented that coordination number can be determined by X-ray diffraction only as quite inaccurate values. The distance to the first coordination sphere was of 0.239 nm. In the second coordination sphere, at $r = 0.455$ nm, 11.2 (1 mol/L) and 9.2 (2 mol/L) methanol molecules were located. In the 1 mol/L solution, solvent separated ion pairs were detected, whereas at 2 mol/L of the salt contact ion pairs were formed with $r(Ca^{2+}–Cl^{-}) = 0.270$ nm. The same solutions were then studied by means of neutron diffraction and molecular dynamics [51]. The following parameters of the first coordination sphere were found: $N = 6.10$ and $r = 0.245$ nm (neutron diffraction, 1 mol/L), $N = 5.50$ and $r = 0.243$ nm (neutron diffraction, 2 mol/L), $N = 6.40$ and $r = 0.242$ nm (molecular dynamics, 1 mol/L), $N = 5.10$ and $r = 0.242$ nm (molecular dynamics, 2 mol/L). The second coordination sphere consisted of 11.5 molecules at $r = 0.487$ nm (1 mol/L) and 9.6 molecules at $r = 0.450$ nm (2 mol/L). Molecular dynamics simulation [52] revealed that about 40% of the cations formed the contact ion pairs in 1 mol/L solution of $CaCl_2$. With the same method [53] it was demonstrated that $CaCl_2$ addition to methanol had smaller influence on the solvent structure than in the case of water, however, the chains of methanol were broken.

From the molecular dynamics study of the $4CaCl_2$ – 400 solvent molecules, the solvent being water–methanol mixtures with varied components ratio, it was shown that hydration of $Ca^{2+}$ was favorable over solvation with methanol [54]. As water was substituted with methanol, the cation coordination number decreased from 10 to <8. Furthermore, transition of methanol decreased the number of solvent molecules in the cation second coordination sphere and increased the distance to coordinated molecules. Methanol molecules coordinated to $Ca^{2+}$ formed less than one hydrogen bond with the neighboring molecules. Some other results are summarized in Table 2.

Thus, in methanol solutions $Ca^{2+}$ coordinated 6 to 8 solvent molecules in the first sphere, $r(Ca^{2+}–O)$ was of 0.239–0.241 nm, the highest and the lowest value being excluded. The second coordination sphere consisted of 7–11.5 methanol molecules at $r = 0.455$–0.487 nm. In contrast to the alkali metal ions ($Li^+$ and $Na^+$), in the cases of $Mg^{2+}$ and $Ca^{2+}$ the number of methanol molecules in the second coordination sphere was somewhat higher than that in the first sphere. This meant that besides hydrogen-bonded methanol molecules, additional solvent was included into the second sphere. No interpretation of this phenomenon was found in the referenced literature; possibly that was due to increased role of the electrostatic interactions of methanol with more charged alkali earth ions. $Ca^{2+}$ and $Cl^-$ formed solvent separated as well as contact ion pairs in methanol solutions depending on the concentration.

In the diluted aqueous solutions, $Ca^{2+}$ coordinated seven to eight water molecules, $r$ being of 0.242–0.246 nm [55]. The second coordination sphere was formed by approximately 18 water molecules at $r$ = 0.425–0.435 nm. In the concentrated solutions, water was expelled from the second coordination sphere that finally disappeared at high concentration of the salt. Moreover, in the concentrated solutions even the coordination number of the first sphere could decrease. Ion association was possible as well with formation of solvent separated or contact ion pairs.

**Table 2.** Structural parameters of the nearest surrounding of $Mg^{2+}$ and $Ca^{2+}$ in methanol

| System | Method | Coordination number *N* | $r(M^{2+}–O)$, nm | References |
|---|---|---|---|---|
| 0.6 mol/L $MgCl_2$[a] | XRD | 6.4 | 206 | [47] |
| | Molecular dynamics | 6.0 | 0.200 | |
| $Mg^{2+}$–260$CH_3OH$ | Monte Carlo | 6 | 0.20 | [56] |
| $Mg^{2+}$–40$CH_3OH$ | Molecular dynamics | 6 | 0.215 | [57] |
| $Ca^{2+}$–260$CH_3OH$ | Monte Carlo | 7 | 0.23 | [56] |
| 0.25 mol/L $CaCl_2$[b] | Molecular dynamics | 7.6 | 0.247 | [58] |
| $Ca^{2+}$–40$CH_3OH$ | Molecular dynamics | 6 | 0.240 | [57] |
| 0.05 mol/L $CaCl_2$[c] | Molecular dynamics | 8 | 0.245 | [52] |
| 1.0 mol/L $CaCl_2$ | | 7.7 | 0.245 | |
| 0.025, 0.2, 2.9 mol/L | Molecular dynamics | 6.0 | 0.240 | [59] |
| $CaCl_2$ | EXAFS | 6.9 | 0.241 | |

[a] $N_{II} = 7$, $r(Mg^{2+}–O_{II}) = 0.400$ nm. [b] $n_{II} = 9.5$, $r(Ca^{2+}–O_{II}) = 0.49$ nm; [c] $N_{II} = 7$, $r(Mg^{2+}–O_{II}) = 0.420$ nm.

From the comparison of $Ca^{2+}$ behavior in aqueous and methanol solutions it was clear that the first coordination sphere was similar in the both solvents. The second coordination sphere consisted of less of solvent molecules in the case of methanol, and they were located farther from the ion as compared with water ($\Delta r = 0.04$ nm).

**$Sr^{2+}$ solvation sphere.** As followed from EXAFS results, in 0.1 mol/L solution of strontium trifluoromethanesulfonate $r(Sr^{2+}–O) = 0.261$ nm, $r(Sr^{2+}–H) = 0.316$ nm, and $r(Sr^{2+}–C) = 0.365$ nm, the number of respective interactions being of 7.2, 8, and 7.4 [60]. The Monte Carlo method revealed $N = 8$ and $r = 0.26$ nm for the 1 $Sr^{2+}$ – 260 $CH_3OH$ system [61].

In the diluted aqueous solutions, $Sr^{2+}$ coordinated eight water molecules in the first sphere, *r* being of 0.260–0.265 nm [62]. The second coordination sphere was formed as well at $r = 0.491–0.496$ nm, consisting of 18–22 water molecules. Ion pairs were readily formed by $Sr^{2+}$.

Basing on the $Sr^{2+}$ behavior in aqueous solution and on the above-deduced common trends, its structural parameters in methanol could be predicted: 7–8 methanol molecules coordinated in the first sphere at $r(Sr^{2+}–O) = 0.260$ nm; 8 or slightly more methanol molecules forming the second coordination sphere at about 0.534 nm; association with counterions was very likely.

**$Ba^{2+}$ solvation sphere.** According to the Monte Carlo simulation of the 1 $Ba^{2+}$ – 260 $CH_3OH$ system, $N = 9$, $r(Ba^{2+}–O) = 0.28$ nm [61].

In the aqueous solution, the first coordination sphere of $Ba^{2+}$ consisting of 9 water molecules was located at $r = 0.280–0.286$ nm [62]. The second coordination sphere was found at $r = 0.500$ nm; it consisted of 24 water molecules in the diluted solution. Ion pair formation occurred as well.

Similarly to the discussed above, $Ba^{2+}$ in methanol solutions likely coordinated 9 alcohol molecules in the first sphere located at about $r = 0.280–0.286$ nm. The second coordination sphere would likely be composed of 9 or somewhat more methanol molecules located at $r \approx 540$ nm. Evidently, ion pairs should be formed in methanol solutions.

From similar considerations and the knowledge on aquatic complexes structure [46] the parameters of $Be^{2+}$ cation nearest surrounding in methanol solutions should be as follows: 4 methanol molecules in the first coordination sphere, at $r = 0.161–0.167$ nm; 4–6 methanol molecules in the second coordination sphere at $r \approx 0.410$ nm; strong tendency to form ion pairs depending on the concentration of salt and the nature of anions. That in methanol solutions $N(Be^{2+}) = 4$, was confirmed in studies of the corresponding solutions thermodynamics [63, 64].

**$Zn^{2+}$ solvation sphere.** By means of EXAFS spectroscopy, 6 solvent molecules were observed coordinated to $Zn^{2+}$ in methanol solution, at $r = 0.208$ nm [40]. Quantum-chemical simulation, molecular dynamics, and EXAFS studies of diluted solution of zinc salt in methanol [65] revealed that the first coordination sphere consisted of six solvent molecules at $r = 0.204$ nm, being very similar to the first aquatic coordination sphere of the same cation. The second coordination sphere, located at $r = 0.394$ nm, consisted of six methanol molecules as well. It was underlined that the first coordination sphere in methanol was more structured than in water, likely due to larger volume of methanol molecule and thus less density of oxygen atoms packing. The quantitative analysis of XANES spectrum confirmed [66] that the structure of the second coordination sphere was mostly determined by the solvent–solvent interaction and bulk solvent structure.

In diluted and semi-concentrated aqueous solutions, $Zn^{2+}$ first coordination sphere of six water molecules formed an octahedron at $r = 0.208–0.215$ nm; the second sphere of 12 water molecules was located at $r = 0.420$ nm. Ion association process was dependent of the salt concentration and the anion nature.

Again, the similarity of the first coordination spheres in water and in methanol was evident, whereas the second spheres were different.

**$Ni^{2+}$ solvation sphere.** As shown by neutron diffraction with isotopic substitution, in 1 mol/L solutions of $NiCl_2$ in methanol, the cation coordinated on the average 3.7 methanol molecules and 0.8 chloride ion; $r(Ni^{2+}–O) = 0.207$ nm, $r(Ni^{2+}–C) = 0.316$, and $r(Ni^{2+}–H_O) = 0.262$ nm [67]. The formation of the second sphere was observed as well at $r = 0.46$ nm, it consisted of 9.5 methanol molecules. The contact ion pairs were formed in that solution as well, in contrast to the case of aqueous solution (in water, no contact associates were found at concentrations of up to 4.35 mol/L). EXAFS spectroscopy revealed coordination of six methanol molecules at $r = 0.205$ nm by $Ni^{2+}$ [40]. By neutron scattering from 1.4 mol/L solution of $NiCl_2$ in methanol, five coordinated methanol molecules were found along with one coordinated chlorine; $r(Ni^{2+}–O) = 0.2057$ nm, $r(Ni^{2+}–Cl) = 0.2348$ nm, and $r(Ni^{2+}–H_O) = 0.2619$ nm [68]. The ions were associated much stronger than in the case of aqueous solutions. The formation of contact ion pairs in the same methanol solution was confirmed in [69]. Minor amount of solvated linear ionic triplets $Cl^-–Ni^{2+}–Cl^-$ were observed.

To sum up, in methanol $Ni^{2+}$ coordinated six solvent molecules in the first sphere at $r = 0.206$ nm, and approximately nine molecules in the second sphere at $r = 0.46$ nm; contact ion pairs were observed even in relatively diluted solutions. In aqueous solutions, the first coordination sphere was exactly the same as in methanol solution, whereas the second sphere consisted of 12 water molecules at $r = 0.410$ nm; ion pairs could be formed as well. Thus, comparison of $Ni^{2+}$ behavior in the two solvents confirms the above-made deductions.

Unfortunately, the quantitative descriptions of the coordination of triply charged cations in methanol solutions were practically absent. The reported studies were mainly limited to the ion association evaluation in the cases of lanthanide ions. For instance, the ultrasound absorption was applied to study aqueous-methanol solutions of erbium(III) chloride [70], nitrate [71], and perchlorate [72]. In the cases of nitrate and perchlorate anions, the ion associates formation was accompanied with decrease of the coordination number, whereas such effect was not observed in the case of chloride. Similar studies of neodymium and gadolinium chlorides (in 0.2 mol/L solutions) revealed that the change of coordination number due to ion association was dependent on the sizes of both cation and anion [73]. In 1.95 mol/L lanthanum chloride solution in methanol, the inner sphere associates $LaCl_3(CH_3OH)_5$ with $r(La^{3+}–O) = 0.248$ nm and $r(La^{3+}–Cl) = 0.295$ nm were revealed by combination of X-ray diffraction and NMR experiments [74]. From NMR studies of the solutions in the mixed water–methanol solvent it was concluded that with increasing the ratio of alcohol in the mixture, formation of the inner sphere $La^{3+}–Cl^-$ ion pairs was enhanced [75].

NMR studies of dysprosium chloride in methanol revealed the coordination number of eight in the first sphere: five solvent molecules and three chloride ions [76]. Similar studies of dysprosium trifluoromethylsulfonate in methanol showed that only one or two of anions were found in the first coordination sphere of the cation along with the solvent molecules; rest of the anions were located in the second sphere [77]. In the aqueous solutions of the both dysprosium salts mentioned above, the anions were never found in the first coordination sphere [78].

In general, for triply charged cations the number of molecules in the second coordination sphere could be higher than that in the first sphere, due to additional electrostatic interaction.

To conclude, the first coordination sphere parameters were practically the same in aqueous and methanol solutions as far as doubly charged cations, $Li^+$, and $Na^+$ were considered; slightly higher number of methanol molecules could be coordinated as compared to water in the cases of $Rb^+$ and $Cs^+$. Similarity of the first coordination sphere in methanol and water was also confirmed by EXAFS for $Mn^{2+}$, $Fe^{2+}$ and $Co^{2+}$ ions [40]. In the cases of alkali metal ions, the number of methanol molecules in the second sphere was no more than that in the first sphere; however, with increasing the cation charge, the difference of $N_{2nd}$ and $N_{1st}$ would likely increase. The distance to methanol molecules coordinated in the second sphere was longer than that in the case of water. The tendency to form ion associates was more pronounced in methanol solutions.

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