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# Structure of the Nearest Surrounding of the $Na^+$ Ion in Aqueous Solutions of Its Salts

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**Abstract**—Published data obtained by various research methods on structural characteristics of sodium ion hydration in aqueous solutions of its salts and authors, X-ray diffraction data have been generalized. Structural parameters of the nearest surrounding of $Na^+$ ion, such as its coordination number, interparticle distances, and types of ion association, have been discussed. It has been noted that the coordination number of the cation changes from four to six upon dilution of the solutions.

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Solutions of sodium salts, along with their extensive use in industry, play an important role in the vital activity of humans. The $Na^+$ ion takes part in the excitation of nervous cells and muscles in the human organism, since it is transported along ion channels of corresponding cells. The selectivity of these channels depends on the hydrate structure of the ion [1]. This is one of the reasons for a large scientific interest to the structure of the hydrate complex of sodium ion. The behavior of this ion in aqueous solutions was studied by a great variety of physicochemical methods, both in terms of its structure-strengthening properties and with the aim of determining its structural hydration parameters and special features of ion association. Nevertheless, in the published works there are a number of discrepancies concerning the interpretation of the resulting data, and even presently no unambiguous conclusion can be drawn about quantitative characteristics of the structure of the nearest surrounding of this ion in solutions.

This work is a continuation of the cycle of works on the structure of aqueous electrolyte solutions under standard conditions [2]. Its aim was to generalize available published data and own experimental X-ray diffraction results on such structural parameters of $Na^+$ hydration as coordination number, interparticle distances, and characteristics of ion pairs. The first review covered Group I–III ions in a concentration range in which no structural changes in the nearest surrounding of cations seem to occur [3]. In that case the effect of concentration on the structure of the $Na^+$ hydrate complex was not set as an object to trace. A more complete material covering a wide concentration range is given below. The results of structural studies including aqueous solutions of sodium salts are summarized up to 1986 in [4] and up to 1993 in [5].

By its action on the structure of water $Na^+$ belongs to positively hydrated ions [6, 7], and this effect is rather weakly pronounced. According to NMR spectral data, the ratio of the mean durations of stay of water molecules near an ion and in pure water ($\tau_i/\tau_0$) for $Na^+$ is 1.6 (for comparison, the respective values for $Li^+$, $K^+$, and $Mg^{2+}$ are 2.3, 0.9, and 5.2) [8]. The mean duration of stay of water molecules in the first coordination sphere of $Na^+$ estimated in [9], was $1.2 \times 10^{-9}$ s. The average duration of stay of water molecules in the first coordination sphere of lithium is $2.2 \times 10^{-9}$ s. Based on these data we can conclude that, unlike $Li^+$, the $Na^+$ ion has a weaker ordering effect on the structure of the solvent. The radius of a hypothetical ion corresponding to the boundary between positive and negative hydration is 0.12 nm [10], whereas the radius of sodium ions is slightly smaller (0.095 nm) [11], which provides evidence to show that this ion belongs to positively hydrated ions.

*Coordination number.* At present there is no unambiguous answer to the question about the coordination number of the $Na^+$ ion. The nature of its electron orbitals suggests a tetrahedral $sp^3$ hybridization, i.e. the coordination number is four [12]. Such value was predicted by Lyushchenko [13] who assumed, on the basis of his developed structural model of solutions and judjing from the type of replacement of water molecules by ions and their penetration into the solvent network, that $Na^+$ coordinates four water molecules in a tetrahedral fashion. This hypothesis was also supported experimentally. An X-ray diffraction study of a 7M aqueous solution of sodium iodide showed that the cation is hydrated with four water molecules, the average $Na^+–OH_2$ distance being 0.24 nm [14]. Similar results were obtained for solutions of sodium iodide by neutron and X-ray diffraction [15]. In the latter case, it was noted that the structure of the hydration shell is independent of temperature and concentration. Valeev et al. [16] performed an X-ray diffraction analysis of an aqueous solution of NaBr with a 1 : 25 salt : water ratio to find that the cation is hydrated with four water molecules, the average $Na^+–OH_2$ distance being 0.230 nm. The presence of the $Na(OH_2)_4^+$ hydrate complex was also established by double-ray differential Raman spectroscopy from examination of the difference spectra of aqueous solutions of sodium chloride or bromide of various concentrations and pure water [17].

A number of other studies provided evidence for the coordination number six for sodium ions. Thus, even in an early X-ray diffraction study of aqueous solutions of sodium tetrafluoroborate (*m* 2.65, 4.59, and 9.05 mol kg$^{-1}$) the coordination number six (5.7 in the most concentrated solution) was deduced from the peak areas in the radial distribution function [18]. The same value was obtained by X-ray diffraction for 5 and 7 M aqueous solutions of $NaNO_3$ [19]. Monte–Carlo calculations for dilute aqueous solutions (1 : 125) under standard conditions, too, resulted in 6 for the coordination number of sodium ion [20]. We performed a comprehensive X-ray diffraction study of aqueous solutions of sodium salts over a wide concentration range [21–24]. The coordination number six was found for aqueous solutions of sodium perchlorate (molar ratios from 1 : 25 to 1 : 100), nitrate (from 1 : 15 to 1 : 40), and sulfate (1 : 100).

The coordination number eight was also suggested. Ohtomo and Arakawa [25] in a neutron diffraction study on a 1 M solution of sodium chloride in heavy water established that the coordination number of the $Na^+$ ion is eight and the distance from the ion to coordinated water molecules, 0.250 ± 0.010 nm.

To illustrate the diversity of coordination numbers found for the $Na^+$ ion in various aqueous solutions, we give the results of certain X-ray and neutron diffraction studies (Table 1).

**Table 1.** Parameters of the first coordination sphere of $Na^+$ ions in aqueous solutions as given by the X-ray and neutron diffraction methods

| Solution | $Na^+$–O destance, nm | Coordination number | References |
|---|---|---|---|
| 1 M NaCl | 0.250 | 8 | [25] (neutron diffraction) |
| 2 M NaCl | 0.242 | 4 | [26] |
| 4 M NaCl | 0.242 | 4 | [26] |
| 3 M NaOH | 0.238 | 4–6 | [27] |
| 6 M NaOH | 0.238 | 4–6 | [27] |
| 2.65 M $NaBF_4$ | 0.240 | 6 | [18] |
| 4.59 M $NaBF_4$ | 0.240 | 6 | [18] |
| 9.05 M $NaBF_4$ | 0.240 | 5.7 | [18] |
| 5 M $NaNO_3$ | 0.240 | 6 | [19] |
| 7 M NaI | 0.240 | 4 | [14] |

The structure of a nearly saturated aqueous solution of sodium chloride (*m* 6.18 mol kg$^{-1}$) was studied at 298 K by X-ray diffraction. Approximately 30% of ions in the solution form ion pairs with the $Na^+–Cl^-$ distance of 0.282 nm. The hydration numbers of the $Na^+$ and $Cl^-$ ions were found to be 4.6 and 5.3, respectively [28]. A 15 mol% aqueous solution of HCOONa was studied by neutron and X-ray diffraction, and also by Raman spectroscopy. The hydration number of $Na^+$ ions was found to be 4.6 ± 0.2 with the $Na^+–OH_2$ distance of 0.237 ± 0.001 nm [29].

The molecular dynamics and Monte–Carlo methods gave more unambiguous evidence showing that the coordination number of the $Na^+$ ion is close to six (Table 2).

Computer simulation of the $Na^+–(1–6)H_2O$ systems at 298 K was carried out by the Monte–Carlo method. The $Na^+–OH_2$ distance remained almost unchanged as the number of water molecules increased. The computations showed that the most probable surrounding of sodium ions is a distorted octahedron of six solvent molecules at an average distance close to 0.240 nm [41].

In some works, the coordination number was found close to five on the basis of molecular dynamics calculations [42–44]. The values obtained by computer methods can vary depending on the interaction potential. It was shown in [45] that the use of combined quantum-mechanic and molecular-mechanic potentials in molecular dynamics computations results in the estimate of 5.6 ± 0.3 for the coordination number of the $Na^+$ ion, which is somewhat lower that the value (6.5 ± 0.2) obtained with pair potentials.

To sum up the aforesaid, we can note that, according to the results of various works, the coordination number of the $Na^+$ ion can be four [12–16, 26], six [18–20], and eight [25]. The value found in [25] did

**Table 2.** Parameters of the first coordination sphere of the $Na^+$ ion in aqueous solutions as given by the MonteσCarlo (MC) and molecular dynamics (MD) methods

| Solvent | $T$, K | $r$, nm | Coordination number | Method | References |
|---|---|---|---|---|---|
| NaCl–25$H_2O$ | 298 | 0.236 | 6.5 | MD | [30] |
| NaCl–79$H_2O$ | 313 | 0.224 | 6 | MD | [31] |
| NaCl–64$H_2O$ | 287 | 0.235 | 6.2 | MD | [32] |
| 16NaCl–200$H_2O$ | 298 | 0.230 | 6.6 | MD | [33] |
| $NaClO_4$–25$H_2O$ | 298 | 0.236 | 6 | MD | [34] |
| $Na^+$–215$H_2O$ | 282 | 0.235 | 5.96 | MK | [35] |
| $Na^+$–125$H_2O$ | 298 | 0.229 | 6 | MK | [36] |
| $Na^+$–64$H_2O$ | 298 | 0.230 | 5–6 | MK | [37] |
| $Na^+$–64$H_2O$ | 348 | 0.230 | –6 | MK | [37] |
| $Na^+$–100$H_2O$ | 298 | 0.230 | 6.1 | MK | [38] |
| $Na^+$–50$H_2O$ | 298 | – | 6 | MK | [39] |
| $Na^+$–200$H_2O$ | 298 | 0.233 | 5.4 | MK | [40] |

not find theoretical and experimental confirmations even for dilute solutions. Hence we consider this coordination number improbable.

Therefore, two main hypotheses and two possible main configurations of the coordination sphere of the ion under study were recognized: (1) coordination sphere consisting of four water molecules arranged as a tetrahedron around the cation and (2) coordination sphere consisting of six water molecules arranged as an octahedron.

If we assume that the coordination number of the $Na^+$ ion is affected by the chemical nature of the anions, no evidence for this assumption can be found in the above-cited works. It was shown that the cation coordination number six can be realized in solutions of chlorides, perchlorates, sulfates, and some other sodium salts, and the value of four was found for solutions of sodium chlorides, iodides, and bromides.

The controversy in the structural parameters of the first coordination sphere may result from the fact that the coordination number of $Na^+$ varies with concentration. The structure of aqueous solutions of NaCl (0.2 to 5.0 M ) was studies in terms of the RISM (Reference Interaction Site Model) theory [46]. As the concentration increases, the cation–oxygen distance almost does not change (0.230–0.231 nm), and the coordination number of the cation decreases from 3.91 (0.2 M solution of NaCl) to 2.74 (5 M solution of NaCl). The $Na^+$ coordination number 3.51 found by the integral equations method is lower than the number obtained by the molecular dynamics and Monte–Carlo methods. This discrepancy seems to be associated with the specific features of the method used in [46]. The fact that the cation coordination number decreases with increasing concentration of aqueous solutions of NaCl was established by the integral equations method in our laboratory [47].

In [48, 49], on the basis of NMR relaxation data for aqueous solutions of sodium hydroxide it was noted that the coordination number of the $Na^+$ ion is six and decreases to four only in highly concentrated solutions (NaOH–14$H_2O$). A similar effect was found in an X-ray diffraction study of aqueous solutions of NaOH and NaCl: The coordination number was close to six at concentrations of 1–2 M and close to four at higher concentrations [27]. A decrease in the coordination number of the cation with increasing concentration was found by X-ray diffraction analysis also in concentrated solutions of sodium aluminate, but the average value remained unchanged until contact ion pairs are formed [50].

Consequently, one more hypothesis appears that the coordination number of the $Na^+$ ion increases from four to six with dilution of the solution. It is evident that in highly concentrated and saturated solutions the nearest surrounding of the cation cannot include six molecules because of the deficit of the solvent. Hence, this hypothesis seems to be the most probable. Moreover, we emphasize that the fractional values of the coordination number of the sodium ion, obtained in some diffraction studies [18, 28, 29], are averaged values of the numbers of interactions of the cation with water molecules from the first coordination sphere. Consequently, these values can provide additional evidence showing that the equilibrium in the solutions between the $Na(H_2O)_4^+$ and $Na(H_2O)_6^+$ hydrate complexes shifts to one or another side, depending on concentration. We suggest that the effect of anions in concentrated solutions shows up in a shift of concentration zones in which the coordination number of the sodium ion changes.

In our research, the coordination number of the cation changed from four in aqueous solutions of sodium chromate with 1:25 and 1:40 molar ratios to six in a 1:100 solution. It also changed in aqueous solutions of sodium perchlorate from four (contact ion pair is formed) in a 1:5 solution to six in a 1:25 and more dilute solutions [21, 22].

*$Na^+$–$OH_2$ interparticle distance.* Marcus [4] gave the $Na^+$–O internuclear distance of $0.235 \pm 0.006$ nm and noted that no evidence that this parameter is concentration-dependent is available. Later Ohtaki and Radnai [5] reported the distance varying from 0.240 to 0.250 nm at the coordination number varying from four to eight, obtained by diffraction studies, and the distance 0.230–0.240 nm (the coordination number is equal or close to six), obtained by computations. Examination of Tables 1 and 2 confirms these ranges. X-ray diffraction studies showed that the $Na^+$–$OH_2$ distance spans the range 0.238–0.249 nm (Table 1). According to compution results, this distance appeared to be slightly shorter, 0.230–0.236 nm (Table 2), whereas the coordination number varies between five and six. We emphasize that the distance between the cation and coordinated water molecules can depend on solution concentration, counterions, ion association, and some other reasons. At present there is no unambiguous experimental evidence for dependence of the $Na^+$–$OH_2$ distance on on the concentration and the type of the counterion. Hence, we can speak about a precise value of this parameter only for highly dilute solutions, since in concentrated systems it can take unique values. In our works, the $Na^+$–$OH_2$ distance was found to be 0.248 nm for sodium nitrate solutions, 0.235–0.237 nm for sodium perchlorate solutions, 0.235 nm for sodium sulfate solutions, and 0.230–0.249 nm for sodium chromate solutions [21–24].

*Second coordination sphere.* Published information points to the fact that $Na^+$ ions form the second coordination sphere [31, 48], the latter contributing about 10% into the total $Na^+$ hydration energy [31]. On the basis of NMR relaxation data for aqueous NaOH solutions, a conclusion was drawn that the second coordination sphere of the cation includes 12 water molecules [48]. Molecular dynamics computations for aqueous sodium perchlorate revealed a fairly well-defined second sphere with the $Na^+$–$OH_{2(II)}$ distance of 0.445 nm [31]. The second hydration shell of sodium ions amounts up to 20 water molecules at 313 K, which seems to be rather strange taking account of a comparatively low coordination ability of the cation. Donets and Chizik [51], based on NMR studies of aqueous solutions of sodium nitrate over a wide concentration range, noted that, as the concentration of the salt increases, a deficit of solvent molecules is observed for forming the second hydration shell of the $Na^+$ ion, which results gradual decomposition of the shell. At $m$ 4.6 mol kg$^{-1}$ ($NaNO_3 : D_2O$ molar ratio 1:12), the second coordination sphere of $Na^+$ disappears completely.

We found that the $Na^+$ ion forms its second coordination sphere in the range of distances 0.410–0.420 nm. The number of water molecules in it strongly depends on the solution concentration, attains the maximum of twelve at medium concentrations, and decreases the concentration of the solutions increases [21–24]. The number of water molecules in the second coordination sphere of sodium ions decreases simultaneously with decreasinng hydration number of the anions.

*Ion association.* The problem of ion association in solutions of sodium salts, too, remains controversial. The chemical nature and steric configuration of the anions affect ion pair formation. For example, the study of the $H_2PO_4^-$–$Na^+$–$nH_2O$ system ($n$ = 9, 12, 14) by the molecular dynamics method revealed strong interaction between the $Na^+$ and $H_2PO_4^-$ ions [52], which makes hydration of sodium ions difficult to consider.

When studying aqueous solutions of sodium perchlorate by means of vibrational spectroscopy, Miller and Macklin [53] found that up $m$ 8 mol kg$^{-1}$ independently hydrated ions are predominantly present in the solution [53]. In the region $8 < m < 12$, solvent-separated ion pairs are formed, and at $m > 12$ contact ion pairs become the main structural units. Among the three structures capable of forming in the solution, a contact associate of $C_{2v}$ symmetry is the most probable.

In a 22 molal $NaClO_4$ solution, the $Na^+$–$ClO_4^-$ pair distribution function was found to have a maimum corresponding to the presence of solvent-separated ion pairs in the system [31]. According to NMR data, contact ion pairs are formed in aqueous solutions of sodium perchlorate at molar fractions higher than 0.2 [54]. The IR spectra of aqueous solutions of sodium perchlorate in the concentration range 1–10 M were found to be adequately interpreted on the assumption that the solution contains $Na^+(H_2O)$–$ClO_4^-$ aggregates [55]. The preservation of the symmetrical shape of the $\nu_3$ band of perchlorate ions at salt concentrations of up to 6 M points to the fact that the surrounding of $ClO_4^-$ ions is not changed and, consequently, the probability of formation of contact ion pairs is very low.

This result was confirmed by the same method for aqueous solutions of sodium perchlorate in the concentration range 0–3.0 M [56]. The distance of the closest approach of the $Na^+$ and $ClO_4^-$ ions in aqueous solutions, calculated from the activity coefficients, appeared to be 0.404 nm [57]. In our studies, contact ion pairs in sodium perchlorate solutions were found only at a 1 : 15 molar ratio [21, 22].

It was found by the X-ray diffraction analysis of 5 and 7 M aqueous solutions of $NaNO_3$ that the experimental data are best described by a model in which an octahedrally hydrated $Na^+$ ion correlates with the $NO_3^-$ anion, probably in the form of a solvent-separated ion pair [19]. It was noted on the basis of NMR data that at m 5.6 mol $kg^{-1}$ (1 : 10) complexes in the form of separated ion pairs seem to form in the solution [51]. Our results, too, provide evidence for the presence of noncontact ion pairs in aqueous solutions of sodium nitrate at 1 : 5 to 1 : 40 molar ratios [23].

Vasin et al. [58, 59] concluded from the thermochemistry of salting out that non-contact ion pairs are present in aqueous solutions of both sodium sulfate and sulfuric acid. We did not find ion pairs of any kind in 1 : 100 aqueous solutions of sodium sulfate, which is probably accounted for by the low concentration of the system [24].

Pytkowicz [60] on the basis of experimental data (Raman spectroscopy and potentiometry) and their correlation with the thermodynamic properties of the $Cl^-$ and $ClO_4^-$ ions obtained evidence in favor of the formation in aqueous solutions of $NaCl^-$ ion pairs, and the association constant of the latter higher than for $NaClO_4^-$.

Berkowitz et al. [61] calculated by molecular dynamics medium-force potentials, to conclud that in aqueous solutions of sodium chloride both contact and hydration-separated ion pair can form, but the former ones are are more favored by energy. The $Na^+$–$Cl^-$ distance in the contact pair found in this work is approximately 0.270 nm. The presence of such types of ion pairs in aqueous solutions of sodium chloride was confirmed by Uchida and Matsuoka [62] by molecular dynamics data for dilute through supersaturated solutions. The number of contact ion pairs was noted to increase as the concentration increases up to saturation. The formation of ion pairs in a 1 M aqueous solution of sodium chloride was confirmed by Monte–Carlo computations [63]. On the contrary, Zasetsky and Svishchev [64] established the presence of only hydration-separated ion pairs with the Na–Cl distance of approximately 0.5 nm in a 1 M NaCl aqueous solution by the molecular dynamics method. The $Na^+OCl^-$ angle was found to be 106°.

In a concentrated solution of sodium chromate (1 : 15), contact $Na^+OCrO_3{}^{2-}$ ion pairs are formed with the $Na^+$–CrO distance of 0.349 nm [65].

The aforesaid allows us to speak about a tendency for ion associates in aqueous solutions of sodium salts, at concentrations starting from 1 : 15 molar ratios and higher. The difference between the types of ion pairs and their quantitative ratios to independently hydrated ions is defined by the difference in the steric configurations and chemical nature of the anions. In the case of sodium chloride solutions, a tendency to form contact ion pairs is observed with gradual trasition to solvent-separated associates and then to independent hydration on dilution. At comparatively high concentrations, solutions of sodium perchlorate and nitrate contain noncontact ion pairs.

Summing up the available information we suggest that in highly concentrated solutions, $Na^+$ ions have the coordination number four and a tetrahedral arrangement of coordinated molecules. Dilution of the solutions increases the number of water molecules in the first coordination sphere of the cation to six with their octahedral arrangement. The distance to water molecules in the first sphere remains almost unchanged in the range 0.230–0.245 nm. The concentration region in which the coordination number of the $Na^+$ ion changes depends on the chemical nature of the anion. As the concentration decreases, the second coordination sphere of $Na^+$ ions forms at a distance of 0.410–0.420 nm. The number of water molecules in it depends on the type of the counterions and on the electrolyte concentration, the maximum being 12. Ion pairs of various types are formed in concentrated solutions, and their form and quantity depends both on the chemical nature of the anions and on the concentration. In dilute and medium-concentration solutions, ion pairs do not determine the structure of aqueous solutions of sodium salts.

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