# Molecular dynamics simulation of an aqueous Na$_2$SO$_4$ solution

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The structure of sodium sulfate in TIP3P water solution with the concentration of 0.1191 mol/dm$^3$ was studied by means of classical molecular dynamics. Both ions have clear hydration shells. The comparison between radial distribution functions and cumulative numbers of selected atoms around the reference one makes it possible to precisely describe the structure of investigated system. Applying such tools geometrical parameters of the hydrogen bond of the dimer SO$_4^{2-}$/H$_2$O have been obtained.

**Keywords**: hydrogen bond, sulfate, water, solvation structure, TIP3P, radial distribution function, hydration shell

## 1. INTRODUCTION

Recently the activity of Hofmeister anions attracted scientists' attention again due to the development of modern experimental techniques. In 2003 Omta et al.[1] showed experimentally that the hydrogen-bond network in aqueous perchlorate and sulfate solutions is affected by anions only in the range of the first solvation shells. These

results were in opposition to the common view on the activity of Hofmeister anions. The for years commonly accepted view that different physical properties of "chaotropic" and "kosmotropic" ions come from their interactions with hydrogen bond network in aqueous solutions appeared to be wrong. Thus, the only reason for quite different influence of perchlorate and sulfate on the solubility of proteins can be explained by effects occurring in their solvation shells. A few years later Laage et al.[2] showed by means of classical molecular dynamics, that the hydrogen-bond network in pure water is constantly changing. The process of hydrogen bond making and breaking is accompanied by non-diffusive jump-reorientation mechanism. Further studies showed that such jump-reorientation of water molecules during hydrogen bond switching has been also observed in solvation shells of simple ions[3, 4, 5]. Stirnemann et al. [6] showed that the impact of salt on water dynamics is ion specific. Ions have strong but short-range influence on the behavior of water molecules located in the solvation shells. Moreover, the hydroxyl and dipole reorientation time correlation functions of water bonded to ions have different shapes and their inclinations change according to Hofmeister series.

It is very interesting that perchlorate and sulfate anions have similar geometrical shape. Both of the ions are regular rigid tetrahedrons with four oxygens located at vertices, six edges and four triangular faces. But the physical properties of their water solutions are quite different – perchlorate is the most chaotropic and sulfate is the most kosmotropic anion in Hofmeister series. The present paper deals with the physical structure of the sulfate anion. Although it is already known how ions influence the solution properties, it is worth investigating the relationship between solution structure and physical properties of ions. The obtained results can help better understand Hofmeister ions activity.

## 2.  DETAILS OF SIMULATION

The sulfate anion is assumed to be of a regular rigid tetrahedron with S-O distance of 0.1487 nm. The atomic charges for $SO_4^{2-}$ were obtained by R.E.D. Server [7] using the RESP-A1A (HF/6-31G*) charge model and the Gaussian 09 quantum mechanics program. The GAFF topology for perchlorate anion was generated using ACPYPE [8]. Atomic partial charges are as follows: S: +1.540804 e, O: -0.885201 e; the Lennard-Jones parameters: O: $\sigma = 0.356359$ nm; $\varepsilon = 1.04600$ kJ/mol; O: $\sigma = 0.295992$ nm;

$\varepsilon = 0.878640$ kJ/mol. The charges of sulphur are different from those reported by Cannon et al. [9]. It is probably due to the differences in methods for charge fitting. It is worth to mentioning that the obtained partial charges for $SO_4^{2-}$ ion are in agreement with the data determined by fluorescence methods [10].

The solution of sodium sulfate in TIP3P (transferable intermolecular potential with 3 points) water with the concentration of 0.1191 mol/dm$^3$ was prepared by placing twenty $Na^+$ cations and ten $SO_4^{2-}$ anions in 4980 water molecules into a cubic box of the length of 5.19 nm. The periodic boundary conditions were applied. Simulations were performed using Gromacs 2016.4 software [11–13]. The smooth particle-mesh Ewald (PME) algorithm was used to describe the long-range electrostatic interactions. After 50 ps equilibration period in isothermal-isobaric ensemble a 2 ns (1 fs time step, coordinates saved every 5 fs) classical MD trajectory was generated in the canonical ensemble using the Nose-Hoover thermostat at the temperature of 295.95 K. The calculated density of simulation system was 1.085 g/cm$^3$, whereas the experimentally determined one was 1.006 g/cm$^3$.

# 3. RESULTS AND DISCUSSION

The aim of presented study is to investigate the structure of an aqueous sodium sulfate solution. It can be determined using the radial distribution function (RDF). Figure 1 shows RDF function of pair sulphur – water's oxygen calculated in relation to the position of sulphur atom. The comparison of the first maximum of RDF with the cumulative number of water molecules at given distance is equal to the coordination number for the first solvation shell. Thus, the first minimum of the RDF is located at 0.434 nm and then the coordination number for the first hydration shell of $SO_4^{2-}$ is 13.4. Moreover, also the second solvation shell of $SO_4^{2-}$ can be observed at 0.67 nm. The corresponding coordination number is 46.
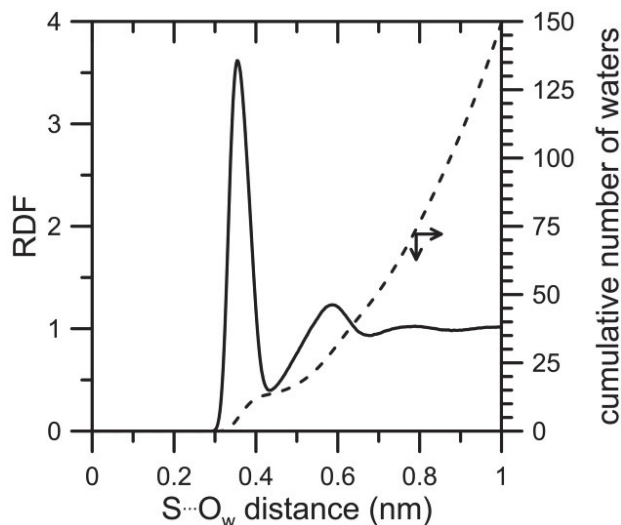
Fig. 1. The comparison between the radial distribution function of the pair sulphur –
water's oxygen and the cumulative number of waters around the sulphate anion.

Then, Fig. 2 shows $Na^{...}O_w$ and $Na^{...}H$ RDFs. The first minimum of RDF function for $Na^{...}O_w$ pair is located at 0.32 nm. The comparison with the cumulative number of $O_w$ around $Na^+$ gives the coordination number of the first solvation shell 6.88. Next, the first minimum of the RDF of the pair $Na^{...}H$ is located at 0.3 nm and the cumulative number of H is 8.1. This information makes it possible to imagine how most water molecules in the first $Na^+$ solvation shell are oriented as the trimer $Na$-$O_w$-$H$ forms triangle with known sides. Thus, the calculations give the angle $NaO_wH$ equal to 69.36°.

The second solvation shell of hydration sphere is less clear and occurs at the distance of 0.56 nm. The corresponding coordination number is 26.25 water molecules.
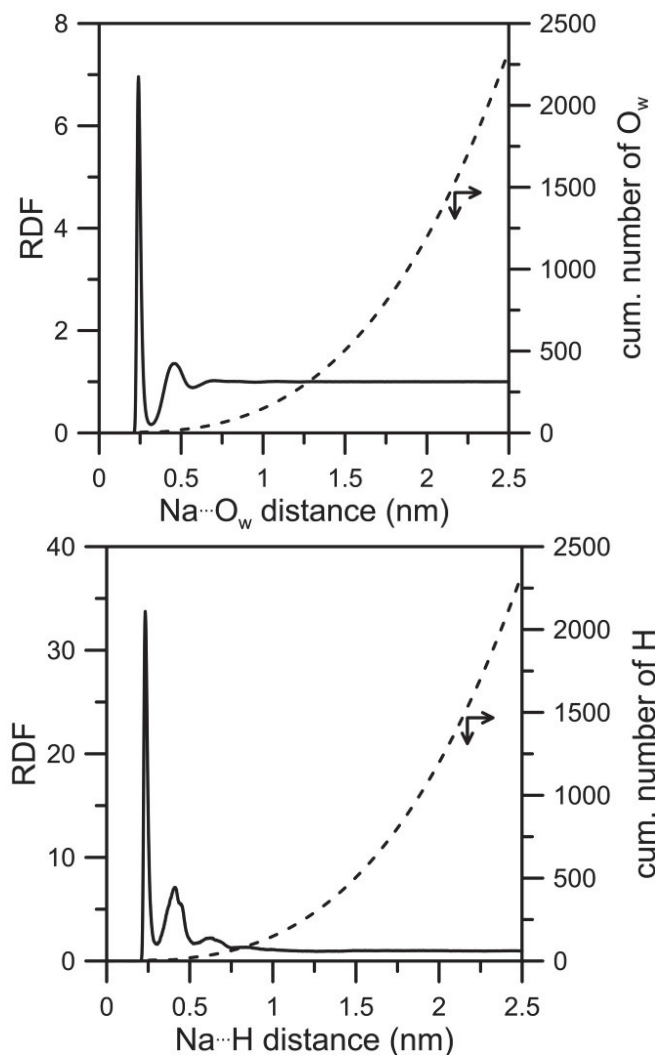
Fig. 2. Radial distribution functions and cumulative numbers of O$_w$ and H atoms around the sodium cation.

Figure 3 shows the distribution of ions in the investigated system. It can be seen that Na$\cdots$Na RDF has two visible minima at 0.48 nm and 0.7 nm. But in this case, due to the low number of sodium cations in system, even an incidental approach of two atoms results in RDF peaks. Thus in this case we can find the distance where the cumulative number of Na$^+$ is equal to 1.

We can see that the average distance between two Na$^+$ cations is about 1.25 nm. At this distance Na$\cdots$Na RDF has an almost stable value. Such a configuration corresponds to the situation when two sodium cations are separated by approximately two water molecules. Similarly, the analysis of the second part of Fig. 3 makes it possible to obtain the

average distance between two sulphate anions. RDF of S⋯S has stable value at the distance of 1.77 nm. This is the average distance between two sulphate anions.
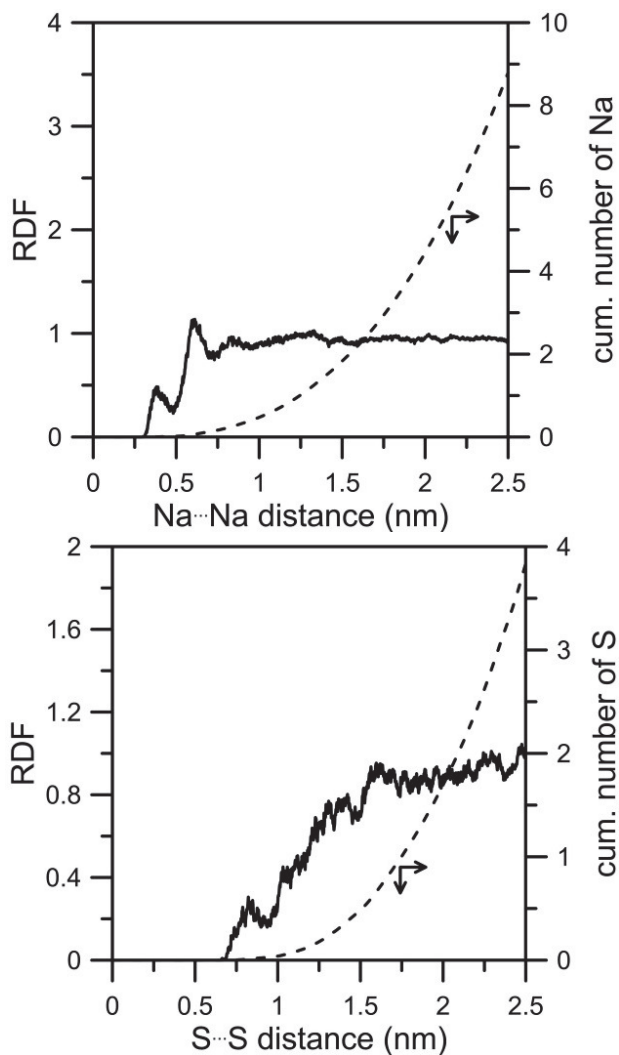


Fig. 3. RDFs and cumulative numbers of pairs Na⋯Na and S⋯S.

The next RDF and cumulative number of sulphur atoms around the sodium cation are showed in Fig. 4. It can be seen that the average distance between these two atoms in simulated system is 0.94 nm. It means that $Na^+$ and $SO_4^{2-}$ can approach each other to distance at which about two water molecules are located between them.
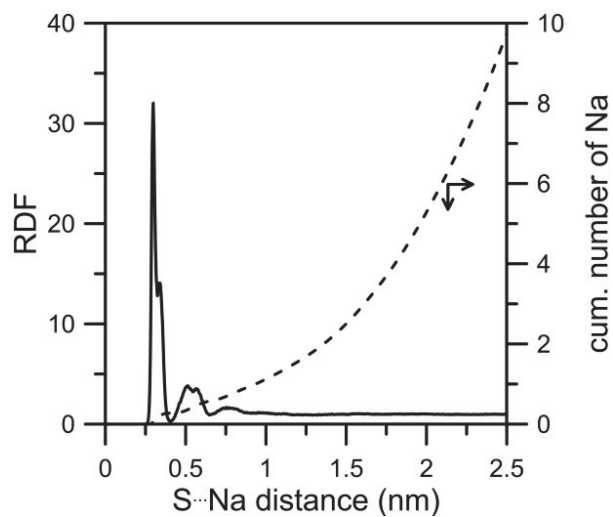
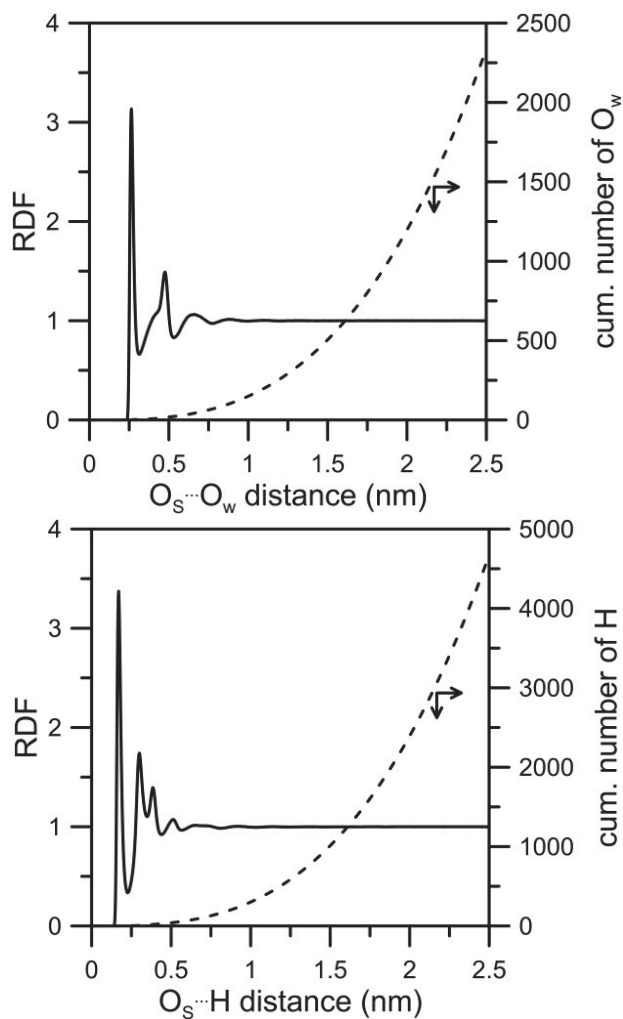Fig. 4. RDF and cumulative number of Na$^+$ cations around sulphur atom.



Fig. 5. RDFs and cumulative numbers of O$_w$ and H around O$_s$ atoms.

The last Fig. 5 shows how water surrounds sulphate anion. Radial distribution function of $O_s^{...}O_w$ has two minima at 0.32 nm and 0.54 nm and the corresponding cumulative numbers of $O_w$ atoms are 3.12 and 22.5 respectively.

The second part of Fig. 5 shows a few minima in $O_s^{...}H$ RDF function at 0.23 nm, 0.34 nm and 0.44 nm. The corresponding cumulative numbers of hydrogen atoms are as follows: 6.25, 13.75 and 28.75. Again, if we consider that three atoms $O_s$, $O_w$ and H form a triangle with known sides, we can calculate in this way the average hydrogen bond geometric parameters for dimer $SO_4^{2-}$ and hydroxyl group $-O_wH$. $O_w-O_s$ distance is, as it was mentioned above, 0.32 nm whereas the average $O_sO_wH$ angle is 15.7°. Taking into account the Jeffrey's classification [14], this is a moderate, mostly electrostatic hydrogen bridge.

## 4. SUMMARY

From molecular dynamics insights the structure of sodium sulphate water solution in TIP3P water has been demonstrated. Both ions have well-formed solvation shells. The information collected by using the radial distribution function makes it possible to precisely describe the structure of the solution e.q. the average distances between all system components. It also enables to determine the average values of geometric parameters of hydrogen bond between sulfate anion and water. All determined data are in agreement with one presented in the literature [9].

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