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## Group ion-water interactions in aqueous solutions $\text{Na}_2\text{SO}_4$ and $\text{K}_2\text{SO}_4$

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In this work, for the first time, studies of aqueous solutions of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  were carried out based on the determination of the parameters of radiothermal radiation in the millimeter (mm) region of the spectrum. The developed method is based on the determination of the static dielectric constant of aqueous solutions - the absorption coefficient at a frequency of 61.2 GHz. Experimental data have been obtained to determine the value of the absorption coefficients of aqueous solutions of substances in a wide range of concentrations. A monotonous increase in the values of the absorption coefficients of solutions with a decrease in the concentration of base substances in the region of high dilutions was established with individual dynamics for each base substance. The changes in the dielectric constant recorded in the experiments reflect the total hydration changes in salt solutions outside the first hydration shell.

**Keywords:** aqueous solutions, absorption coefficient, hydration shell.

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Variations of physical properties of aqueous solutions reflect the evolution of their dielectric parameters, including the spectra of centimeter and millimeter ranges of electromagnetic waves (EMWs) [1–3], which attract attention due to the fact that here lies the boundary between collective molecular processes in solutions (specifying the statistical values of dielectric constants) and individual reactions of water molecules (due to the redistribution of H bonds) [4]. Waveguide methods for measurement of the permittivity of aqueous solutions of sulfates as a function of their concentration were discussed, with a focus on the decimeter EMW range, in [5]. Quasi-optical techniques for measurement of absorbed and reflected plane electromagnetic waves were used to determine the properties of aqueous solutions [6,7]. The EMW absorption in aqueous solutions of lithium and sodium sulfates was associated in these studies with relaxation processes of ionic pairs in the decimeter spectral range. The results of examination of aqueous solutions of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  were presented in [8]. It was found that the influence of  $\text{Na}^+$  and  $\text{K}^+$  ions on the water network is not limited to the first hydration layer. The interest in  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  stems from the fact that sulfate solutions are used widely as prototype systems for studying complex structural and dynamic properties of aqueous solutions of ions [1,2,8].

The papers cited above cover solutions with high concentrations of the base substance (from 1% upward), since the sensitivity of instruments used in experiments is insufficient to probe lower values. An average of no more than four water molecules are positioned in this case between cations and anions of the dissolved substance. This hampers the construction of hydration shells with more than a single layer. The present study is aimed at examining the dynamics

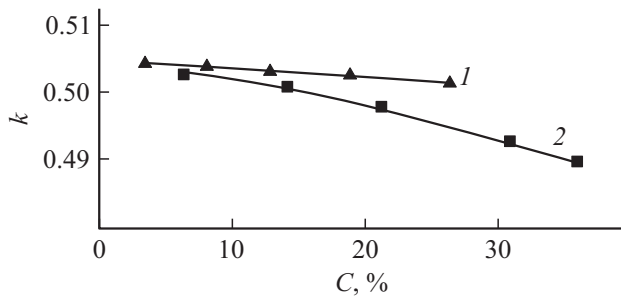
of dielectric properties of aqueous solutions at high (from 1 to 35%) and low (down to  $10^{-9}$ ) concentrations of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  at a frequency of 61.2 GHz and analyzing the influence of ions on the formation of hydration shells.

The following substances were used to prepare solutions: sodium sulfate  $\text{Na}_2\text{SO}_4$  (high purity), STP TU KOMP 3-47857, and potassium sulfate  $\text{K}_2\text{SO}_4$  (high purity), GOST 24147–87. Water of the first grade of purity with a resistance of  $17.5 \text{ M}\Omega \cdot \text{cm}$  at the moment of preparation, which was produced by an Aquapur MLW, VEB MLW LABORTECHNIK 85005 (ILMENAU, Germany) ion exchanger, was used to prepare the initial solutions and all samples of each substance with subsequent dilutions. Samples with a normal (1–35%) concentration of base substances  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  were formed by weighing with scales with an accuracy of 0.01 g. Solutions were prepared by weighing specific amounts of substances and dissolving them in distilled water. Samples of highly dilute solutions were prepared via consecutive decimal dilutions. A 10% solution (D1) was made first, and solutions with concentrations from  $10^{-2}$  (D2) to  $10^{-9}$  (D9) were derived from it via consecutive decimal dilutions.

The specifics of interaction of aqueous solutions with an EMW are defined by their dielectric properties. The complex permittivity of a solution may be presented as a sum of two components [1]:

$$\varepsilon^*(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu),$$

where  $\varepsilon'(\nu)$  is permittivity and  $\varepsilon''(\nu)$  are dielectric losses,  $i = \sqrt{-1}$ . Dielectric losses in electrolyte solutions are specified by the reorientation of water molecules and the



**Figure 1.** Variation of the absorption coefficient of aqueous solutions of  $\text{K}_2\text{SO}_4$  (1) and  $\text{Na}_2\text{SO}_4$  (2) with concentration of the base substance, which increases from 1 to 35%.

shift of charged ions:

$$\varepsilon''(\nu) = \varepsilon_d''(\nu) + \varepsilon_i''(\nu),$$

where  $\varepsilon_d''(\nu)$  and  $\varepsilon_i''(\nu)$  are dipole and ionic losses. At experimental frequency  $\nu = 61.2$  GHz, which is much higher than Debye frequency  $\nu_D = (2\pi\tau)^{-1} \approx 2 \cdot 10^{10}$  Hz with relaxation time  $\tau = 10^{-11}$  s, the dipole mechanism of EMW absorption should be in effect.

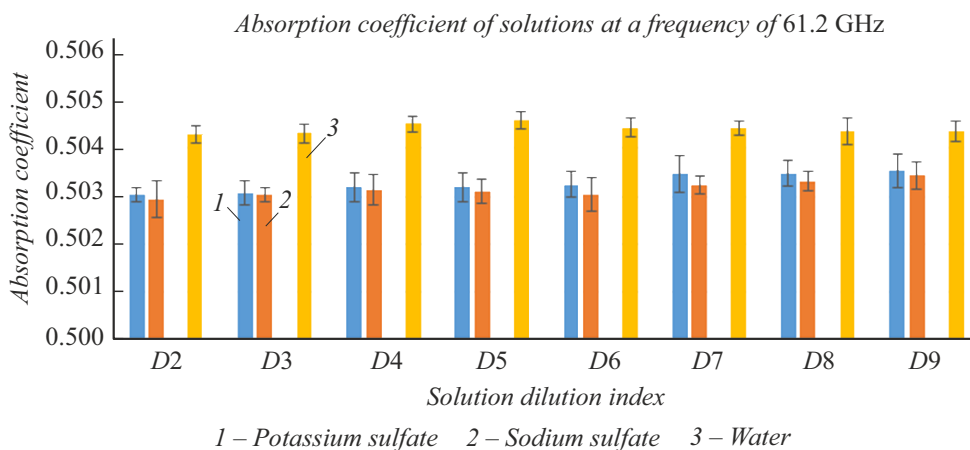
The method for measurement of thermal radio radiation of solutions, which was detailed in [9], was used to determine the absorption coefficient. The dielectric characteristics of solutions were measured with a high-sensitivity radiometer at frequency  $\nu = 61.2$  GHz. Its parameters were as follows: the accuracy of the heterodyne frequency setting and maintenance was 100 MHz, the input operating frequency band was 100 MHz, the fluctuation sensitivity of the receiver did not exceed 0.15 K at a time constant of 1 s, and the minimum power measured by the radiometer was  $4.1 \cdot 10^{-16}$  W [10]. The radiometer antenna was a horn with flare angles of  $15^\circ$  and an overall length of 42 mm. Its perimeter was in contact with the solution in a cuvette, and the cuvette size was sufficient to consider the studied samples of solutions to be half-space ones. Prior to measurements, the radiometer was calibrated against a perfect black body at three temperatures: 273, 296, and

373 K (ice melting point, temperature of the experiment, and water boiling point, respectively). The absorption coefficients were calculated as  $k(\nu) = T_R/T$ , where  $T_R$  is the measured radio brightness temperature of the solution and  $T$  is the thermodynamic temperature.

Figure 1 presents the variations of absorption coefficients with concentration of solutions of sulfates of alkali metals  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  at high concentrations. The dependences of absorption coefficients on concentration of these solutions are similar in nature, although the affinities for water of their ions differ. The absorption coefficients for the  $\text{K}_2\text{SO}_4$  solution differ insignificantly from those for pure water in the considered scale; as for the  $\text{Na}_2\text{SO}_4$  solution, its absorption coefficient, which governs the intrinsic emission, changes from 0.501 to 0.490 in transition from water to the solution.

The variation of radio brightness temperatures from one solution to the other is less pronounced for solutions with low (lower than 1%) concentrations. It was demonstrated in [9] that computer processing of temporal variations of radio brightness temperatures of the studied solutions provides an opportunity to determine accurately the actual values of absorption coefficients.

The radiometer used in our experiment is an EMW receiver connected to a personal computer, which records and processes the radiometer signal. The low-frequency radiometer signal (in volts) corresponds to the radio brightness temperature of the sample being studied. The average voltage value in a 30-min-long measurement was determined in Excel 2013 to obtain the actual values of radio brightness contrasts. The number of readings of radio brightness contrasts was 1800 for a time constant of 1 s of the low-frequency radiometer channel. These values were introduced into a database in Excel 2013, where the average value and the standard deviation were then calculated. Experiments on measurement of the absorption coefficient of water were carried out to verify the measurement procedure. The resulting dynamics of variation of the absorption coefficients of the studied solutions and water is presented in the form of a diagram in Fig. 2.



**Figure 2.** Absorption coefficients of aqueous solutions of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  and water.

The presented data reveal a significant difference between the absorption coefficients of the studied electrolyte solutions and water. At equal concentrations of substances, the absorption coefficients of Na<sub>2</sub>SO<sub>4</sub> solutions are significantly lower than the values for K<sub>2</sub>SO<sub>4</sub> solutions; this suggests that the structural network of water undergoes different perturbations by ions in an aqueous solution. Cations of substances have the same charge, but the radius of a Na<sup>+</sup> ion is smaller than the radius of K<sup>+</sup>; therefore, Na<sup>+</sup> has a higher charge density and a smaller radius of the first hydration layer. It then follows from the diagram in Fig. 2 (and the assertion that lower absorption coefficients correspond to greater numbers of ions of water molecules perturbed by Coulomb interactions) that an isolated network of water molecules, which is perturbed by each ion of the dissolved substance, with a permittivity differing from the one typical of water outside of the first hydration shell forms in low-concentration solutions.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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