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Structural-kinetic changes of water in salt solutions and their dielectric and radio brightness characteristics

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Abstract. General approach to the analysis of the structure and dynamics of aqueous solutions of electrolytes is proposed. In the first region, which includes solutions of a wide range of concentrations, changes in solutions occur on the original matrix of the solvent, which is the water itself with its unique tetrahedral structure. The configurations of the hydrate shell are considered on the basis of the model of formation of structures of substitution and introduction of ions and long-lived hydrate complexes in the initial water structure. On its basis, the volume and other properties of solutions are explained and calculated. The method of dielectric spectroscopy in the centimeter (cm) and millimeter (mm) regions of the spectrum is used to establish new orientation patterns of the original network of H-bonds of water in salt solutions. On the basis of an experimental study of about 50 water-electrolyte systems at frequencies in the region of the main maximum dispersion of water and solutions, a systematics of changes in static dielectric constants and relaxation effects in electrolyte solutions is given. The features and molecular mechanisms of hydrophobic and hydrophilic ion hydration are separated. In the latter case, both distortion and stabilization of the water structure in the solution are possible (with structural correspondences with the hydrate shell). The development of the approach allows us to characterize the parameters of the intrinsic radiation of solutions with different ions in the mm range of the spectrum. Their change in relation to clean water may even differ in sign. This is due to the presence of contributions to the complex dielectric permittivity of both dipole and ion losses. The latter still remain significant at frequencies in the mm range. A new distant laboratory method for analysis of solutions and complex water-electrolyte systems based on their radiobrightness characteristics in the mm range is proposed.

Keywords: structure, solution, dielectric properties

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1. INTRODUCTION

Anomalous properties of water are repeatedly described in the literature. They also include the stability of the tetrahedral net of water not only in dilute, but also in solutions of a wide range of concentrations. The main question that arises

here is: how and who determines the system of connections and ordering of solutions - ions or water molecules. So far, there are no unambiguous interpretations on this issue. In quantum chemical calculations, the "gas-like" scheme of hydration is most often used, when ions determine the formation of hydrate shells. The Frank and Wen model considers a three-layer model with different zones of hydration and volume water. We have developed a general model for solutions of electrolytes and nonelectrolytes in a wide range of concentrations for the formation of

replacement and introduction structures on the basis of the initial structure of water [1]. There is no blurred transition layer on the border of the hydrate shell and bulk water.

2. MAIN PART

As the main principle of the organization of the system under consideration, the principle of complementarity of the configurations of the bulk water, the hydrate shell and the dissolved particle itself is highlighted. In the very first approximation, the regularities of translational and orientational ordering are considered separately. Accordingly, geometric models (solid sphere potential) are used to analyze new spatial relationships and translational structure. The placed particle is contoured using ionic radii, data from crystalhydrates and other crystal structures, as well as general crystal-chemical regularities. This is possible, since in the condensed state, the spatial configurations of solid and liquid solutions have much in common (in the area of near-ordering of the system). In the framework of the accepted model, the packing coefficients and volumetric properties of salt solutions are described without empirical parameters using simple geometric models of substitution and introduction (including the free volume of internodes). On the same basis, the compressibility of electrolyte solutions is considered [2]. The boundary of the first structural region of solutions is highlighted, where the ordering is based on the initial structure of water. Changes in the system during the transition to high concentrations correspond to reduced values of static permittivity, found on the basis of experimental data of microwave and HF spectroscopy (HF-extremely high frequencies). The second structural zone is characterized by configurations with significantly smaller dielectric constants. We will not consider its interesting regularities here.

The dielectric method in this interpretation comes to the fore. It characterizes changes in the orientation relations and structural-kinetic

reactions of water in the transition to a solution. The inclusion of the mm range in measurements and calculations clarifies the data describing the main maximum dispersion in water and solutions, but they do not lead to new qualitative patterns.[3] (Fig. 1).

The complex permittivity $\varepsilon^*(V)$ at the frequency V is determined in dielectric measurements and is represented as two components: the permittivity $\varepsilon'(V)$ and the losses $\varepsilon''(V)$: $\varepsilon^*(V) = \varepsilon'(V) - i\varepsilon''(V)$, where $i = \sqrt{-1}$.

The value of $\varepsilon''(V)$ in the case of solutions of nonelectrolytes is completely determined by the dipole relaxation of the molecules. In the case of electrolyte solutions, absorption follows two mechanisms related to the reorientation of dipole water molecules and the displacement of charged ions. For electrolyte solutions:

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

where $\varepsilon_d''(\nu)$ is dipole, and $\varepsilon_i''(\nu)$ is the ionic loss of the dielectric spectrum. The contribution of ion losses, which remains significant in the mm range of the spectrum, is taken into account using available low-frequency electrical conductivity data:

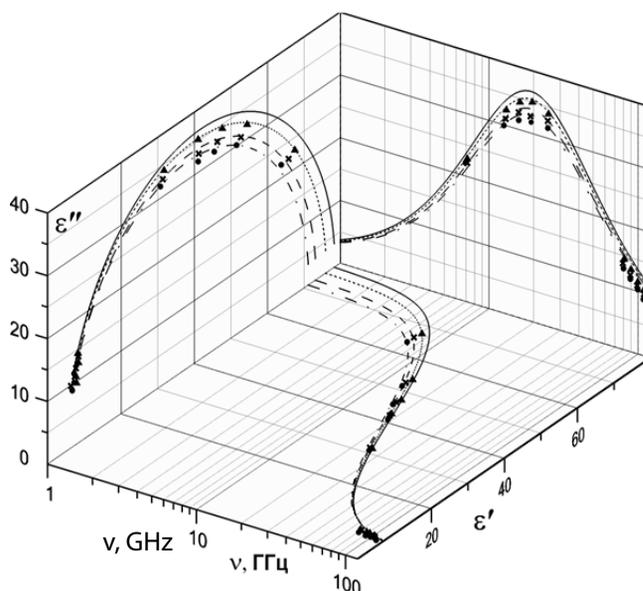


Fig. 1. Three-dimensional representation of the relaxation process. Approximations of frequency dependences $\varepsilon'(V)$ and $\varepsilon''d(V)$ for aqueous solutions K_2SO_4 at 298 K. Experimental data for 0.11 m (\blacktriangle), 0.32 m (\times), 0.46 m (\bullet).

$$\varepsilon_i''(\nu) = \frac{\sigma}{2\pi\varepsilon_0\nu},$$

where σ is the electrical conductivity (Cm/m), ε_0 is the dielectric constant of the vacuum. To determine the values of the complex dielectric permittivity (ε' and ε'') of solutions in the mm range of the spectrum, we used our experimental data on the absorption coefficients (k) and reflection coefficients (R) of solutions at frequencies $\nu = 80-110$ GHz [4, 5]. The complex dielectric permittivity of the test solution is associated with the measured parameters that determine R and k , the Fresnel formulas (with a normal incidence of an electromagnetic wave on the surface of the dielectric):

$$k = \frac{4\pi}{\lambda} \text{Im} \sqrt{\varepsilon^*}, \quad R = \left| \frac{\sqrt{\varepsilon^*} - 1}{\sqrt{\varepsilon^*} + 1} \right|.$$

To establish the applicability of various relaxation models describing spectra in the cm and mm regions, the analysis of dielectric data was carried out using the variational selection of parameter values of the spectrum model components using the method of nonlinear least squares. For each spectrum, models containing 1 to 3 Cole-Cole functions were tested. The numerical solution of these relations allows us to determine the real (ε') and imaginary (ε'') part of the complex permittivity.

$$\varepsilon^*(\nu) = \varepsilon_\infty + \sum_{k=1}^K \frac{\Delta\varepsilon_k}{1 + (i2\pi\nu\tau_k)^{1-\alpha_k}},$$

where ν is the frequency, $\varepsilon^*(\nu)$ is the complex permittivity, ε_∞ is the high-frequency limit of the permittivity, K is the number of components in the model, $\Delta\varepsilon$ and τ are the relaxation force and relaxation time for the k -component, and α is an empirical parameter. At $\alpha = 0$, the empirical Cole-Cole function (CC) becomes the Debye function (D). Thus, the values of α obtained as a result of computer approximation of the experiment allow us to make an objective conclusion about the type of spectral components (Cole-Cole or Debye).

In this paper, in many cases, already in the calculation of the model with a single Cole-Cole function was obtained $\alpha = 0$, which is equivalent to the model 1D from a single Debye function. At the same time, calculations using the 2CC model show that the second component is redundant. This case corresponds to solutions of K_2SO_4 , Cs_2SO_4 and solutions of Li_2SO_4 and Na_2SO_4 low concentrations and other systems.

For more concentrated solutions of Li_2SO_4 and Na_2SO_4 , a slightly different decomposition of the dielectric spectrum is possible. The calculation of the 2CC model gives an additional component. However, it stands out separately.

Thus, the Debye or Cole-Cole equations with a small parameter of the relaxation time distribution are applicable in the first concentration zone to describe the relaxation times. They are analyzed in several aspects. The data of the high-frequency limit of the main maximum of dispersion are used to establish the high-frequency boundary of the total collective processes in the H -bond net (> 150 GHz). Elementary and collective molecular-kinetic reactions occur at high frequencies. A model of a set of restricted rotators or other schemes can be used to describe them [6]. The low-frequency limit is set by static dielectric constants in salt solutions. In the absence of an association of ions, they directly determine the hydration process. In this case, they can be used to describe and calculate the thermodynamic coefficients of activity of solutions [7, 8] (without fitting parameters). This is possible in a fairly wide range of concentrations. Examples are solutions of aluminum chloride, lithium chloride and other systems.

The analysis of the spectra of complex dielectric permittivity of aqueous salt solutions in the Laboratory of Aqueous Solution Structure IGIC RAS was initiated by P.S. Yastremsky and O.Y. Samoilov. First measurements were made at the Volgograd Pedagogical Institute. In the IGIC RAS, the experimental complex for

measurements in the cm range was established by A.S. Lileev (the method of a cylindrical rod in a waveguide), and in the mm range - A.Yu. Zasetsky (measurement of reflection coefficients of solutions). Currently, more than 50 double and triple systems of different types have been studied at the frequencies of 7-25 or 7-120 GHz at 298 K [9]. A small temperature range has been studied for many solutions. In the region of low concentrations, it was found that in the considered frequency range of 7-110 GHz, only one component is observed, reflecting the total hydration changes of water in salt solutions. At the same time, there is no separation of the maximum dispersion into the hydrate shell, the transition layer and the bulk water. From the data of the complex dielectric permittivity and the Debye or Cole-Cole equations, the high-frequency and low-frequency limits of the considered dispersion region and relaxation times are determined, reflecting the dynamics of water molecules during the formation of a hydrated ion shell.

According to the data of dielectric relaxation in the temperature range, changes in the enthalpy and entropy of activation are determined, transmitting changes in the degree of connectivity and structure of the system. Despite the high values of the hydration energies of ions in their hydrophilic hydration, the net of hydrogen bonds is more mobile and less structured in comparison with pure water [9]. This case is realized for the majority of such solutions (more than 30 systems). Reverse effects are observed in hydrophobic ion hydration [9, etc.]. In the case of solutions of tetraalkylammonium and allylammonium salts with different anions, there is an increase in the times and enthalpy of activation of dielectric relaxation compared to water under the action of nonpolar groups. This is a typical variant of hydrophobic hydration. In some cases, it is possible to note the stabilization of the bond network in hydrophilic hydration. An example is solutions of hydrophosphates or ammonium fluoride. In the latter case, solid

solutions are also implemented in ice (up to 7.44 mol.%[10]).

Another experimentally measured property is directly related to the high-frequency dielectric characteristics of solutions. These are radiobrightness parameters that characterize the proper radiation of solutions. Quasi-optical coefficients and radiofrequency characteristics of solutions in the mm range of the spectrum were determined on the example of solutions of chlorides and sulphates of alkali metals and a number of other systems [11-14]. Using Fresnel formulas and developed computer programs, they are calculated from the dielectric data of the cm region. In some cases, they are also found experimentally. The reflection coefficients of solutions at frequencies of 80-120 GHz (special technique [4, 5]) and (or) radiation coefficients at a frequency of 61.2 GHz [11] were measured using a radiometer (IRE RAS technique, NPO "Istok", Fryazino [14]). They are consistent with the calculated data. This confirms the correctness of the choice of the relaxation model for the main maximum of water dispersion in salt solutions. As a result, a new approach to the study of aqueous solutions based on their radiation in the millimeter range of the dielectric permittivity spectrum is developed.

3. CONCLUSION

The theoretical justification and quantitative description of the measured effects are given using the data of the complex dielectric permittivity of solutions. It is shown that the radiation reflects the contributions of both dipole and ion losses, which still remain significant at the considered frequencies. They can even detect the presence of different sign radiation effects compared to water. There are examples of different variations of reflection and radiation coefficients. This is observed for aqueous solutions of alkali metals in the mm region. For example, at a frequency of 100 GHz, the reflection coefficient of sodium chloride solutions falls, and potassium chloride increases

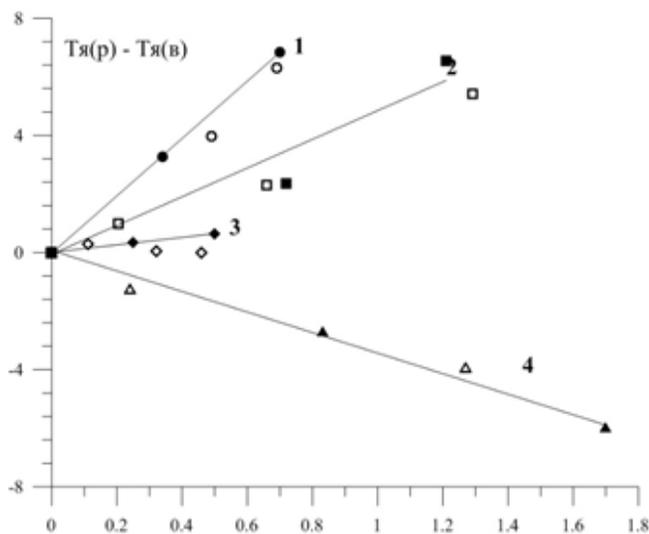


Fig. 2. Radiobrightness contrasts $\Delta T = T_i - T_w$ of solutions $Li_2SO_4(1)$, $Na_2SO_4(2)$, $K_2SO_4(3)$, $Cs_2SO_4(4)$ at 298 K (abscissa — molarity, mol/1000 g. H_2O). Dark points — calculation data from radiometric measurements, light points — calculation data from dielectric parameters.

in comparison with water. This means that the radiation coefficient in the first case increases, and in the second case decreases during the transition from water to solution. The **Fig. 2** shows changes in radiobrightness temperature for solutions of alkali metal sulfates. The observed radiobrightness contrasts of different salt solutions are quite large, so that the proposed method of rapid analysis of solutions can be used in laboratory practice.

The presence of different changes in radiation and absorption during the transition from water to solutions of sodium and potassium chlorides, hydrochloric acid and a number of other electrolytes can be significant for biological objects, characterizing the differences in radio brightness and energy redistribution of intracellular (K^+ ions) and extracellular (Na^+ ions) liquids. This may serve to explain the medical effects of millimeter waves.

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