

Dielectric Characteristics of Water and Electric Conductivity of Aqueous Electrolytes

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Abstract—The specific electric conductivities (ECs) of concentrated aqueous solutions of electrolytes were shown to be comparable to the limiting high-frequency (HF) EC of water. The limiting HF EC of water is determined by the ratio of the absolute dielectric constant to the dipole dielectric relaxation time. It was assumed that the specific EC of an aqueous solution cannot exceed the limiting HF EC of water. The specific ECs of the 1.0 M aqueous solutions of lithium, sodium, and potassium chlorides were calculated from the limiting HF EC of water. At elevated temperatures, the specific ECs of aqueous salts were shown to increase in direct proportion to the limiting HF EC of water.

Keywords: water, electrolyte solutions, static dielectric permittivity, dielectric relaxation time, high-frequency electric conductivity

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The static dielectric constant (DC) ϵ_s and dipole dielectric relaxation time τ are very important physicochemical characteristics that determine the rate and mechanism of processes in water and aqueous solutions. The electric properties of water and aqueous solutions in a wide range of frequencies of the electromagnetic field are generally described in terms of complex DC: $\epsilon^* = \epsilon' - j\epsilon''$ (ϵ' is the active component of the complex DC, and ϵ'' is its reactive component; $j \equiv \sqrt{-1}$). These properties can also be described in terms of complex conductivity $\kappa^* = \kappa' + j\kappa''$ [κ' is the active component of complex conductivity, and κ'' is its reactive component). The complex quantities ϵ^* and κ^* are related by the equations [2]

$$\epsilon^* = \kappa^*/(j\omega\epsilon_0) = \kappa''/(\omega\epsilon_0) + \kappa'/(j\omega\epsilon_0) = \epsilon' - j\epsilon'', \quad (1)$$

$$\kappa^* = j\omega\epsilon_0\epsilon^* = \omega\epsilon_0\epsilon'' + j\omega\epsilon_0\epsilon' = \kappa' + j\kappa'', \quad (2)$$

where ϵ_0 is the absolute DC of vacuum ($\epsilon_0 = 8.85 \times 10^{-12}$ F/m), and ω is the circular frequency.

The high-frequency (HF) electric conductivity (EC) defines the absorption of the microwave energy by a substance [2, 3]. In particular, the power of electromagnetic radiation absorbed by the substance P is directly proportional to the HF EC κ' and the square of the field strength E [2]:

$$P = \kappa'E^2 = \omega\epsilon''\epsilon_0E^2. \quad (3)$$

Therefore, it was interesting to analyze the dependence of HF EC of water and aqueous solutions on the frequency of the electromagnetic field.

The frequency dependence of the conductivity of electrolytic solutions was first predicted by P. Debye and H. Falkenhagen [4]. Based on the Debye–Hückel theory, they showed that the asymmetry of an ionic atmosphere vanishes in high-frequency fields provided that the circular frequency of the electromagnetic field ω ($\omega = 2\pi F$) is comparable to the reciprocal relaxation time of the ionic atmosphere θ , i.e., when $\omega\theta \approx 1$. As a result, the electric conductivity of solutions increases. The experimental proof of the theory of dispersion of conductance was given in the monograph by H. Falkenhagen [5]. Although the Debye–Falkenhagen theory is described in manuals on physical chemistry and electrochemistry [6, 7], it was not developed further for concentrated solutions. It should be noted, however, that the relaxation time of the ionic atmosphere in dilute solutions of electrolytes is the relaxation time of space charges θ according to the Maxwell [8]:

$$\theta = \frac{\epsilon_0\epsilon_s}{\kappa}, \quad (4)$$

where ϵ_s is the static dielectric constant of the solution, and κ is its specific electric conductivity.

As the solution concentration increases, the relaxation time θ decreases, and in concentrated solutions it approaches the dipole dielectric relaxation time of water. For example, for the 1.0 M aqueous solution of KCl at 25°C, $\epsilon = 68.5$ [9], and $\kappa = 11.2$ S/m [10]. Substituting these values in (4), we obtain $\theta = 5.4 \times 10^{-11}$ s. The dipole dielectric relaxation time of water is $8.3 \times$

10^{-12} s at this temperature [11]. This fact requires joint analysis of the solution and solvent relaxation in concentrated solutions.

The dipole dielectric relaxation time of a solvent for describing the EC of electrolyte solutions was used by R. Zwanzig in his dielectric friction model [12, 13]. According to this model, an analysis of the ion motion in solution should take into account the dipole orientation of solvent molecules, which gives rise to a retarding force. This force increases with hydration and dipole relaxation time. R. Zwanzig used his concept for describing the dependence of the Walden product $\Lambda_0\eta_0 = \text{const}$ [7] (Λ_0 is the molar EC for infinite dilution, and η_0 is the solvent viscosity) on the ion size. The theoretical and experimental verification of the Zwanzig theory by D. Evans et al. [14] showed that the dielectric friction effect is exaggerated more than tenfold.

In the Hubbard–Onsager model of limited polarization [15, 16], the reorientations of solvent molecules characterized by the dipole dielectric relaxation time $\tau(\text{H}_2\text{O})$ have not enough time to settle in the presence of ions in solution. This leads to a deficiency of kinetic polarization, which increases with ion concentration in solution. In the Hubbard–Onsager model [15, 16], the ion conductivity of solutions is described by the equation

$$\kappa_\infty = \kappa_0 + \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{\tau(\text{H}_2\text{O})}, \quad (5)$$

and the dielectric permeability is described by the equation

$$\varepsilon_s = \varepsilon_s(\text{H}_2\text{O}) - \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{\varepsilon_s} \tau \kappa_0. \quad (6)$$

Here κ_∞ is the high-frequency limit of the specific EC of the solution, and κ_0 is its low-frequency limit; ε_s is the low-frequency limit of the dielectric constant of solution, and ε_∞ is its high-frequency limit. Regrettably, Eq. (5) does not contain the electromagnetic field frequency and hence does not describe the increase in the EC of solution with an increase in frequency. In addition, the authors did not explain the physical meaning of conductivity at infinite frequency κ_∞ . According to (6), the static DC of solution ε_s in the limited polarization model [15, 16] should be the same in solutions with equal specific conductivities. As a matter of fact, the slopes of the curves $\varepsilon_s - \kappa_0$ differ by a factor of three for aqueous solutions, which was explained in [15] by dielectric saturation (a decrease in the static DC in the nearest environment of the ion), which was neglected in their model.

Using the concepts of dipole ion relaxation and ion relaxation described by (4), it can easily be shown that in electrolytic solutions with equal conductivities, the relaxation times rather than DCs will be equal [17]. Summing the ionic $1/\theta$ and dipole $1/\tau(\text{H}_2\text{O})$ relax-

ation rates, we obtain the relaxation time of the solution τ taking into account (4):

$$\frac{1}{\tau} = \frac{1}{\tau(\text{H}_2\text{O})} + \frac{1}{\theta} = \frac{1}{\tau(\text{H}_2\text{O})} + \frac{\kappa}{\varepsilon_0\varepsilon_s}. \quad (7)$$

Equation (7) describes well the decrease in the relaxation time τ of aqueous solutions of electrolytes with an increase in their specific EC κ , and solutions with the same conductivity have almost identical relaxation times [17, p. 259].

The high-frequency dielectric permittivity and electric conductivity of water and aqueous solutions can be described using the Debye DC dispersion theory of polar solvents [18]. According to this theory, the dependence of the active and reactive components of complex dielectric permittivity of water and other polar solvents on the frequency in the dipole relaxation region is described by the Debye equations:

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + (\omega\tau)^2}, \quad \varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)}{1 + (\omega\tau)^2}(\omega\tau). \quad (8)$$

Substituting (1) and (2) into (8), we obtain the active κ' and reactive κ'' components of the complex EC:

$$\kappa'' = \frac{\omega\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{1 + (\omega\tau)^2}(\omega\tau), \quad (9)$$

$$\kappa' = \omega\varepsilon_0\varepsilon_s + \frac{\omega\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{1 + (\omega\tau)^2}. \quad (10)$$

As the absorption of microwave energy is determined by the active component of conductivity, below we consider the dependence of only κ' on frequency and dielectric properties. Multiplying the numerator and denominator of (9) by the relaxation time, we obtain

$$\kappa' = \frac{\kappa_{d\infty}}{1 + (\omega\tau)^2}(\omega\tau)^2. \quad (11)$$

Here, $\kappa_{d\infty}$ is the dipole component of the limiting HF EC of a polar solvent [19]:

$$\kappa_{d\infty} = \frac{\varepsilon_0(\varepsilon_s - \varepsilon_\infty)}{\tau}. \quad (12)$$

Thus, the second term of (5) is the dipole component of the limiting HF EC of water. It also follows from (11) that the HF EC κ' of a polar solvent increases with frequency. At low frequencies when $\omega\tau \ll 1$, the active conductivity increases in proportion to the square of the frequency F :

$$\kappa'_{(\omega\tau \ll 1)} = \varepsilon_0(\varepsilon_s - \varepsilon_\infty)\omega^2\tau = KF^2. \quad (13)$$

Here, $K = 2\pi\varepsilon_0(\varepsilon_s - \varepsilon_\infty)\tau$. For water at 25°C, $\varepsilon_s = 78.3$, $\varepsilon_\infty = 5.0$, and $\tau = 8.3$ ps [11]. Then at a frequency of 10 kHz, for example, substituting the dielectric characteristics of water in (13), we obtain $\kappa' = 2.11 \times 10^{-11}$ S/m. This is much smaller than the intrinsic specific conductivity of pure water (6.33×10^{-6} S/m [10])

and may be neglected in conductometric studies of solutions. However, already at a frequency of 10 MHz, the HF EC of water is 2.11×10^{-5} S/m; i.e., the HF EC of water already exceeds its LF EC and should be taken into account in studies of water and aqueous solutions at high frequencies. At very high frequencies when $\omega\tau \gg 1$, the active conductivity κ' reaches its limiting maximum value $\kappa_{d\infty}$, which is independent of frequency.

The physical reason for the increase in the active component κ' of the complex conductivity κ^* when the frequency increases in the dipole relaxation range is as follows. In contrast to the electronic and atomic polarizations, the orientational polarization is accompanied by energy scattering in the substance because the dipoles of the polar solvent can no longer follow the change in the external field. This leads to a decrease in the active component of the complex DC ϵ' and, according to (1) and (2), to an increase in the active component of the complex EC κ' .

The dipole component of the limiting high-frequency EC of water (12) was used by V.G. Artemov et al. [20–24] for describing some of its physicochemical characteristics and the conductivity of the concentrated aqueous solutions of some electrolytes. The Artemov's model is based on the assumption about autoionization of water and its proton conductivity. According to [20–24], as a result of autoionization, the concentration of H^+ (H_3O^+) and OH^- ions in water is seven orders of magnitude higher than their real concentration ($\sim 10^{-7}$ M at room temperature). The ion concentrations as high as these were obtained in [20–24] because the limiting HF EC of water that is due to the Debye dipole relaxation (~ 80 S/m) is seven orders of magnitude higher than the specific EC of pure water (5.5×10^{-6} S/m [20]). Here it should be emphasized that the dipole component of the limiting HF EC of the polar solvent calculated by (12) [20–24] is due to the hindered orientational polarization of its molecules, but not to their dissociation into ions. This is indicated by the fact that $\kappa_{d\infty}$ is of the same order of magnitude, for example, for acetone (~ 60 S/m) [25] and acetonitrile (~ 70 S/m) [26], in which protons do not form in the possible dissociation, which explain, according to [20–24], the high dipole conductivity of the solvent. In addition, the HF EC increases with frequency due to dipole relaxation not only in water and nonaqueous solvents [25], but also in ionic liquids [27].

The anomalously high DC of water was also explained in [20–24] by the proton motion [21], but not by the high degree of cross-linking in the structure of water due to hydrogen bonding. The Artemov's model regrettably neglects the hydrogen bonds in water, which explain the existing anomalies of its properties [22]. Then using the idea of the anomalously high concentration of H^+ (H_3O^+) and OH^- ions in water, the authors of [23] derived the equations for the concentration dependences of the specific EC of

aqueous HCl, NaOH, and NaCl, which are consistent with experiment. The results of these calculations would be acceptable if the “high ion concentration” in the concept of the authors were replaced by the concentration of the solvent molecules polarized by the electrolyte ions. In our opinion, the motion of H^+ (H_3O^+) ions (“proton transitions” in terms of [20–24]) that formed as a result of water dissociation cannot be used to explain the specific EC of aqueous solutions of inorganic acids, alkalis, and salts because the temperature coefficient and, accordingly, the activation energy of the EC E_κ of these solutions differ significantly [28, 29]. In particular, the activation energy E_κ depends on the nature of electrolyte ($E_{\kappa(\text{NaCl})} > E_{\kappa(\text{NaOH})} > E_{\kappa(\text{HCl})}$) and its concentration (E_κ generally increases with the concentration) [29]. According to [24], the activation energy of conductivity remains constant at any concentrations, and the differences in the character of conduction of HCl, NaOH, and NaCl solutions are described using the “numerical specific parameters” α , β , and γ , whose physical meaning was not explained in [23]. The conclusion of the authors that “the concentrations of H_3O^+ and OH^- ions are independent of temperature” cannot be explained either [24]. This fact is denied by the temperature dependence of the ion product of K_w of water: e.g., when the temperature increases from 0 to 100°C, the ion concentration in water increases by a factor of more than 20. It is also not clear why the authors write about the absence of the “fundamental justification of the hydrogen index concept,” which they believe to be based on the “assumption about the existence of proton conductivity of $\sim 10^{-7}$ S/cm in water” [20, p. 636]. The equilibrium between the dissociation of water molecules (and its pH) is explained by the authors by the “thermal activation” of H_3O^+ and OH^- ions [24]. Here it should be noted that the ion product of water determined by electrometric (pH-metric) measurements was studied in detail in the ranges of temperatures 0–1000°C and pressures 1–10000 bar. The results of these studies were summarized in [30], and the analytical dependence of K_w on the temperature and density of water was approved by the special commission of IAPS (International Association for the Properties of Steam) in the late 20th century [30]. The only fact that has not yet been explained is the existence of a maximum on the temperature dependence of K_w , which shifts toward higher temperatures at elevated pressure [30].

Considering from a single standpoint the electric relaxation processes described by (4) and (7) in solutions whose complex conductivity is $\kappa^* = j\omega\epsilon_0\epsilon^*$, we think that the calculation of the limiting HF EC of the solvent should use the total DC ϵ_s , rather than its dipole component ($\epsilon_s - \epsilon_\infty$) [25]:

$$\kappa_\infty = \frac{\epsilon_0\epsilon_s}{\tau} \quad (14)$$

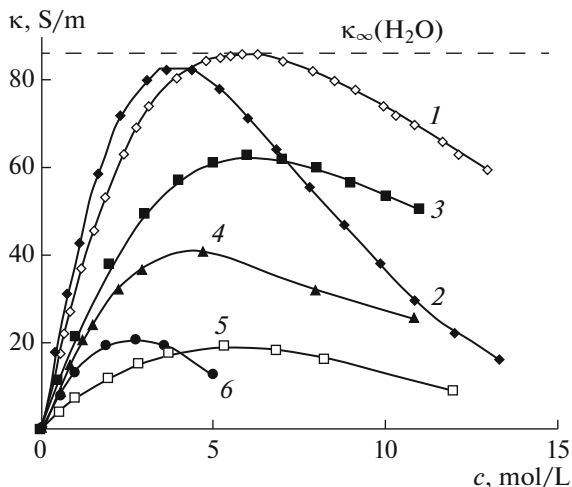


Fig. 1. Concentration dependences of the specific EC of aqueous (1) HNO_3 , (2) H_2SO_4 , (3) KOH , (4) NaOH , (5) LiCl , and (6) CaCl_2 solutions according to the data of [31]; $t = 25^\circ\text{C}$.

According to our concept [25], the specific EC of an electrolyte solution cannot exceed the limiting HF EC of water κ_∞ and generally amounts only to some part of it, which depends on the fraction of water molecules polarized by electrolyte ions [25] (Fig. 1). Figure 1 shows the concentration dependences of the specific EC of some aqueous solutions of acids, alkalis, and salts. We can see that the specific EC of alkali and salt solutions is smaller than $\kappa_\infty(\text{H}_2\text{O})$, which is 84.0 S/m. The specific EC of the concentrated aqueous solutions of inorganic acids approaches this value. In particular, at 25°C the maximum specific EC of aqueous HCl , HBr , HNO_3 , and H_2SO_4 is 84 ± 2 S/m [31]. The dipole component of the limiting HF EC of water $\kappa_{d\infty}(\text{H}_2\text{O})$ determined by (12) at this temperature is 78.7 S/m, i.e., is smaller than the maximum specific EC of the concentrated solutions of inorganic acids (84 S/m).

The use of ϵ_s instead of the difference $\epsilon_s - \epsilon_\infty$ when calculating the limiting HF EC is also preferable because it is the static DC (ϵ_s) but not its dipole component ($\epsilon_s - \epsilon_\infty$) that characterizes the total bias current of the polar solvent ($\omega\epsilon_s\epsilon_0$). In addition, the procedure for calculating the limiting HF EC of polar solvents is considerably simplified because a reliable value of the optical component of complex DC ϵ_∞ is now available only for water [32]. For other polar solvents, the ϵ_∞ values differ significantly [11]. Also note that as $\epsilon_s \gg \epsilon_\infty$, the difference between the calculated κ_∞ and $\kappa_{d\infty}$ values of water does not exceed 5–10%, i.e., lies within the error of the dipole dielectric relaxation time [11].

As the limiting HF EC of water is determined by its dielectric characteristics, we can see that they limit the maximum conductivity of aqueous electrolytes (Fig. 1), which does not exceed the κ_∞ value of water.

Our studies of the specific EC of aqueous solutions of mixtures of HCl and H_2SO_4 showed that a change in the composition of these mixtures leads only to a shift of the maximum of the specific EC along the concentration axis, while its maximum value remains constant (83 ± 1 S/m) (Fig. 2).

A maximum of specific EC is observed at a concentration of ~ 6 M in aqueous HCl and at ~ 4 M in a H_2SO_4 solution. The 6 M HCl solution (density 1.098 g/cm³) contains 48.0 M water. At this concentration, there are eight water molecules per molecule of electrolyte in the HCl solution. In the 4 M solution of sulfuric acid (density 1.220 g/cm³), the concentration of water is 47.5 M. There are ~ 12 water molecules per H_2SO_4 molecule at this concentration. The positions of the specific EC maxima in the mixtures of acids in question can be calculated from these values. Thus, for the HCl solution in 2 M sulfuric acid, a specific EC maximum should be observed at a concentration of HCl of $(48.0 - 2 \times 12)/8 = 3.0$ M. For the H_2SO_4 solution in a 2 M HCl solution, a maximum should be observed at a concentration of H_2SO_4 of $(47.5 - 2 \times 8)/12 = 2.6$ M. The extrema on curves 2 and 4 in Fig. 2 are observed at exactly these concentrations.

As indicated above, the specific EC of an electrolyte solution should not exceed $\kappa_\infty(\text{H}_2\text{O})$; generally it amounts only to some part of it, which depends on the fraction of water molecules bonded with the electrolyte ions [25]:

$$\kappa = \frac{cN}{c_0} \frac{\epsilon_0 \epsilon_s}{\tau} = K \kappa_\infty. \quad (15)$$

Here, c is the concentration of the solution (M), c_0 is the concentration of the solvent (55.5 M for water), N is the number of moles of water bonded to one mole of electrolyte, and τ is the relaxation time of solution;

the constant $K = \frac{cN}{c_0}$ is the fraction of water molecules bonded with electrolyte ions. In the solutions of acids and their mixtures (Fig. 2) at the maximum of specific EC, almost all water molecules are bonded with electrolyte ions. Therefore, the K value approaches unity and the specific EC of these solutions equals the limiting HF EC of water (84.0 S/m).

In inorganic salt solutions, K is smaller than unity, and the specific EC of these solutions is only some part of the κ_∞ of water. Using (15), we can evaluate the specific EC of the aqueous 1.0 M solutions of lithium, sodium, and potassium chlorides. For LiCl , NaCl , and KCl solutions, we take that $N = 5, 6,$ and 8 . These values are close to the coordination numbers of lithium, sodium, and potassium ions [33]. For dilute solutions, κ_∞ of water can be substituted into (15) [25]. For concentrated solutions, it is necessary to take into account the electrolyte effect on the dielectric characteristics (ϵ_s and τ) of solution and the concentration of solvent molecules in it.

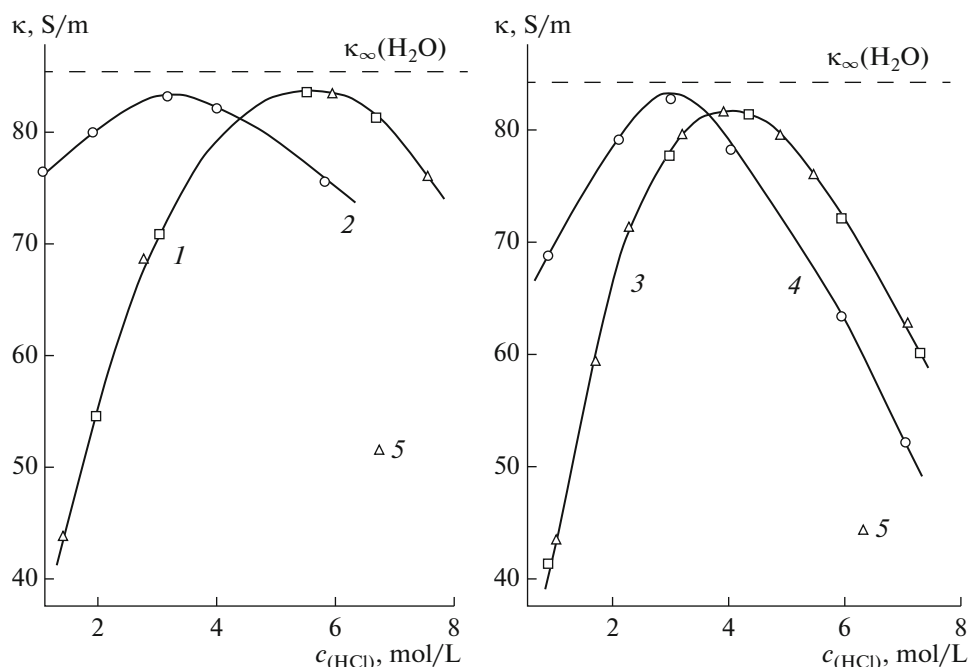


Fig. 2. Specific EC of aqueous (1) HCl and (3) H₂SO₄ solutions and mixtures: (2) HCl + 2 M H₂SO₄ and (4) H₂SO₄ + 2 M HCl; (5) according to the data of [31]; $t = 25^\circ\text{C}$.

Table 1 compares the experimental ([31]) specific electric conductivities with those calculated by (15) for 1.0 M aqueous lithium, sodium, and potassium chloride solutions. The κ_∞ values of the solutions were determined using the data of the handbook [9], and the concentration of water molecules c_0 (M) in the solutions was determined from their densities [10].

The discrepancy between the experimental specific ECs and those calculated by (15) for 1.0 M aqueous lithium, sodium, and potassium solutions did not exceed 5%. Surprisingly, the specific conductivity of the 1.0 M LiCl, NaCl, and KCl solutions was calculated using their dielectric characteristics (ϵ_s and τ). The N coefficient in (15) is the only parameter whose meaning has to be clarified. Note that for NaCl and KCl, N coincides with the coordination number of ions in the crystal lattice of the solid salts.

According to (15), at elevated temperature the specific EC of the electrolyte solution should increase in direct proportion to the limiting HF EC. An analysis of the temperature dependences of the specific EC of dilute aqueous solutions of inorganic salts shows that

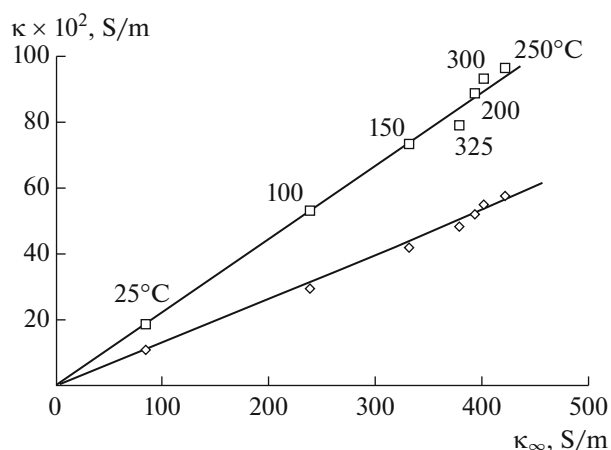


Fig. 3. Dependences of the specific EC of the (1) 0.005 and (2) 0.01 M Na₂HPO₄ solutions [34] on the limiting HF EC of water [19] in the temperature range 25–325°C.

the proportion described by (15) is valid over a wide temperature range. Figure 3 shows as an example the dependence $\kappa - \kappa_\infty$ constructed using the experimen-

Table 1. Experimental specific electric conductivities [31] and those calculated by (15) (S/m) for 1.0 M aqueous LiCl, NaCl, and KCl solutions; $t = 25^\circ\text{C}$

Solution	N	c_0	κ_∞	$\kappa_{(\text{calc})}$	$\kappa_{(\text{exp})}$ [31]	$\delta, \%$
LiCl	5	54.4	75	6.89	7.22	4.6
NaCl	6	54.5	77	8.48	8.61	1.5
KCl	8	53.9	78	11.6	11.20	3.6

tal specific ECs of the 0.005 and 0.01 M Na₂HPO₄ solutions from [34] and the κ_{∞} values of water [35]. According to Fig. 3, in the temperature range 25–325°C the specific EC of the solutions increases in direct proportion to the limiting HF EC of water not only in the range in which the specific EC of the solution increases with temperature (25–250°C), but also in the range in which the EC decreases when the temperature increases (250–325°C). Thus, the temperature dependence of specific EC is determined by the temperature dependence of the static dielectric permittivity and dipole dielectric relaxation time (Eq. (15)).

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