

## FREQUENCY DISPERSION OF THE SPECIFIC CONDUCTANCE COEFFICIENT IN AQUEOUS ELECTROLYTE SOLUTIONS

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Analytical expressions for the dynamic specific conductance coefficient  $\sigma(\omega)$  and the dynamic electroelasticity modulus  $\epsilon(\omega)$  are obtained by solving kinetic equations using specific expressions for the potential energy  $\Phi_{ab}(r)$  of the interaction between structural units of the solution and the equilibrium radial distribution function  $g_{ab}(r)$ . Friction coefficients  $\beta_a$  and  $\beta_b$  are calculated numerically; relaxation times  $\tau_a$ ,  $\tau_b$ ,  $\tau_{ab}$  along with  $\epsilon(\omega)$  and  $\sigma(\omega)$  values are determined for aqueous solutions of LiCl, NaCl, KCl, and CsCl as functions of the concentration  $c$ , density  $\rho$ , and temperature  $T$  in a wide frequency range  $\omega$ . The obtained theoretical data are presented in the form of tables and graphs and are compared with experimental results show a satisfactory agreement between them.

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**Keywords:** friction coefficient, relaxation times, potential energy of interparticle interaction, radial distribution function, electroelasticity modulus, electrical conductivity coefficient.

Non-reversible processes in liquids and solutions involving the transfer of mass, impulse, energy, and electrical charge are due to the gradients of speed, temperature, chemical and electric potentials. Depending on the physical state and conditions, the transfer processes make different contributions to the total flow, and the presence of one type transfer in the medium makes other type processes to appear. Considering individual types of transfer phenomena is justified in theoretical studies. Therefore, important relationships are introduced to exclude the difficulties arising when all these phenomena are studied together.

Electrical conductivity of solutions can be described experimentally using relations between macroscopically measured parameters without taking into account molecular mechanisms of transfer processes, which makes it possible to measure the processes with high accuracy. The works [1-3] present detailed reviews of experimental studies concerning the nature of internal relaxation processes, transport phenomena, elastic, acoustic, dielectric, and electrically conductive properties of liquids and solutions. In recent years, dielectric and electrically conductive properties (along with other physical properties) of electrolyte solutions and their frequency dispersions have been widely studied experimentally in terms of their dependence on the density, concentration, and temperature [4-13].

The temperature dependence of the limiting high-frequency (HF) electrical conductivity (EC) and dielectric

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properties of water and aqueous solutions of alkali chlorides were analyzed in [4-6]. It was shown that specific electrical conductivity of solutions increases with increasing temperature directly proportional to the limiting value of the solvent's HF conductivity. Also, as the concentration of aqueous NaCl solutions increases, their electric capacity increases multiply, first at low (10÷30) kHz and then at higher (100÷300) kHz frequencies, as compared to that of distilled water. It is assumed that suchlike changes in NaCl solutions depend on the ratios between the number and size of water associates and the degree of ion hydration.

The limiting HF EC value of water, methanol, ethanol, and propanol, as well as the HF EC dependence on the composition of aqueous acetone and dimethyl sulfoxide solutions at 2.45 GHz were studied over a wide range of temperatures [7, 8]. It was established that the limiting HF EC value passes through a minimum and reaches the maximum at 2.45 GHz as the content of the organic component increases. It was also shown that the temperature maximum of the limiting HF EC value is reached when the relative temperature coefficients of static permittivity are equal to those of the time of dipole dielectric relaxation.

The frequency dependence of the relaxation time in Debye models of permittivity and specific conductivity dispersions were studied in [9]. The frequency dependencies built for the electrical conductivity  $\sigma(\omega)$  are described by a power function  $\sim\omega^\alpha$ , while the frequency dependences of relaxation times have the form  $\tau \sim \tau_0\omega^{-\beta}$ . The parameters of power functions depend on the temperature and impurity concentrations. Also, the effect of the HF electromagnetic field on the properties of alkali chloride solutions (LiCl, NaCl, KCl, and CsCl) was investigated in [10] and it was found that the changes of the properties depend on the frequency of the field, the nature of the electrolyte, and the time of exposure.

The works [11-13] reported temperature dependences of super high frequency (SHF) dielectric properties and relaxation processes in KI, CsI, and LiI aqueous solutions in a wide concentration range (0.50-4.01 M) at 288-323 K for the dispersion of water permittivity at seven frequencies ranging from 7.5 GHz to 25 GHz. The low-frequency conductivity of these solutions required to calculate the ion loss was measured. It was found that the temperature dependence of static permittivity disappears in high-concentration solutions. The values of static permittivity  $\epsilon_s$  and dielectric relaxation times  $\tau$  calculated from the formula (2) reported in [4] can be used to calculate the limiting HF EC value  $k_\infty$  of the polar solvent. The latter is further used in formula (2) of the work [7] to determine the frequency dispersion of electrical conductivity  $k$ , i.e. the active component of the EC complex coefficient of electrolyte solutions.

Theoretical studies of kinetic coefficients, elastic, acoustic, and dielectric parameters of liquids and solutions with the methods of time correlation functions (TCF), projection operators (PO), nonequilibrium statistical operators (NSO), collective variables (CV), and kinetic equations (KE) were reported in [3, 14-21]. It was shown in these studies that the expressions derived for the corresponding coefficients and physical parameters are of the most general form and impose no restrictions on the nature of interparticle interactions. To determine them, the problems concerning irreversibility and detailed microscopic evolution of the system are to be solved. Because of the common nature of TCF, PO, NSO, CV, and KE methods, transfer coefficients and other physical parameters of classical liquids and their solutions can hardly be determined explicitly this way. However, these nonequilibrium thermodynamic functions and transport coefficients can be relatively easily studied using the molecular dynamics method [22-24]. According to the results obtained with this method, the kinetic coefficients and acoustic parameters of liquids have low-frequency asymptotics  $\sim\omega^{1/2}$ , while elastic moduli are not frequency-dependent at high frequencies [16, 23].

## **INITIAL EXPRESSIONS FOR THE ELECTRIC ELASTICITY MODULUS $\epsilon(\omega)$ AND THE SPECIFIC CONDUCTANCE COEFFICIENT $\sigma(\omega)$**

The method of kinetic equations was used to study viscoelastic, thermoelastic, acoustic, and dielectric properties of electrolyte solutions depending on the thermodynamic parameters, as well as their frequency dispersion in a wide frequency range [25-29]. It is of interest to study and determine the frequency dispersion of the specific conductance coefficient of electrolyte solutions and to carry out numerical calculations.

Dynamic analytical expressions for the electroelastic modulus  $\epsilon(\omega)$  and the specific conductivity coefficient  $\sigma(\omega)$  were obtained using kinetic equations for one-particle  $f_a(\mathbf{x}_a, t)$  and two-particle  $f_{ab}(\mathbf{x}_a, \mathbf{x}_b, t)$  distribution functions (designated as  $a$ - and  $b$ -type particles) depending on the nature of the attenuation of relaxing flows [30]. We used these formulas as the starting equations.

In the case of the power-law flow relaxation  $t^{-d/2}$  ( $d$  is the dimension of the space), the following analytical expressions were obtained for  $\epsilon(\omega)$  and  $\sigma(\omega)$ :

$$\epsilon(\omega) = \sum_a \omega \hat{\sigma}_a(\omega) \left\{ \omega \tau_a + \sum_b n_b^* q_{ab} \int_0^\infty \frac{\partial \Phi_{ab}(r)}{\partial r} \left[ \int_0^\infty G_2^{ab}(r, r_1, \omega) \frac{\partial g_{ab}^0(r_1)}{\partial r_1} r_1 dr_1 \right] r dr \right\}, \quad (1)$$

$$\sigma(\omega) = \sum_a \hat{\sigma}_a(\omega) \left\{ 1 + \sum_b n_b^* q_{ab} \int_0^\infty \frac{\partial \Phi_{ab}^*(r)}{\partial r} \left[ \int_0^\infty G_1^{ab}(r, r_1, \omega) \frac{\partial g_{ab}^0(r_1)}{\partial r_1} r_1 dr_1 \right] r dr \right\}, \quad (2)$$

where  $\hat{\sigma}_a(\omega) = \frac{\sigma_a}{1 + (\omega \tau_a)^2}$ ;  $\sigma_a = \frac{n_a^0 e_a^2}{\beta_a} = \frac{n_a^0 e_a^2 \tau_a}{m_a}$ ;  $\tau_a = \frac{m_a}{\beta_a}$ ;  $n_b^* = \frac{\pi}{6} n_b d_{ab}^3$ ;  $\Phi_{ab}^*(r) = \frac{\Phi_{ab}(r)}{kT_0}$ ;

$$q_{ab} = \frac{4 e_a \beta_b - e_b \beta_a}{\pi e_a (\beta_a + \beta_b)}.$$

$$G_{1,2}^{ab}(r, r_1, \omega) = \left( \frac{\omega \tau_a}{2} \right)^{-1/2} [e^{-\varphi_1} (\cos \varphi_1 \mp \sin \varphi_1) - e^{-\varphi_2} (\cos \varphi_2 \mp \sin \varphi_2)], \quad (3)$$

where  $\varphi_{1,2} = \varphi_{1,2}^{ab}(r, r_1, \omega) = \left( \frac{\omega \tau_{ab}}{2} \right)^{1/2} (r \mp r_1)$ ;  $\mathbf{r} = \mathbf{r}_{ab}/d_{ab}$ ;  $\mathbf{r}_{ab} = \mathbf{q}_b - \mathbf{q}_a = \mathbf{q}_2 - \mathbf{q}_1$  is the mutual distance;  $d_{ab} = (d_{aa} + d_{bb})/2$

is the average diameter of  $a$  and  $b$  ions;  $n_a^0 = N_a/V$  is the equilibrium number density of  $a$  ions;  $\omega = 2\pi\nu$  is the angular frequency;  $\nu$  is the frequency of the process,  $k$  is the Boltzmann constant;  $T_0$  is the equilibrium temperature;

$\tau_{ab} = \frac{d_{ab}^2}{kT_0} \frac{\beta_a \beta_b}{\beta_a + \beta_b}$  is a phenomenological parameter, an analogue of the time of structural relaxation;  $e_a = z_a e$ ,  $z_a$ ,  $n_a$ ,  $\beta_a$ ,  $\beta_b$

are the charge, valence, mass, and friction coefficients of ions;  $\Phi_{ab}(r)$  is the potential energy of interparticle interactions, and  $g_{ab}^0(r)$  is the equilibrium radial distribution function. Functions  $G_1^{ab}(r, r_1, \omega)$  and  $G_2^{ab}(r, r_1, \omega)$ , defined according to the formula (3) are fundamental solutions (Green's functions) of the Smoluchowski equation for the binary density in the configuration space  $n_{ab}(\mathbf{q}_1, \mathbf{q}_2, t)$  obtained earlier in our work [26].

Equations (1) and (2) describe dynamic processes of electrically conductive properties and, as far as their form, correspond to viscoelastic and thermoelastic properties of electrolyte solutions [26, 27], since  $\epsilon(\omega)$  (by analogy of bulk  $K(\omega)$ , share  $\mu(\omega)$ , and thermal  $Z(\omega)$  moduli) contain function  $G_2^{ab}(r, r_1, \omega)$  under the integral signs, and the corresponding kinetic coefficients  $\eta_v(\omega)$ ,  $\eta_s(\omega)$ , and  $\lambda(\omega)$  are determined by the function  $G_1^{ab}(r, r_1, \omega)$ , as in the case of the specific conductance coefficient  $\sigma(\omega)$ . With a certain choice of the model solution (i.e.  $\Phi_{ab}(r)$  and  $g_{ab}^0(r)$  functions), equations (1) and (2) allow studying frequency dispersions of the electroelastic modulus  $\epsilon(\omega)$  and the specific conductance coefficient  $\sigma(\omega)$  depending on the thermodynamic parameters of the state (density, concentration, and temperature) and to calculate these parameters for aqueous solutions of electrolytes.

Below are the analytical expressions for the electroelasticity modulus  $\epsilon(\omega)$  and the dynamic specific conductance coefficient  $\sigma(\omega)$  of electrolyte solutions obtained in [30] for the case of exponentially relaxing flows:

$$\epsilon(\omega) = \sum_a \frac{(\omega \tau_a)^2 \epsilon_{\infty a}}{1 + (\omega \tau_a)^2} \left[ 1 + \sum_b \frac{(1 + \tau_{ab} / \tau_a) G_0^{ab}(r)}{1 + (\omega \tau_a)^2 (\tau_{ab} / \tau_a)^2} \right], \quad (4)$$

$$\sigma(\omega) = \sum_a \frac{\sigma_a}{1 + (\omega\tau_a)^2} \left[ 1 + \sum_b \frac{1 - (\omega\tau_a)^2 (\tau_{ab} / \tau_a)}{1 + (\omega\tau_a)^2 (\tau_{ab} / \tau_a)^2} G_0^{ab}(r) \right], \quad (5)$$

$$\text{where } \epsilon_{\infty a} = \frac{n_a^0 e_a^2}{m_a}; \quad \sigma_a = \epsilon_{\infty a} \tau_a = \frac{n_a^0 e_a^2 \tau_a}{m_a} = \frac{n_a^0 e_a^2}{\beta_a}; \quad G_0^{ab}(r) = 2\pi n_b^* q_{ab} \int \frac{\partial \Phi_{ab}^*(r)}{\partial r} \frac{\partial g_{ab}^0(r)}{\partial r} r^2 dr. \quad (6)$$

Equations (4) and (5), along with the account of (6), describe electrically conductive properties of electrolyte solutions and have the simplest form as compared to equations (1) and (2). Expressions (4) and (5) contain the times of translational  $\tau_a$ ,  $\tau_b$  and structural  $\tau_{ab}$  relaxation processes, and the function  $G_0^{ab}(r)$  under the integral sign is defined by the interparticle interaction potential  $\Phi_{ab}(r)$  and the equilibrium radial distribution function  $g_{ab}(r)$ , taking into account the contribution of the solution structure to these coefficients.

Therefore, we will restrict our study of the frequency dispersion and numerical calculations of  $\epsilon(\omega)$  and  $\sigma(\omega)$  to using equations (4) and (5) which, along with other molecular parameters, contain friction coefficients of ions  $\beta_a$  and  $\beta_b$ . The latter can be used to determine relaxation times  $\tau_a$ ,  $\tau_b$ , and  $\tau_{ab}$ . However, determining  $\beta_a$ ,  $\beta_b$ ,  $\tau_a$ ,  $\tau_b$ ,  $\tau_{ab}$ ,  $G_0^{ab}(r)$  requires a model solution as well as functions  $\Phi_{ab}(r)$  and  $g_{ab}(r)$  to be chosen, the latter are commonly considered to be known.

## MODEL SELECTION AND NUMERICAL CALCULATIONS

Relaxation times  $\tau_a$ ,  $\tau_b$ , and  $\tau_{ab}$  are expressed through friction coefficients  $\beta_a$  and  $\beta_b$  defined as follows [29]:

$$\beta_a^2 = \sum_a \frac{4\pi}{3} \rho_a \sum_b d_{ab} \int_0^\infty \nabla^2 \Phi_{ab}(r) g_{ab}(r) r^2 dr, \quad (7)$$

$$\beta_b^2 = \sum_b \frac{4\pi}{3} \rho_b \sum_a d_{ab} \int_0^\infty \nabla^2 \Phi_{ab}(r) g_{ab}(r) r^2 dr,$$

where  $\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)$  is the radial part of the Laplace operator;  $\rho_a = m_a n_a$  and  $\rho_b = m_b n_b$  are mass densities of particles  $a$  and  $b$ .

Following the previously reported data [29],  $\Phi_{ab}(r)$  was taken as the sum of the Lennard-Jones potential and the generalized Debye potential taking into account the configuration and size of ions (i.e. in the MacMillan–Maier approximation). These approximations take into account only the interaction between ions, and the contribution of the solvent was considered using the  $\epsilon_{ss}$  coefficient:

$$\Phi_{ab} = \frac{4\epsilon_{ab}}{\epsilon_{ss}} (r^{-12} - r^{-6}) + R_{ab} \frac{e^{-\kappa^* r}}{r}, \quad (8)$$

where  $d_{ab} = (d_{aa} + d_{bb})/2$ ;  $R_{ab} = \frac{f z_a z_b e^2 e^{\kappa^*}}{kT \epsilon_{ss} d_{ab} (1 + \kappa^*)}$ ;  $\epsilon_{ab} = (\epsilon_{aa} \epsilon_{bb})^{1/2}$  is the depth of the potential well of the interparticle

interaction energy;  $f = (4\pi\epsilon_0)^{-1} = 9 \cdot 10^9$  F/m;  $\epsilon_0$  is the electric constant;  $\epsilon_{ss}$  is the specific conductance coefficient of the solvent;  $e$  is the elementary charge;  $d_{ab}$ ,  $d_{bb}$  and  $z_a$ ,  $z_b$  are the diameter and the valence of ions  $a$  and  $b$ ;  $\kappa^* = \kappa_a d_{ab}$  is the inverse of the reduced Debye length where  $\kappa$  is defined as  $\kappa^2 = \sum_a n_a e_a^2 / \epsilon_r \epsilon_0 kT$  [31].

According to [21],  $g_{ab}(r)$  of the ionic subsystem has the form:

$$g_{ab}^0(r) = y(r, \rho^*) e^{-\frac{\Phi_{ab}(r)}{kT}}, \quad (9)$$

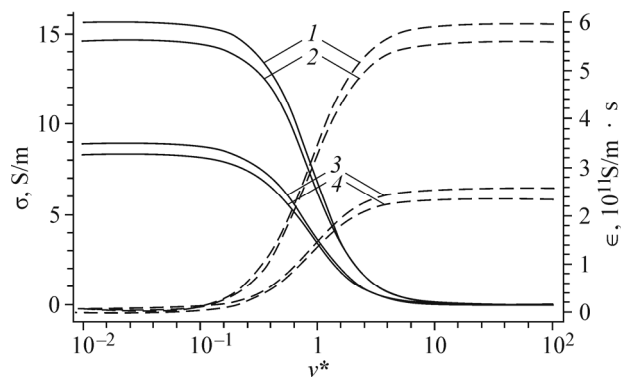
where  $y(r, \rho^*)$  is a binary function for the distribution of two cavities (we consider only its contact value  $y(r, \rho^*) \approx y(\rho^*)$  at a distance  $r = 1$  ( $r_{ab} = d_{ab}$ )). This function was obtained by Carnahan and Starling in the form

$$y(\rho^*) = (2 - \rho^*) / 2(1 - \rho^*)^3, \quad (10)$$

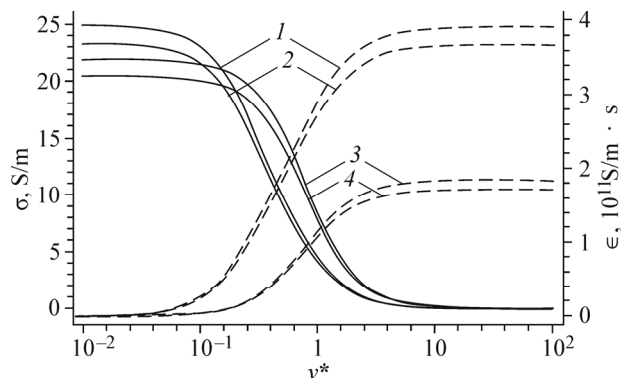
where  $\rho^* = \pi n d_{ab}^3 / 6 = \pi \rho d_{ab}^3 N_0 / 6M$  is the reduced density;  $\rho$  is the solution density;  $N_0$  is the Avogadro number;  $M$  is the molar mass.

Equations (8)-(10) allow calculating friction coefficients  $\beta_a$ ,  $\beta_b$ , relaxation times  $\tau_a$ ,  $\tau_b$  and  $\tau_{ab}$  as well as the electroelastic modulus  $\epsilon(\omega)$  and the specific conductance coefficient  $\sigma(\omega)$  in a wide range of densities  $\rho$ , concentrations  $c$ , temperatures  $T$ , and frequencies  $\omega$ .

Tables 1 and 2 and Figs. 1-3 show the results of numerical calculations of friction coefficients  $\beta_a$  and  $\beta_b$ , relaxation times  $\tau_a$ ,  $\tau_b$  and  $\tau_{ab}$ , as well as the dynamic electroelasticity modulus  $\epsilon(\omega)$  and the specific conductance coefficient  $\sigma(\omega)$  obtained from equations (4)-(6) taking into account expressions (7)-(10) for LiCl, NaCl, KCl, CsCl aqueous solutions.



**Fig. 1.** Frequency dependence of the specific conductance coefficient  $\sigma(\nu)$  (solid lines) and the electroelasticity modulus  $\epsilon(\nu)$  (dashed lines) for aqueous solutions of LiCl (lines 3, 4) and NaCl (lines 1, 2) at 20 °C (2, 4) and 35 °C (1, 3) and fixed concentrations  $c = 0.113$  for LiCl and  $c = 0.149$  for NaCl.



**Fig. 2.** Frequency dependence of the specific conductance coefficient  $\sigma(\nu)$  (solid lines) and the electroelasticity modulus  $\epsilon(\nu)$  (dashed lines) for aqueous solutions of KCl (lines 3, 4) and CsCl (lines 1, 2) at 20 °C (2, 4) and 35 °C (1, 3) and fixed concentrations  $c = 0.183$  for KCl and  $c = 0.574$  for CsCl.

**TABLE 1.** Friction Coefficients  $\beta_1, \beta_2$ , Relaxation Times  $\tau_1, \tau_2, \tau_{11}, \tau_{12} = \tau_{21}, \tau_{22}$  of LiCl, NaCl, KCl, CsCl Aqueous Solutions as Functions of Concentration and Density at a Fixed Temperature  $t = 18^\circ\text{C}$

| $c, \%$ | $\rho, \text{kg/m}^3$ | $\beta_1 \cdot 10^{13}, \text{kg/s}$ | $\beta_2 \cdot 10^{13}, \text{kg/s}$ | $\tau_1 \cdot 10^{13}, \text{s}$ | $\tau_2 \cdot 10^{12}, \text{s}$ | $\tau_{11} \cdot 10^{12}, \text{s}$ | $\tau_{12} = \tau_{21} \cdot 10^{12}, \text{s}$ | $\tau_{22} \cdot 10^{12}, \text{s}$ |
|---------|-----------------------|--------------------------------------|--------------------------------------|----------------------------------|----------------------------------|-------------------------------------|-------------------------------------------------|-------------------------------------|
| LiCl    |                       |                                      |                                      |                                  |                                  |                                     |                                                 |                                     |
| 2.5     | 1011.8                | 0.424                                | 0.986                                | 1.371                            | 2.992                            | 0.295                               | 0.958                                           | 2.879                               |
| 5       | 1026                  | 0.606                                | 1.452                                | 0.959                            | 2.031                            | 0.421                               | 1.382                                           | 2.932                               |
| 10      | 1056                  | 0.854                                | 2.168                                | 0.681                            | 1.360                            | 0.593                               | 1.980                                           | 3.047                               |
| 20      | 1117                  | 1.251                                | 3.333                                | 0.465                            | 0.885                            | 0.869                               | 2.940                                           | 3.295                               |
| 30      | 1183                  | 1.632                                | 4.435                                | 0.356                            | 0.665                            | 1.133                               | 3.855                                           | 3.585                               |
| 40      | 1251                  | 2.026                                | 5.572                                | 0.287                            | 0.529                            | 1.407                               | 4.802                                           | 3.911                               |
| NaCl    |                       |                                      |                                      |                                  |                                  |                                     |                                                 |                                     |
| 5       | 1033.5                | 1.157                                | 1.256                                | 1.651                            | 2.348                            | 1.066                               | 2.145                                           | 3.668                               |
| 10      | 1070                  | 1.665                                | 1.877                                | 1.148                            | 1.571                            | 1.534                               | 3.142                                           | 5.481                               |
| 15      | 1108.5                | 2.093                                | 2.406                                | 0.913                            | 1.225                            | 1.929                               | 3.987                                           | 7.027                               |
| 20      | 1148                  | 2.496                                | 2.901                                | 0.765                            | 1.016                            | 2.300                               | 4.779                                           | 8.473                               |
| 25      | 1188.5                | 2.892                                | 3.385                                | 0.661                            | 0.871                            | 2.665                               | 5.555                                           | 9.885                               |
| 26      | 1197                  | 2.972                                | 3.482                                | 0.643                            | 0.847                            | 2.739                               | 5.711                                           | 10.171                              |
| KCl     |                       |                                      |                                      |                                  |                                  |                                     |                                                 |                                     |
| 5       | 1029.5                | 1.014                                | 0.565                                | 3.194                            | 5.219                            | 1.416                               | 0.884                                           | 1.650                               |
| 10      | 1063                  | 1.448                                | 0.865                                | 2.237                            | 3.411                            | 2.022                               | 1.294                                           | 2.525                               |
| 15      | 1097                  | 1.970                                | 1.226                                | 1.644                            | 2.406                            | 2.750                               | 1.786                                           | 3.579                               |
| 20      | 1132                  | 2.139                                | 1.340                                | 1.515                            | 2.200                            | 2.986                               | 1.944                                           | 3.915                               |
| 21      | 1139.5                | 2.204                                | 1.385                                | 1.470                            | 2.129                            | 3.077                               | 2.005                                           | 4.044                               |
| CsCl    |                       |                                      |                                      |                                  |                                  |                                     |                                                 |                                     |
| 1.66    | 1011.1                | 0.779                                | 0.216                                | 14.183                           | 3.786                            | 1.428                               | 0.831                                           | 0.653                               |
| 14.4    | 1020.4                | 2.520                                | 0.673                                | 4.383                            | 1.170                            | 4.584                               | 2.588                                           | 2.017                               |
| 25.2    | 1231.5                | 3.508                                | 0.973                                | 3.149                            | 0.841                            | 6.429                               | 3.717                                           | 2.915                               |
| 33.6    | 1332.4                | 4.273                                | 1.201                                | 2.585                            | 0.690                            | 7.837                               | 4.572                                           | 3.594                               |
| 40.2    | 1425.2                | 4.911                                | 1.390                                | 2.249                            | 0.600                            | 9.006                               | 5.279                                           | 4.155                               |
| 50.3    | 1589.3                | 6.102                                | 1.741                                | 1.810                            | 0.483                            | 10.967                              | 6.461                                           | 5.091                               |
| 57.4    | 1728.8                | 6.853                                | 1.961                                | 1.612                            | 0.430                            | 12.575                              | 7.424                                           | 5.854                               |

Molecular parameters participating in Lennard-Jones and generalized Debye potentials ( $d_{aa}, d_{bb}, \varepsilon_{aa}/k, \varepsilon_{bb}/k, \kappa^*$ ) were taken from [32] and the corresponding experimental values of density  $\rho$ , solution concentrations  $c_a, c_b$ , and temperature  $T$  were taken from [33, 34].

According to Table 2, the values of the dynamic specific conductance coefficient  $\sigma(\omega)$  of LiCl, NaCl, KCl, CsCl theoretically calculated from equations (5) as a function of reduced frequency  $\nu^*$  are in satisfactory agreement with the experimental values reported for the static specific conductance coefficient [33, 34] for the corresponding values of concentration  $c$ , density  $\rho$ , and temperature  $T$ . Theoretically calculated values  $\sigma(\omega)$  are slightly underestimated at low frequencies as compared to experimental values of the static specific conductance coefficient  $\sigma_s$  reported in [33, 34], which is apparently due to the choice of the approximation for the interaction potential  $\Phi_{ab}(r)$  and radial distribution function  $g_{ab}(r)$  according to equations (8) and (9).

Figs. 1 and 2 show the dependencies of  $\varepsilon(\omega)$  and  $\sigma(\omega)$  on the reduced frequency  $\nu^* = \nu\tau_a$  at  $29^\circ\text{C}$ ,  $35^\circ\text{C}$  and for the corresponding concentrations of KCl, CsCl and LiCl, NaCl. The obtained frequency dependencies of the electroelasticity

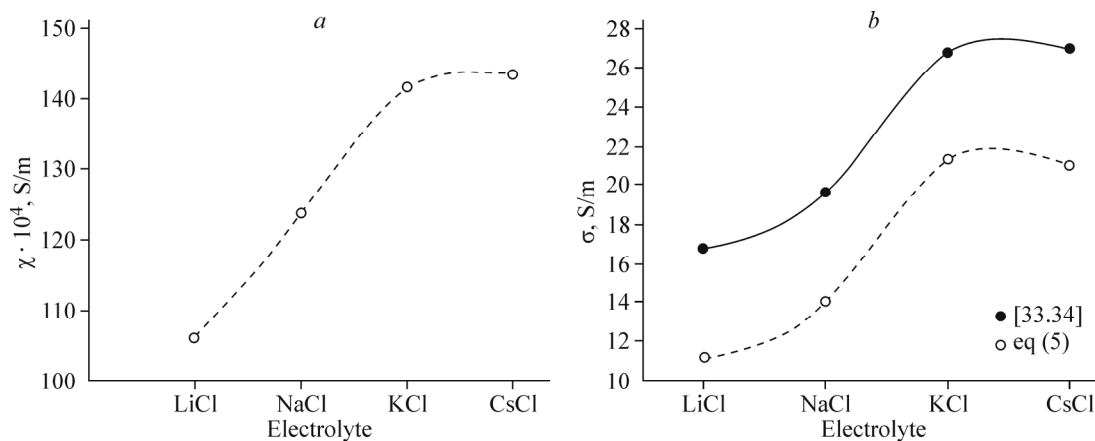
**TABLE 2.** Specific Conductance Coefficient  $\sigma(\nu)$  of LiCl, NaCl, KCl, CsCl Aqueous Solutions as a Function of Concentration and Density at a Fixed Temperature  $t = 18\text{ }^{\circ}\text{C}$  and Reduced Frequencies  $10^{-6} \leq \nu^* \leq 1$  ( $\nu^* = \nu \cdot \tau_1$ ;  $10^6 \leq \nu \leq 10^{12}$  Hz)

| $c, \%$ | $\rho, \text{kg/m}^3$ | $\sigma, \text{S/m [33]}^*$ | $\sigma, \text{S/m}$ |                   |                   |                   |                   |                   |             |
|---------|-----------------------|-----------------------------|----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------|
|         |                       |                             | $\nu^* = 10^{-6}$    | $\nu^* = 10^{-5}$ | $\nu^* = 10^{-4}$ | $\nu^* = 10^{-3}$ | $\nu^* = 10^{-2}$ | $\nu^* = 10^{-1}$ | $\nu^* = 1$ |
| LiCl    |                       |                             |                      |                   |                   |                   |                   |                   |             |
| 2.5     | 1011.8                | 4.10                        | 3.86                 | 3.86              | 3.86              | 3.86              | 3.86              | 3.78              | 1.55        |
| 5       | 1026.0                | 7.33                        | 5.43                 | 5.43              | 5.43              | 5.43              | 5.42              | 5.32              | 2.20        |
| 10      | 1056.0                | 12.18                       | 7.80                 | 7.80              | 7.80              | 7.80              | 7.80              | 7.66              | 3.24        |
| 20      | 1117.0                | 16.76                       | 11.12                | 11.12             | 11.12             | 11.12             | 11.12             | 10.93             | 4.69        |
| 30      | 1183.0                | 13.99                       | 13.47                | 13.47             | 13.47             | 13.47             | 13.46             | 13.25             | 5.73        |
| 40      | 1251.0                | 8.44                        | 15.24                | 15.24             | 15.24             | 15.24             | 15.24             | 15.00             | 6.51        |
| NaCl    |                       |                             |                      |                   |                   |                   |                   |                   |             |
| 5       | 1033.5                | 6.72                        | 7.24                 | 7.24              | 7.24              | 7.24              | 7.24              | 7.18              | 3.96        |
| 10      | 1070.0                | 12.11                       | 10.15                | 10.15             | 10.15             | 10.15             | 10.15             | 10.06             | 5.60        |
| 15      | 1108.5                | 16.42                       | 12.29                | 12.29             | 12.29             | 12.29             | 12.29             | 12.19             | 6.83        |
| 20      | 1148.0                | 19.57                       | 14.00                | 14.00             | 14.00             | 14.00             | 14.00             | 13.89             | 7.80        |
| 25      | 1188.5                | 21.35                       | 15.40                | 15.40             | 15.40             | 15.40             | 15.40             | 15.28             | 8.59        |
| 26      | 1197.0                | 21.51                       | 15.65                | 15.65             | 15.65             | 15.65             | 15.65             | 15.52             | 8.73        |
| KCl     |                       |                             |                      |                   |                   |                   |                   |                   |             |
| 5       | 1029.5                | 6.90                        | 10.99                | 10.99             | 10.99             | 10.99             | 10.98             | 10.76             | 3.89        |
| 10      | 1063.0                | 13.59                       | 15.21                | 15.21             | 15.21             | 15.21             | 15.21             | 14.94             | 5.70        |
| 15      | 1097.0                | 20.20                       | 18.41                | 18.41             | 18.41             | 18.41             | 18.40             | 18.10             | 7.14        |
| 20      | 1132.0                | 26.77                       | 21.28                | 21.28             | 21.28             | 21.28             | 21.28             | 20.93             | 8.30        |
| 21      | 1139.5                | 28.10                       | 21.80                | 21.8              | 21.80             | 21.80             | 21.79             | 21.44             | 8.52        |
| CsCl    |                       |                             |                      |                   |                   |                   |                   |                   |             |
| 1.66    | 1011.1                | 1.18                        | 3.30                 | 3.30              | 3.30              | 3.30              | 3.30              | 3.27              | 1.72        |
| 14.4    | 1020.4                | 9.59                        | 10.18                | 10.18             | 10.18             | 10.18             | 10.18             | 10.08             | 5.16        |
| 25.2    | 1231.5                | 18.36                       | 13.63                | 13.63             | 13.63             | 13.63             | 13.63             | 13.51             | 7.07        |
| 33.6    | 1332.4                | 25.5                        | 15.99                | 15.99             | 15.99             | 15.99             | 15.99             | 15.84             | 8.35        |
| 40.2    | 1425.2                | 31.41                       | 17.72                | 17.72             | 17.72             | 17.72             | 17.72             | 17.56             | 9.30        |
| 50.3    | 1589.3                | 39.5                        | 20.20                | 20.20             | 20.20             | 20.20             | 20.20             | 20.02             | 10.64       |
| 57.4    | 1728.8                | 43.41                       | 21.82                | 21.82             | 21.82             | 21.82             | 21.82             | 21.63             | 11.52       |

\* Hydrates In the case of CsCl, the data for  $\sigma$  are cited according to [34].

modulus  $\epsilon(\omega)$  and the dynamic specific conductance coefficient  $\sigma(\omega)$  correspond to the general conclusions of the statistical theory of transfer coefficients and elastic properties of liquids and solutions: elastic moduli  $\epsilon_{\infty}$  increases monotonously with increasing frequency and remains constant at high frequencies of  $10^{12}$ - $10^{13}$  Hz, while the specific conductance coefficient decreases and tends to the asymptotic value  $\sigma_{\min}$  [16, 20, 22—24]. Numerical values and the order of  $\epsilon(\omega)$  and  $\sigma(\omega)$  coincide with reported experimental data.

Fig. 3a shows the dependency of the specific conductance coefficient  $\sigma$  on the properties of aqueous solutions of alkali metals LiCl, NaCl, KCl, and CsCl subjected to the influence of HF EC according to the experimental data reported in [10]. Fig. 3b shows the same dependency for the theoretical values obtained from equation (5) using the data of Table 2 at a fixed concentration  $c = 20\%$  corresponding to the density  $\rho$  and the temperature  $t = 20\text{ }^{\circ}\text{C}$ ; the plot also shows the comparison



**Fig. 3.** Specific conductance of various electrolytes at a temperature of 20 °C and the concentration  $c = 20\%$ .

of these results with experimental data reported in [33, 34]. As can be seen from the graphs, the curves demonstrate the same qualitative behavior. A better agreement between theoretical and experimental  $\sigma(\omega)$  values can be achieved by considering ion-dipole and dipole-dipole interactions in the  $\Phi_{ab}(r)$  potential and the radial distribution function  $g_{ab}(r)$  rather than ion-ion interactions only. Unfortunately, theoretical consideration of these contributions is a very difficult problem.

### CONFLICT OF INTERESTS

The authors declare that they have no conflict of interests.

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