MECHANISM OF FREQUENCY-INDEPENDENT CONDUCTIVITY IN AQUEOUS SOLUTIONS OF ELECTROLYTES

L.A. BULAVIN, A.N. ALEKSEEV, YU.F. ZABASHTA, S.YU. TKACHEV

Taras Shevchenko National University of Kyiv, Faculty of Physics
(4, Academician Glushkov Prosp., Kyiv 03680, Ukraine; e-mail: `tkachevserg@gmail.com`*)*

PACS 82.45.Gj

It is shown that the dependence of the resistance of a cell filled with a NaCl aqueous solution on the ac frequency cannot be explained as a result of only polarization phenomena in the boundary region at the electrode–electrolyte interface. A physical mechanism is proposed, which explains the monotonous increase of the solution specific conductivity at frequencies below 10^4 Hz, and its constant value in the frequency interval of 10^4–10^5 Hz. The temperature dependences for the diffusion coefficients of Na^+ and Cl^- ions in NaCl aqueous solutions and for the dimension of an physically infinitesimal volume (a region, where the local equilibrium is established) in this electrolyte are calculated. The space-time hierarchies in the NaCl aqueous solution are analyzed, and a relationship between a connection of the ac period with certain time characteristics, on the one hand, and the frequency dependence of the specific conductivity in this electrolyte, on the other hand, is demonstrated.

1. Introduction

It is known [1] that, when the frequency of an alternating current through an electrolyte solution is initially lower than 10^4 Hz, the frequency growth is accompanied by a monotonous increase of the specific conductivity of the electrolyte solution followed by its saturation within the frequency interval of $10^4 - 10^5$ Hz. Such a behavior is supposed to be a manifestation of polarization phenomena in the boundary region between the electrolyte and the electrode, when the contact technique is used for measurements. In this work, we demonstrate that this model results in only a qualitative agreement with experimental data. The aim of this work is to propose a physical mechanism, which could explain the constant electroconductivity in the indicated frequency interval.

2. Experimental Technique

We studied the ac resistance of sodium chloride aqueous solutions with salt concentrations of 0.9, 1.8, 4.5, and 9 g/l in the frequency range of 0.1–100 kHz and the temperature interval 30–70 °C. The measurements were carried out with a P5083 alternating current bridge.

The resistance was measured, by using a two-electrode cell, with a liquid system to study being poured into. Such a cell is usually represented in the form of an equivalent circuit [1], which includes, besides the electrolyte resistance, double layer capacitance, Warburg impedance, electrochemical polarization resistance, parasitic capacitance between electrodes, and resistance formed as a result of the ion adsorption on the electrode surface. The parameters of the cell and the electrolyte can be so selected that the parasitic capacitance, the adsorption resistance, and the electrochemical polarization resistance could be considered equal to zero. For instance, in order to minimize the parasitic capacitance, we used a cell with probe platinum electrodes rather than ordinary electrodes in the form of plates. Owing to this simplification of the equivalent circuit, the measured resistance of the cell filled with the electrolyte, R_{meas}, and the resistance of the electrolyte, R, are connected as follows:

$$R_{\text{meas}} = R + \Delta R_s, \tag{1}$$

where

$$\Delta R_s = \frac{1}{\eta C^2}\omega^{-3/2}, \tag{2}$$

is an error inserted by polarization phenomena [1], η is a constant, C is the capacitance of the double layer, $\omega = 2\pi f$ is the cyclic frequency of the alternating current, and f is the ac frequency.

The cell diameter was much smaller than its length ($l_0 = 10.1$ cm and $d = 0.2$ cm), which favored a better thermostabilization, when measuring the temperature dependence of electroconductivity.

The frequency dependence of the resistance of a cell filled with the NaCl aqueous solution of a concentration of 9 g/l, which was measured in the indicated frequency interval, is depicted in Fig. 1. Let us replot it in the $(\omega^{-3/2}, R_{\text{meas}})$-coordinates and approximate by a linear

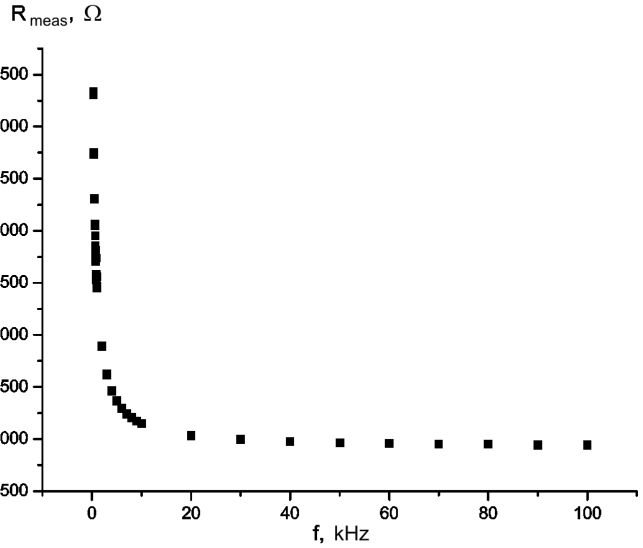

Fig. 1. Resistance of a cell filled with a sodium chloride aqueous solution with a NaCl concentration of 9 g/l as a function of the ac frequency

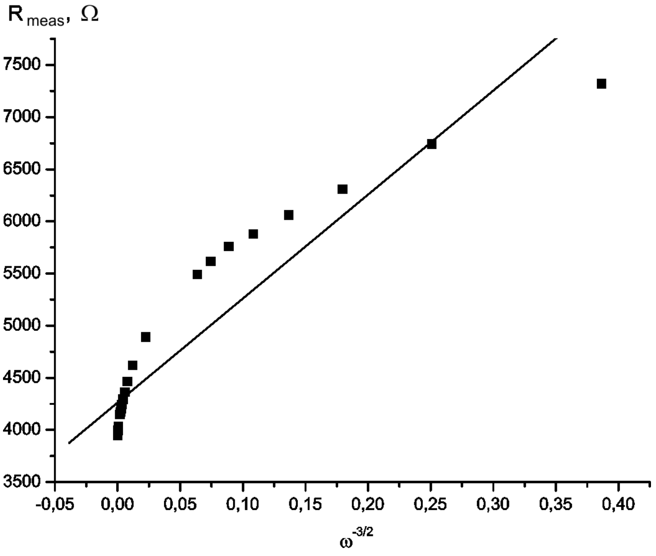

Fig. 2. The same as in Fig. 1, but in the $(\omega^{-3/2}, R_{\mathrm{meas}})$-coordinates and the corresponding approximation by formula (1)

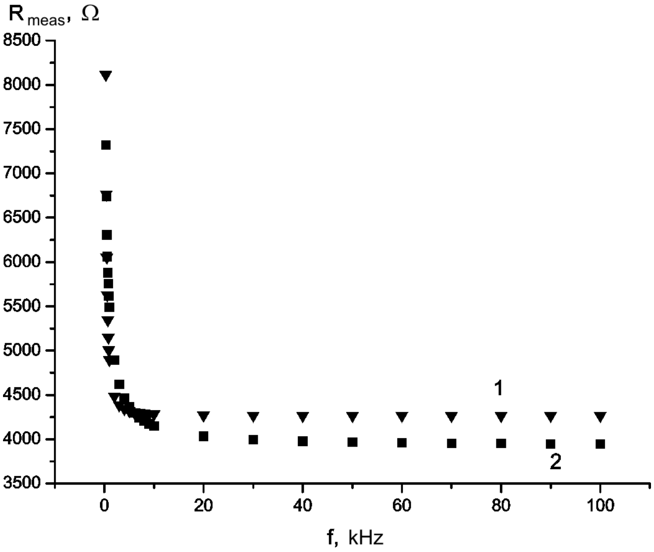

Fig. 3. Dependences of the resistance of a cell filled with a sodium chloride aqueous solution with a NaCl concentration of 9 g/l on the ac frequency: (*1*) calculated by formula (1) and (*2*) experimentally measured

dependence, to which formula (1) corresponds in these coordinates (see Fig. 2).

Consider this dependence (the experimental curve) and its approximation (the theoretical curve) in the (f, R_{meas})-coordinates (see Fig. 3). It is evident that the curves are only in qualitative agreement. This afforded ground for supposing that, besides polarization phenomena, there exists another reason for the frequency dependence of the measured resistance to have a form presented in Fig. 1.

3. Experimental Results

In Figs. 4 and 5, the frequency and temperature dependences of the specific conductivity in sodium chloride aqueous solutions calculated from the experimentally obtained values of the cell resistance are given.

4. Discussion of Experimental Results

While interpreting our experimental data, we use the continual model. Any continual theory [2–4] is based on the idea of local equilibrium. It is adopted that an incomplete equilibrium, i.e. with respect to a definite confined set of dynamic variables, is established in a certain region of the dimension l and the volume $v \sim l^3$. It is this equilibrium that is called local, and the region itself is called a physically infinitesimal volume. The emergence of the latter term is explained by the fact that the continual theory considers the dimension l as an infinitesimal quantity. Accordingly, the physical infinitesimal volume transforms into a mathematical infinitesimal volume $d\mathbf{x}$ in the continual approximation.

The existence of local equilibrium allows one to ascribe a certain free energy to the physically infinitesimal volume and, therefore, a certain macroscopic parameter. In the case of electrolyte solutions, such a parameter

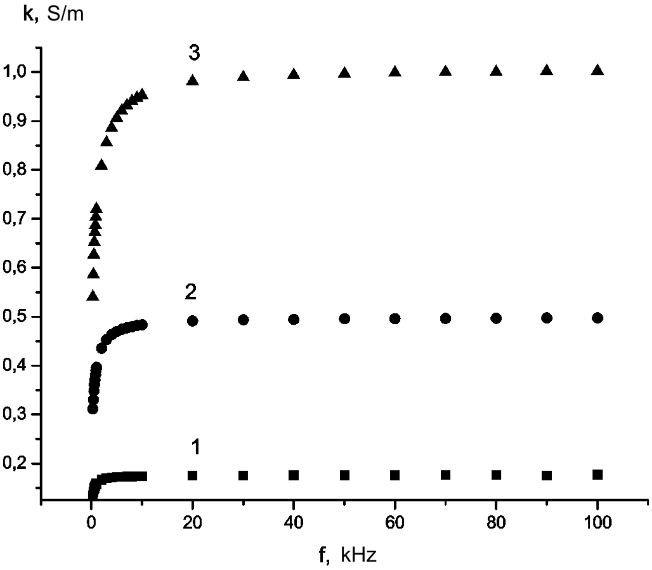

Fig. 4. Dependences of the specific conductivity on the ac frequency in sodium chloride aqueous solutions with concentrations of 1.8 (*1*), 4.5 (*2*), and 9 g/l (*3*)

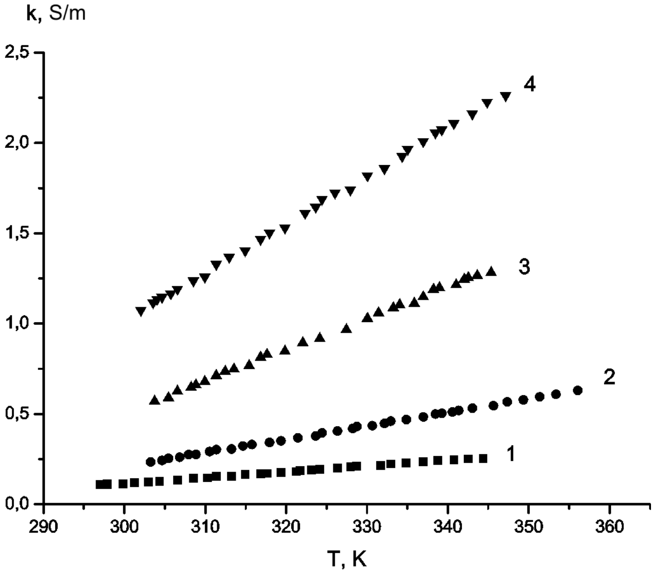

Fig. 5. Temperature dependences of the specific conductivity in sodium chloride aqueous solutions with NaCl concentrations of 0.9 (*1*), 1.8 (*2*), 4.5 (*3*), and 9 g/l (4). The ac frequency is 80 kHz

can be, e.g., the concentration of ions n. This quantity is considered to be a continuous function of coordinates in the continual approximation. Respectively, the number of ions in the physically infinitesimal volume with the center of mass at $\mathbf{x}$ is determined by the expression $n(\mathbf{x})d\mathbf{x}$.

By definition [2], the number of particles in the physically infinitesimal volume must be considerably larger than one. In our case, the following inequality holds:

$$nv \gg 1. \tag{3}$$

Just this inequality determines the eligibility of applications of the continual approach. The introduction of the local equilibrium concept results in the appearance of a certain minimal size l, below which the continual approach becomes ineligible.

In the absence of external field [2], the diffusion process in the one-dimensional case is described by the equation

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}, \tag{4}$$

where D is the diffusion coefficient. The solution of this equation with zero boundary conditions is written down in the form of an infinite series

$$n = \sum_{q=1}^{\infty} A_q \sin\frac{\pi q x}{L} \exp\left(-t/\tau_q\right), \tag{5}$$

where L is the system size, and τ_q is the relaxation time for the q-th diffusion mode, which is determined by the expression

$$\tau_q = \frac{L^2}{\pi^2 q^2 D}. \tag{6}$$

However, expression (5) is, generally speaking, an approximation, because, as was already mentioned, the continual representations are valid only for spatial intervals larger than l. Taking this fact into account, it would be more exact to write down the mentioned solution in the form of a finite series,

$$n = \sum_{q=1}^{Q} A_q \sin\frac{\pi q x}{L} \exp(-t/\tau_q), \tag{7}$$

where Q is the largest value of parameter q; it is determined by the equality

$$Q = \frac{L}{l}. \tag{8}$$

As is seen from formula (6), the existence of the minimal spatial interval l suggests the existence of the minimal time interval

$$\tau_Q = \frac{L^2}{\pi^2 Q^2 D}. \tag{9}$$

To find l, we used the experimental data on the conductivity of electrolyte solutions. This choice of experiments is associated with the fact that ions are charge carriers in electrolytes. Accordingly, for the current density amplitude I, we obtain the expression

$$I = eJ, \tag{10}$$

where e is the ion charge, and J is the density of ionic flow. As is known [6], under the action of an external force, the ionic flow density J can be written down as a sum

$$J = J_\mathrm{D} + J_\mathrm{K}, \tag{11}$$

where J_D and J_K correspond to the densities of the diffusion and convective flows, respectively. They look like

$$J_\mathrm{D} = -D\frac{\partial n}{\partial x}, \tag{12}$$

$$J_\mathrm{K} = nbF, \tag{13}$$

respectively, where $F = eE$ is a force acting on an ion, E is the electric field strength, and b is the ion mobility, which is coupled with the diffusion coefficient by the Einstein relation

$$bk_\mathrm{B}T = D. \tag{14}$$

We consider the alternating current, so that

$$E = E_0 \exp(-i\omega t). \tag{15}$$

Figure 4 shows that the conductivity increases with the ac frequency, but only until a certain frequency ω_Q of the order of 10^{-4} s^{-1}. At frequencies higher than ω_Q, the electroconductivity remains practically invariable. Such a behavior of the electroconductivity can be explained as follows. According to formulas (11)–(13), the diffusion flow counteracts the convective one and reduces it. At high frequencies of the external force, when the inequality

$$\omega\tau_Q \gg 1 \tag{16}$$

is obeyed, diffusion modes are too slow to "trace" the external field, and, provided that inequality (16) holds, the diffusion flow is practically absent. Only the convective flow survives, so that formula (10) reads

$$I = \frac{e^2 nD}{k_\mathrm{B}T}E. \tag{17}$$

Hence, if condition (16) is satisfied, the specific conductivity k is determined by the expression

$$k = \frac{e^2 nD}{k_\mathrm{B}T}. \tag{18}$$

According to the last expression, the electroconductivity is frequency independent. Hence, the section of the constant conductivity corresponds to inequality (16). It means that the frequency ω_Q at the beginning of this section is determined by the condition

$$\omega_Q\tau_Q = 1. \tag{19}$$

According to formula (7), the concentration is written down as a sum, every term of which is a collective fluctuation, which is sinusoidal in space and exponentially damps in time with the relaxation time (6). As was already mentioned, such a damped collective fluctuation is called a diffusion mode. Its appearance is associated with the constant concentration of particles (now, these are ions). Accordingly, the excess of this quantity cannot disappear locally. It can only relax slowly, expanding over the whole system. The sinusoidal diffusion mode relaxes only through the particle transfer from a region, where there is an excessive concentration, into a region with a concentration deficiency.

When an external field is applied, the initial distribution of ions does not correspond any more to the equilibrium state, i.e. there appears a fluctuation determined by the field with respect to the equilibrium distribution. To be more exact, we deal in this case with the already mentioned set of fluctuations, every of them being characterized by a specific relaxation time (6). The minimal value of these times was defined as τ_Q. It is clear that, under condition (16), collective fluctuations have no time to relax, and the conductivity is determined by formula (18). This formula includes the concentration. This quantity characterizes a certain state of local equilibrium and can be calculated making use of the local-equilibrium distribution function [9]. As was already mentioned, the presence of the concentration in formula (18) means that there is enough time for a local equilibrium to be established at any moment in the system subjected to the action of an external alternating field. In other words, if τ_l stands for the equilibration time, the following inequality must be satisfied:

$$\omega\tau_l \ll 1. \tag{20}$$

Let us make sure of the validity of formula (18). According to it, the frequency-independent value of specific conductivity k must be proportional to the concentration n, provided that the temperature is constant. In Fig. 6, the experimental dependences of the specific conductivity k on the concentration n at various temperatures are depicted. One can see that the experimental dependences can be approximated with a satisfactory accuracy

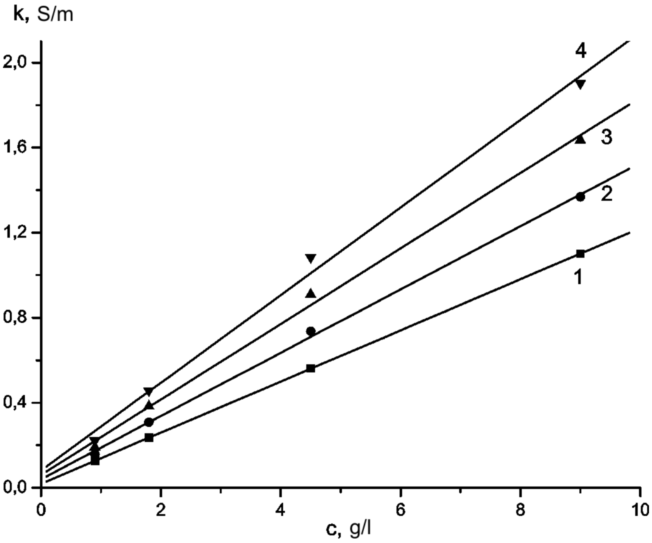

Fig. 6. Concentration dependences of the specific conductivity in a sodium chloride aqueous solution at temperatures of 30 (*1*), 40 (*2*), 50 (*3*), and 60 °C (*4*)

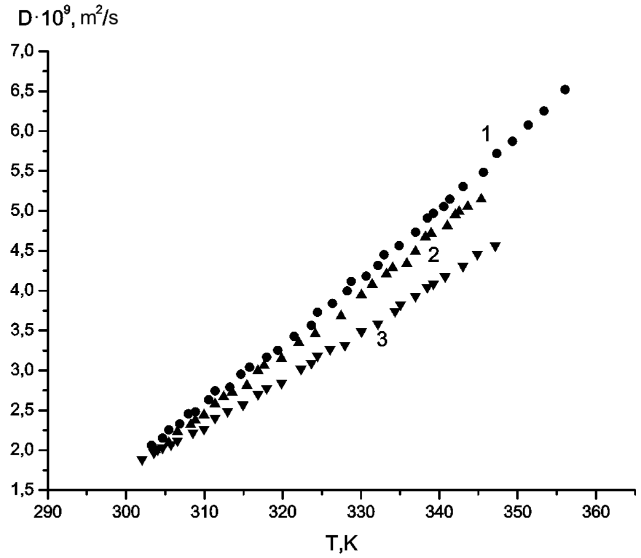

Fig. 7. Temperature dependences of the diffusion coefficient for a sodium chloride aqueous solution with NaCl concentrations of 1.8 (*1*), 4.5 (*2*), and 9 g/l (*3*)

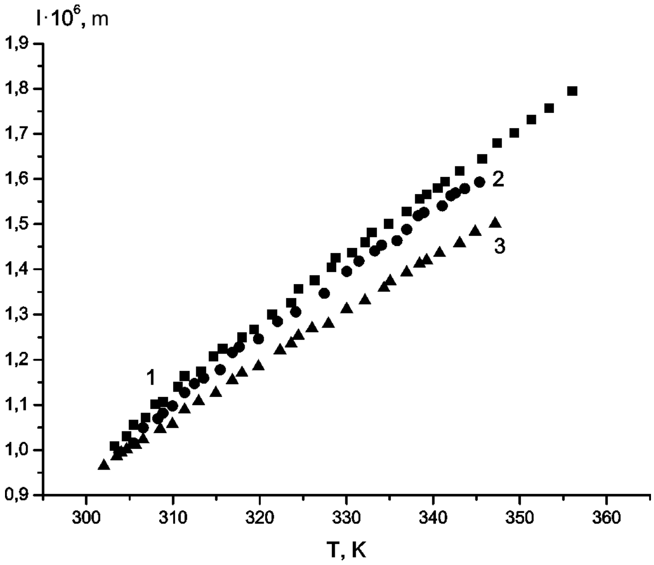

Fig. 8. Temperature dependences of the dimension of a physically infinitesimal volume in sodium chloride aqueous solutions with NaCl concentrations of 1.8 (*1*), 4.5 (*2*), and 9 g/l (*3*)

by linear dependences, which allows the diffusion coefficient D and the infinitesimal volume dimension l for the studied solutions to be calculated by formula (18) and formulas (8) and (9), respectively (see Figs. 7 and 8). As follows from the given plots, the order of magnitude of the quantity l is 10^3 nm.

According to expression (20), there must exist fast relaxation processes in the system, which provide the establishment of a local equilibrium. As such, there may be the processes of Debye atmosphere relaxation proposed by P. Debye in [7,8]. The relaxation time of these processes is 10^{-7}–10^{-6} s. At the same time, it should be emphasized that the size of a physically infinitesimal volume substantially exceeds the Debye radius $r_{\rm D}$. Really, the formula for the Debye radius is [7]

$$r_{\rm D}=\left(\frac{\varepsilon k_{\rm B}T}{8\pi n e^2}\right)^{1/2}, \tag{21}$$

where ε is the dielectric permittivity of a solvent, and e is the ion charge. Substituting the relevant numerical values obtained in our experiment into formula (21), we obtain the estimate $r_{\rm D}\approx 0.8$ nm. The Debye theory is valid, if $l \ll r_{\rm D}$. However, in our case, $r_{\rm D} \ll l$. It means that the Debye theory is inapplicable.

There is another argument that the Debye theory cannot be applied in our case. This theory is good, provided that the interaction energy U of a given ion with the others satisfies the condition $U \ll k_{\rm B}T$. Let us calculate U for the concentrations studied in this work. It is known that, at concentrations that correspond to the Debye theory, the concentration of counterions in a vicinity of the given ion exceeds the concentration of ions with the same sign. In our case, when the Debye radius $r_{\rm D}$ becomes comparable with the ion-to-ion distance $n^{-1/3}$ by the order of magnitude, positive charges are practically absent from the nearest vicinity – the first coordination sphere – of a positive ion, and this ion turns out surrounded only with negative ones. Radiographic researches [9] showed that the number of ions in the first coordination sphere in the solution is approximately the same as in the crystal. This circumstance allows one, while estimating U, to use the calculation results obtained for a NaCl crystal [10], where the following expression was obtained for the electrostatic energy U' per one cell, i.e., in fact, for the energy of interactions of an ion with its environment:

$$U' = 1.75e^2n^{1/3}. \tag{22}$$

Taking into account that solute ions are surrounded by water molecules, this formula should be rewritten in the form

$$U = 1.75\frac{e^2n^{1/3}}{\varepsilon}. \tag{23}$$

Substituting the n-value from the studied concentration interval into this formula, we obtain $U \approx 5 \times 10^{-21}$ J, which is of the same order of magnitude as the energy of thermal motion of ions $k_{\mathrm{B}}T \approx 4 \times 10^{-21}$ J.

Leaving the distance between solvent molecules aside, four characteristic linear dimensions can be distinguished in the electrolyte solution: the average distance between ions $n^{-1/3}$, the dimension of the physically infinitesimal volume l, the Debye radius r_{D}, and the system size L. The Debye theory of electroconductivity is applicable at low concentrations of ions. It is applicable, when the inequalities

$$n^{-1/3} \ll l \ll r_{\mathrm{D}} \ll L \tag{24}$$

are satisfied.

The value for the physically infinitesimal volume obtained from our experiment turned out to be 10^{-6} m by the order of magnitude. In addition, the average distance between ions $n^{-1/3}$ and the Debye radius r_{D} are of the same order of magnitude in the studied concentration range, because $n^{-1/3} = (0.2 \div 0.5)$ nm here. In other words, in the concentration interval studied in this work, the inequalities

$$n^{-1/3}, \quad r_{\mathrm{D}} \ll l \ll L \tag{25}$$

hold true. According to the spatial dimension hierarchy (25), there must exist a temporal hierarchy

$$\tau_{\mathrm{D}} \ll \tau_l \ll \tau_L, \tag{26}$$

where τ_{D} is the duration of the Debye atmosphere formation, τ_l the local equilibration time, and τ_L the equilibration time for the whole system. In fact, in our case where $n^{-1/3} \approx r_{\mathrm{D}}$, the formation of a Debye atmosphere corresponds to the emergence of a short-range ordering in the system of ions. In addition, the equilibration in the whole system is a complex of relaxation processes with relaxation times that are determined by formula (6).

Therefore, when introducing the notion of relaxation time τ_L, we conditionally understand it as a spectrum of relaxation times, the minimal of which is equal to τ_Q; i.e. expression (26) should be rewritten in the form

$$\tau_{\mathrm{D}} \ll \tau_l \ll \tau_Q. \tag{27}$$

Hierarchy (27) determines the frequency range, in which the frequency independence of electroconductivity is observed. In particular, these are frequencies that satisfy the inequalities

$$\tau_l \ll \omega^{-1} \ll \tau_Q. \tag{28}$$

Hence, the appearance of the frequency-independent electrical conductivity in electrolyte solutions is connected with the existence of a relaxation process, which is characterized by the relaxation time τ_l and gives rise to the emergence of a local equilibrium state. This type of conductivity is realized, when the period of an external field becomes much longer than the local equilibration time and, at the same time, remains much shorter than the time of diffusion processes τ_Q.

5. Conclusions

There is a hierarchy of relaxation times in electrolyte solutions. It is a sequence of growing time values, which correspond to the following processes: the formation of a Debye atmosphere, the local equilibration, and the relaxation of the set of diffusion modes. In the case where the period of an external electric field is longer than the time of local equilibration, but shorter than the diffusion-mode relaxation times, the electric conductivity of an electrolyte solution is independent of the external field frequency. In this case, there is no diffusion flow of ions, and only the convective flow is invoked. This circumstance allows the diffusion coefficients of ions to be calculated, knowing the experimentally determined values of conductivity in the concerned frequency interval. The value of the lower limit of the frequency interval, where the conductivity does not depend on the frequency, was used to calculate the dimension of the physically infinitesimal volume, in which the local equilibrium is established.

1. B.A. Lopatin, *Theoretical Bases of Electrochemical Methods of Analysis* (Vysshaya Shkola, Moscow, 1975) (in Russian).
2. L.D. Landau and E.M. Lifshitz, *Fluid Mechanics* (Pergamon Press, Oxford, 1993).
3. Yu.L. Klimontovich, *Statistical Physics* (Harwood, New York, 1986).
4. K.P. Gurov, *Phenomenological Thermodynamics of Irreversible Processes* (Nauka, Moscow, 1978) (in Russian).
5. E.M. Lifshitz and L.P. Pitaevskii, *Physical Kinetics* (Pergamon Press, New York, 1981).
6. P. Debye and E. Hückel, Phys. Z. **24**, 185 (1923).
7. P. Debye and H. Falkenhagen, Phys. Z. **29**, 401 (1928).
8. D.N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Consultants Bureau, New York–London, 1974).
9. A.F. Skryshevskii, *Diffraction of X-Rays, Electrons, and Neutrons in Gases and the Structure of Molecules* (Kyiv Univ., Kyiv, 1961) (in Russian).
10. G. Leibfried, *Gittertheorie der Mechanischen und Thermischen Eigenschaften der Kristalle* (Springer, Berlin, 1955).

Received 28.01.11.
Translated from Ukrainian by O.I. Voitenko

МЕХАНІЗМ ЧАСТОТНО-НЕЗАЛЕЖНОЇ ЕЛЕКТРОПРОВІДНОСТІ ВОДНИХ РОЗЧИНІВ ЕЛЕКТРОЛІТІВ

Л.А. Булавін, О.М. Алексеев, Ю.Ф. Забашта, С.Ю. Ткачов

Резюме

Показано, що поведінка залежності опору комірки з водним розчином NaCl від частоти змінного струму в вибраному наближенні не може бути пояснена тільки поляризаційними явищами в граничних областях електрод–електроліт. Запропоновано фізичний механізм, що пояснює монотонне зростання питомої електропровідності розчину при зростанні частоти, коли частота менша за 10^4 Гц, і сталість питомої електропровідності розчину при частотах в інтервалі (10^4–10^5) Гц. Розраховано температурні залежності коефіцієнта дифузії іонів Na^+ і Cl^- у водних розчинах NaCl та розміру фізичного нескінченно малого об'єму (області встановлення локальної рівноваги) для такого електроліту. Проведено аналіз просторової та часової ієрархії у водному розчині NaCl та показано зв'язок співвідношення періоду змінного струму та певних характерних часів з частотною залежністю питомої електропровідності цього електроліту.