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Development of a model equation for estimating particle oscillations in electrolyte solutions in the ion plasma approximation

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Abstract. *The aim of the work was to develop a unified model equation that makes it possible to estimate the natural vibrations of ions and molecules in electrolyte solutions in the ionic plasma approximation.*

Previously, we have confirmed the analogy of the properties of electrolyte solutions with those of low-temperature gas, solid-state plasmas and semiconductor plasmas, on the basis of which we have shown the possibility of applying the concept of a plasma-like state of ions and molecules (quasi-neutrality condition, density, plasma frequency, Debye screening radius, equilibrium process "Dissociation-association" of electrolytes, the degree of dissociation, etc.), the electrostatic theory of the system of charges (ions) in the transfer processes in solutions of strong and weak electrolytes.

Based on the assumption about the process of "dissociation-reverse recombination into neutral molecules (or the association of hydrated ions)", which takes place in the mode of harmonic oscillations with a certain frequency and mean free path of ions and molecules - the screening parameter (Debye radius), a rather strict a unified and end-to-end model equation for estimating the frequency of natural vibrations of particles in electrolyte solutions using the example of lithium chloride from concentrations of 0.0005 M to 12 M.

Keywords*: plasma-like concept, parameters of electrolyte solutions, model for evaluating the vibration frequencies of particles in solutions.*

Electrolyte solutions can be considered as a system of charges (cations and anions). For electrolyte solutions, the use of the plasma-like state of ions in solutions is shown to be promising. This was achieved through the use of the formal apparatus of plasma in a stricter sense than in the electrostatic theory of Debye-Hückel [1], where the concept of plasma was introduced into the theory, but was not disclosed in essence.

Introduction

Some aspects of the plasma-like concept

The fundamental possibility of using the plasma theory of the state of electrolyte solutions was noted in [2-3], which show the characteristic signs of the plasma state of matter: the condition of quasi-neutrality, density, plasma frequency, Debye screening radius, etc.

In [4], the electrodynamics of conducting media with significant spatial dispersion is consistently presented. Such media, first of all, include gas and solid-state plasma (metals and semiconductors) in constant or alternating electromagnetic fields.

Let us compare some characteristics of low-temperature gas plasma, solid state plasma, semiconductors and electrolyte solutions.

Low temperature gas plasma:T = $10^4…10^5$ K, degree of ionization $\alpha = 0…\infty$, vibration frequency $10^8…10^{16}$ c^{-1}, density $\rho = 10^8…10^{20}$ cm^{-3}, shielding parameter r_D = $10^{-4}…10^{-3}$ cm;

Solid state plasma: $T < 10^4$ K, degree of ionization α = ~1,0, vibration frequency $10^{13}…10^{15}$ c^{-1}, density $\rho = 10^{21}…10^{22}$ cm^{-3}, shielding parameter $r_D = 10^{-7}…10^{-5}$ cm,

Semiconductors: T = <10^2 K, degree of ionization α «1,0, density $\rho = 10^{16}…10^{18}$ cm^{-3}. vibration frequency $10^{13}…10^{15}$ c^{-1},

Electrolyte solutions: T = 273…350 K, degree of ionization α = 0…1,0, vibration frequency $10^{10}…10^{13}$ c^{-1}, density $\rho = 10^{16}…10^{22}$ cm^{-3}, shielding parameter $r_D = 10^{-9}…10^{-7}$ cm.

It can be seen that the main parameters of electrolyte solutions are comparable to those of low-temperature plasma, occupying an intermediate position between gas, solid-state and semiconductor plasma.

Within the framework of this concept, the process of dissociation and reverse recombination in solutions is presented in the form of equilibrium

$$\mathrm{KtAn \cdot ns} \leftrightarrow \mathrm{Kt_s^+} + \mathrm{An_s^-} \qquad (1)$$

where KtAn, $\mathrm{Kt_s^+}$, $\mathrm{An_s^-}$ - solvated molecule of electrolyte, cation and anion.

During dissociation (1), ions run a certain distance with a velocity v_1 and return with a velocity v_2, recombining into neutral molecules.

At a fixed concentration, the mean free path of ions is finite, and their motion is finite [5]. According to the general provisions of classical mechanics, any one-dimensional finite motion is oscillatory, with a certain frequency, having limit cycles characterized by the Debye screening parameter (Debye radius). In this case, oscillatory motion is assumed in the harmonic oscillator mode [5].

Let us represent the vibration frequency, taking into account the equation of continuity, the law of conservation of charge, mass and rates of the process "dissociation - recombination of ions into neutral molecules" (eq. 1), by the method of kinetics.

$$\partial\rho/\partial t + div\, \rho V = 0$$

Here $\rho = CN_A/1000$ – charge density.

Let's reveal the divergence

$$\partial\rho/\partial t + V\, grad\, \rho + \rho\, div\, V = 0$$

Note that ($\partial\rho/\partial t + V\, grad\, \rho$) = $d\rho/dt$ – full derivative, then

$$d\rho/dt + \rho\, div\, V = 0.$$

Introducing $\rho = CN_A/1000,$ considering $C_0 – C_M = C$ (concentration of dissociated ions = total - the initial concentration of the electrolyte minus the concentration of undissociated molecules), for weak electrolytes the inequality takes place $C_0 >> C$.

The rates of forward and reverse reactions of equilibrium can be represented in the form of expressions:

$$V_1 = - d(C_0 – C)/dt = - k_1 (C_0 – C), \qquad (2)$$

$$V_2 = dC/dt = k_2 C^2$$

Based on eq. (2) compose the system

$$dC/dt + C\, div\, V_2 = 0 \qquad (3)$$

$$d(C_0 – C)/dt + (C_0 – C)\cdot div\, V_1 = 0.$$

Comparing system (2) with system (3), we arrive at the form

$$- k_1 (C_0 – C) + (C_0 – C)\, div\, V_1 = 0$$

$$k_2 C^2 + C\, div\, V_2 = 0,\ k_2 = - (1/C_0)\, div\, V_2$$

$$k_1 = div\, V_1 \qquad (4)$$

$$k_2 = - (1/C_0)\, div\, V_2$$

American scientist A.J. Lotka (A.J. Lotka) in 1925, and in 1926 independently of him - the Italian scientist V. Volterra (V. Volterra) derived the so-called equation of persistent population fluctuations "predator - prey", which is used in many areas of science:

$$\omega = (k_1k_2C_0)^{0,5}, \qquad (5)$$

including the rates (or rather, the rate constants of growth and decrease in the prey population, decrease and increase in the population of predators). With regard to the topic under discussion, eq. (5) can be transformed into an expression:

$$\omega = (k_1k_2C_0)^{0,5} = (- div\, V_1 \cdot(1/C_0)\, div\, V_2\cdot C_0)^{0,5}$$

When equilibrium (1) occurs $V_1 = V_2 = V$, which gives the modified equation

$$\omega = [-(div\, V)^2]^{0,5} = div\, V$$

Since ω – the frequency of harmonic oscillations, the *div* operator is represented as

$$div \equiv i \cdot k = i \cdot (1/r_D),$$

where r_D – Debye radius (penetration depth, ion mean free path from equilibrium coordinates, screening parameter, distance at which the oscillation disturbance is screened by a continuous medium).

Introducing this into the formula for the frequency, we get

$$\omega = V/r_D \qquad (6)$$

It is shown that the vibration frequency of the system of charges (cation-anion) was obtained by the kinetic method.

A system of stationary point charges located at finite distances from each other cannot be stable [5]. And this predetermines the reverse movement of counterions with their subsequent recombination into KtAn (or into a molecular associate).

Thus, the proposed concept confirms the oscillatory nature of the "dissociation-association" process.

Experimental part

No unified end-to-end, model, without adjustable parameters, methods for assessing the vibration frequencies of particles in electrolyte solutions have been proposed. In this work, the complete concept of ω estimation in a wide range of electrolyte concentrations is considered and applied.

Since equilibrium (1) takes place in an oscillatory mode, it is necessary to take into account the frequency and spatial dispersion. This is determined by the Vlasov equation [6]

$$\omega = \omega_L(1+\frac{3}{2}\, k^2 r_D{}^2)^{0,5}$$

$$\omega_L = (4\pi Ze Z_d e n_0/M)^{0,5}$$

where: ω_L – Langmuir plasma frequency; Ze, $Z_d e$- the charges of the ion and the dipole of the solvent; n_0 – the density of the dipole charges of the solvent molecules, $n_0 = n_s / \frac{4}{3}\pi r_s{}^3$; M – molar mass of solvent; $Z_d e = p/l$ (l – solvent dipole distance, usually taken as the reduced radius of the solvated ion $r_s = r_{s\,kt} * r_{s\,An}/(r_{s\,kt} + r_{s\,An})$, where $r_{s\,kt}$ and $r_{s\,An}$ – radii of hydrated cation and anion.

The Vlasov equation is the most general dispersion equation for a system of charges (electrolyte solutions).

At $kr_D = 1$ ($0 \le kr_D \le 1$) spatial dispersion is maximum, in this case

$$\omega = \frac{5}{2}(4\pi z_s 3\,/4\, l\pi r_s{}^3 M)^{0,5},$$

Substituting the values of all constants: $e = 4,8 \cdot 10^{-10}$ *e.s.e.*, Avogadro's number $N_A = 6,023 \cdot 10^{23}$, $r_s = r \cdot 10^{-8} cm$, μ – reduced mass of unsolvated electrolyte ions ($\mu \cdot 1,67 \cdot 10^{-24}$), we write it down in CGS units and obtain an expression for the desired frequencies:

$$\omega = (3{,}23\cdot 10^{13}/(z_{kt}z_{An}e^{2}Cf\alpha/\mu\cdot 1000)^{\,0,5}) \qquad (7)$$

$$\alpha = \lambda/\lambda_0,$$

α – degree of dissociation; λ_0 – limiting electrical conductivity of lithium chloride, (λ_0 = 115 $Cm\cdot cm^2/mol$); f – distribution coefficient (activity), estimated according to Davis. The values μ, r_s , $r_{s\,kt}$, $rs_{\,An}$ are borrowed from works [7, 8, 9].

As an example, in tab. 1 shows the initial parameters for the estimates (eq. 7) of the frequencies of harmonic vibrations of particles(ω, c^{-1}) in a solution of lithium chloride.

Table 1

Initial parameters for calculations and frequencies of harmonic vibrations of particles in a lithium chloride solution, estimated by equation (7)

$Cm_{\,lit}$	λ_{lit} [10]	lgf	f	α	$\omega_{\,theor(eq.\,7)}$	ω *by eq.(8)*
0.0005	97.20	-0.0111	0.9746	0.8452	2.721E+11	2.003E+12
0.0010	96.50	-0.0155	0.9647	0.8391	3.815E+11	2.006E+12
0.0050	93.90	-0.0333	0.9261	0.8165	8.247E+11	2.029E+12
0.0100	92.10	-0.0455	0.9004	0.8008	1.138E+12	2.059E+12
0.0500	86.10	-0.0885	0.8155	0.7486	2.343E+12	2.298E+12
0.1000	82.40	-0.1130	0.7708	0.7165	3.152E+12	2.595E+12
0.2366	77.10	-0.1438	0.7179	0.6704	4.526E+12	3.391E+12
0.5000	71.80	-0.1620	0.6885	0.6243	6.217E+12	4.877E+12
0.9630	63.50	-0.1572	0.6961	0.5521	8.160E+12	7.332E+12
1.0000	61.50	-0.1560	0.6982	0.5347	8.195E+12	7.520E+12
1.2101	57.28	-0.1471	0.7125	0.4981	8.790E+12	8.564E+12
1.4604	55.31	-0.1341	0.7343	0.4809	9.632E+12	9.758E+12
1.9687	51.42	-0.1020	0.7905	0.4471	1.118E+13	1.202E+13
2.4879	47.61	-0.0645	0.8618	0.4140	1.263E+13	1.414E+13
3.0183	43.88	-0.0231	0.9481	0.3816	1.401E+13	1.610E+13
3.5600	40.26	0.0213	1.0504	0.3501	1.534E+13	1.792E+13
4.1131	36.75	0.0683	1.1705	0.3195	1.663E+13	1.961E+13
4.6777	33.35	0.1176	1.3111	0.2900	1.788E+13	2.117E+13
5.2544	30.08	0.1689	1.4755	0.2616	1.910E+13	2.262E+13
6.4461	23.98	0.2772	1.8936	0.2085	2.139E+13	2.525E+13
7.6914	18.53	0.3928	2.4707	0.1611	2.347E+13	2.766E+13
9.0081	13.80	0.5167	3.2867	0.1200	2.528E+13	3.009E+13
10.3826	9.99	0.6475	4.4414	0.0869	2.685E+13	3.278E+13
11.8190	7.25	0.7852	6.0992	0.0630	2.859E+13	3.608E+13

12.2615	6.66	0.8278	6.7280	0.0579	2.932E+13	3.726E+13

Discussion of the results

From the data in Table 1 it can be seen that the frequencies calculated according to the theory (equation 7) are comparable with the parameters of electrolyte solutions $10^{10}\ldots10^{13}$ c^{-1}, given at the beginning of the article when comparing the parameters of plasma and electrolyte solutions. In fig. 1 shows the concentration dependence of the oscillation frequency of an aqueous solution of lithium chloride in a wide range from 0.0005 to 12.000 *M*. It can be seen that the dependence has a polynomial form and corresponds to the equation:

$$\omega = 2\cdot10^{10}\cdot C^3 - 5\cdot10^{11}\cdot C^2 + 6\cdot10^{12}\cdot C + 2\cdot10^{12} \quad (R^2 = 0{,}990) \qquad (8)$$

with a sufficiently high coefficient of multiple regression (0.990), indicating the reliability and high reliability of equation (8).

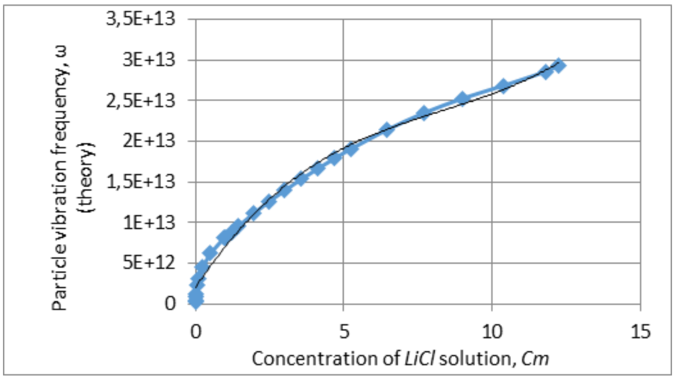

Fig. 1. Dependence of the theoretical vibration frequencies of lithium chloride particles on the concentration of an aqueous solution of *LiCl*.

Note also that equation (7) assumes an almost directly proportional dependence of frequency on concentration, and the graphical dependence (fig. 1) has a curvilinear ascending form. This can be explained by the unequal contribution of the product of $\alpha\cdot f$ by the value of $C\cdot\alpha\cdot f$. This results in a polynomial curve.

In fig. 2 shows the polynomial function of the dependence of the estimated frequency values on the concentration according to equation (8). This is, in essence, an independent way to estimate the vibration frequencies of particles in an aqueous solution of lithium chloride, since the values for eq. (7) and (8), when compared, correlate in a straight line with the slope close to 1.

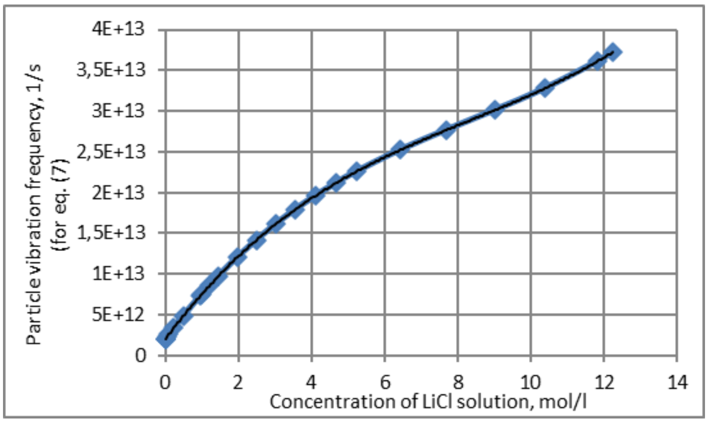

Fig. 2. Dependence calculated by eq. (8) the vibration frequencies of lithium chloride particles on the concentration of an aqueous solution of *LiCl*

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