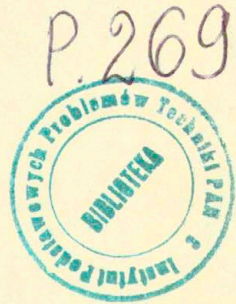


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SPHEROIDAL PARTICLES
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DOUBLE LAYER POLARIZATION OF NONCONDUCTING SPHEROIDAL
PARTICLES AND ITS APPLICATION TO KERR EFFECT
I. LONGITUDINAL POLARIZATION IN A CONSTANT ELECTRIC FIELD.

Abstract

The problem of the double layer polarization of elongated spheroidal charged particles in an electrolyte solution is discussed. The nonconducting elongated ellipsoidal particle, embedded in the electrolyte, is assumed to acquire a surface charge, compensated by the surrounding counterion atmosphere, forming the double layer. The double layer thickness is assumed to be small, $\kappa^{-1}a \gg 1$ where κ^{-1} is the reciprocal Debye radius and a is the particle radius. The electric potential ψ is found inside the particle for the case of the constant external electric field $E \parallel a$, applied parallel to the symmetry axis of the particle. The Laplace equations are solved for the distribution of the potential ψ and the electrolyte concentration C with the boundary condi-

tions describing the diffuse double layer in the model of Dukhin and Shilov / *Kolloidn. Zh.*, 31, no. 5, 706 (1969) and 36, no. 6, 1133 (1974) /. The effective electric field $E_{\text{eff}}(a)$ is then found inside the ellipsoidal particle. The polarization energy, associated with the induced polarization of the ellipsoid and the surrounding medium is calculated, then the steady-state specific Kerr constant is found, following the O'Konski and Krause / *J. Phys. Chem.* 74, no. 17, 3243, (1970) / approach.

1. Introduction

The problem of the polarization of the double layer of particles, embedded in the solution and its influence on the dielectric properties of disperse systems and polyelectrolytes has been widely studied in recent years. The physical and chemical properties of particles in the solution, which are of great interest / for instance DNA, TMV, solutions of biological molecules / can be investigated by means of electrooptic phenomena. In the theory describing the electrooptic properties of the particles in the electrolyte solution the effect of the double layer polarization plays an important role.

In this work we consider the longitudinal / part I / and lateral / part II / polarizability of the nonconducting charged spheroidal particles, embedded in the isotropic dielectric and conducting solvent, placed in a constant electric field E . The double layer polarization model we use is

based on the approach proposed by Dukhin and Shilov [3,4,12]. The results are applied to the theory of the Kerr effect, as developed in works of O'Konski and Krause [9].

When the system of nonspherical macromolecules in the solution is placed in the external constant field E , the molecules tend to orient in the field. The rate of the orientation can be determined by the birefringence effect. For the conducting solutions one has to consider the steady - state effects [10]. The specific Kerr constant K_{sp} for the steady - state birefringence at low electric fields is

$$1.1 \quad K_{sp} = \frac{\Delta n}{n E^2 c_v}$$

where Δn is the difference between the refractive indices parallel and perpendicular to the electric field direction, E - the field, c_v - the volume fraction of the molecule.

Let us consider the system of rigid, nonspherical macromolecules represented in the shape of the prolate ellipsoid of revolution, with the semimajor axis a and the semiminor axes $b=c$, embedded in the dielectric solution. The total energy change caused by inserting a dielectric molecule in the dielectric medium is [9]

$$1.2 \quad U = U_1 + U_2$$

Here U_1 is the dipole interaction energy given as

$$1.3 \quad U_1 = -\mu_a E_a - \mu_b E_b - \mu_c E_c$$

μ_a, μ_b, μ_c are the components of the permanent dipole moment along the molecule axes. E_a, E_b and E_c are the components of the internal effective field - the modified electric field inside the molecule:

$$E_{\text{eff}}(a) \equiv E_a = B_a E \cos \Theta$$

$$E_{\text{eff}}(b) \equiv E_b = -B_b E \sin \Theta \cos \Psi$$

$$1.4 \quad E_{\text{eff}}(c) \equiv E_c = B_c E \sin \Theta \sin \Psi$$

Θ, Ψ are the Eulerian angles.

The polarizability coefficients B_a, B_b , and B_c , introduced in (1,4) determine the electric field inside the molecule. In the case of both dielectric nonconducting media / the molecule and the solvent / these coefficients are [10]

$$B_i(\epsilon) = [1 + \{\epsilon_i / \epsilon_1 - 1\}]^{-1} \quad i = a, b$$

$$1.5 \quad A_a = \frac{ab^2}{2} \int_0^\infty \frac{d\lambda}{(a^2 + \lambda)^{3/2} (b^2 + \lambda)}$$

$$A_c = \frac{a^2c}{2} \int_0^\infty \frac{d\lambda}{(b^2 + \lambda)^2 (a^2 + \lambda)^{3/2}}$$

where ϵ_1 is the dielectric constant of the solvent,

ϵ_i is the principal value of the dielectric constant of the ellipsoid along its i axis.

The energy associated with the induced polarization, denoted as U_2 in (1.2), for the case of nonconducting particles placed in dielectric medium is given [3,9,11]

$$1.6 \quad U_2 = \frac{1}{8\pi} \int [(\epsilon_1 - \epsilon_a)E_a E + (\epsilon_1 - \epsilon_b)E_b E + (\epsilon_1 - \epsilon_c)E_c E] dV$$

where the integration is over the molecule volume v .

E_a, E_b and E_c are the internal effective field components, directed along the axes a, b and c , defined in (1.4). E is the external applied field.

In the case when both media are nonconducting, the polarizability coefficients B_a, B_b and B_c depend only on the geometry of the system and the dielectric constants ϵ_1, ϵ_2 . Having the polarization energy U (1.2), one can calculate the specific Kerr constant K_{sp}

$$1.7 \quad K_{sp} = \frac{2\pi}{15n^2} (g_a - g_b)(P_a - P_b + Q_a - Q_b)$$

where $(g_a - g_b)$ is an optical anisotropy factor, P_a, P_b are the permanent dipole terms and Q_a, Q_b - the induced dipole terms, found as [6, 7, 9 - 12]

$$1.8 \quad P_i = B_i^2(\epsilon) \mu_i^2 / k_B^2 T^2$$

$$1.9 \quad Q_a - Q_b = \frac{\nu \epsilon_0}{k_B T} \{ B_a(\epsilon)(\epsilon_a - \epsilon_1) - B_b(\epsilon)(\epsilon_b - \epsilon_1) \}$$

ϵ_0 - the permittivity of the vacuum.

The model of the nonconducting uncharged molecules immersed in the nonconducting medium, being rather far from the reality, did not give the proper values of the Kerr constant. O'Konski and Krause [9] proposed the approach, in which the conducting molecules were embedded in the conducting medium. Most molecules do not conduct, but they showed, that the

counterions, condensed on the surface of the molecule can contribute to the surface conductivity, which can be interpreted as the volume conductivity. Assuming both media having the conductivity \mathcal{K}_1 and \mathcal{K}_2 they calculated the total energy U (1.2) and then found the dipole moments $P_1(\mathcal{K})$ and $Q_1(\mathcal{K})$ and the corresponding formula for the Kerr constant. In their model the existence of the double layer, surrounding the charged molecules in the solution is manifested only by the counterions, condensed on the molecule surface. The diffuse part of the double layer and its polarization is not included. That picture is close to the Manning theory of counterion condensation (CC) [13, 19]. In the present work we consider the nonconducting, charged molecules, which embedded in the dielectric conducting solvent acquire the double layer. When the external field is imposed, the polarization of the double layer (DL) occur. The processes characterizing the polarized DL are described within the Poisson - Boltzmann theory (PB) [20, 21]. Our aim is to calculate on the basis of (PB) theory the internal effective field E_{eff} inside the molecule and the corresponding polarizability coefficients B_1 , which now would depend not on the dielectric constants ϵ_1, ϵ_2 only, but also on the parameters, characterizing the polarized DL and the electrolyte conductivity properties. Then the induced dipole $Q_a - Q_b$ can be recalculated and the formula for the specific Kerr constant K_{sp} can be found.

The total induced dipole moment $Q_{\text{ab}} = Q_a - Q_b$ consists of two terms : the first one depending on the polarizability coefficients $B_a = B^{\parallel}$ corresponding to the

external field component parallel to the symmetry axis of the molecule and the second, depending on the polarizability coefficient $B_b = B^\perp$, corresponding to the external field component perpendicular to the symmetry axis / longitudinal and lateral polarizability of the particle/. In this paper /part I of our work/ we calculate the electric potential Ψ inside the particle, E_{eff} and the longitudinal polarizability coefficient $B_a = B^{\parallel}$ for the case of the constant external field E applied parallel to the symmetry axis of the spheroidal molecule.

2. Polarization of the double layer. The Dukhin - Shilov model.

Let us consider a system of rigid, dielectric, nonconducting molecules of the elongated spheroidal shape, embedded in the dielectric conducting medium. The double layer is formed then around each charged molecule. The precise description of the DL structure and the phenomena connected with its appearance are given in many excellent reviews [3-5]. Here we will limit ourselves to a simplified model of the quasi-equilibrium DL, as outlined in works of Dukhin, Shilov et al [4, 13 - 15]. We assume, that the thickness of the DL is small, $\kappa^{-1}a \gg 1$ where κ^{-1} is the reciprocal Debye radius and a is the particle radius. That enables us to use the results, obtained for the planar DL, to the DL surrounding a particle of arbitrary shape. We consider the outer, diffuse part of the DL only. That is possible, when the DL is formed by the

dissociation of ionogenic surface groups of the particle and when the counterions are distributed around the particle only diffusely - there is no inner, compact part of the DL. That assumption is valid for sufficiently low electrolyte concentration and when the counterions do not form the ion pairs with the fixed ions on the particle surface.

The processes occurring in the DL and outside its limits, in the neighborhood of the particle are described by the distribution of the electric potential Ψ and the electrolyte concentration c . When the polarization of the DL is not considered, these distributions can be expressed as:

$$2.1 \quad \Psi = \Psi_0 + \Psi_1 \quad c = c_0 + c_1 \quad \left. \nabla \Psi_0 \right|_{r \rightarrow \infty} = E$$

here Ψ_0 and c_0 are the equilibrium values of potential and ion concentrations for the uncharged particle in its vicinity, Ψ_1 is the potential distribution in the diffuse part of the unpolarized DL, satisfying the Poisson - Boltzmann equation, c_1 is the excess concentration of ions in the DL, describing the deviation of the anions and cations concentration within the DL from their bulk concentrations.

The applied external field changes the structure of the system - the polarization of the DL occurs. Then the distribution of the potential and ion concentrations will differ from Ψ_0 and c_0 outside the DL, as the values of Ψ_1 and c_1 will change inside the DL. However when the applied electric field is sufficiently weak, we can use the quasi-equilibrium

model. Within this approximation we still assume, that the polarized DL can be described by the equilibrium distributions φ_0 and c_0 and the small additional terms φ_1' and c_1' , now characterizing the polarized DL :

$$2.2 \quad \varphi = \varphi_0 + \varphi_1' \quad c = c_0 + c_1'$$

the polarized DL is fully described by the set of equations of continuity of the cations and anions currents, Poisson equation and Navier - Stokes equation for viscous incompressible fluids / Dukhin - Shilov [4,5,13] /

$$2.3a-2.3d \quad \begin{aligned} \operatorname{div} j^{\pm} &= 0 \\ \Delta \varphi &= -\frac{4\pi F}{\varepsilon} (z^+ c^+ - z^- c^-) \\ \eta \Delta \vec{v} &= \operatorname{grad} P + \rho \operatorname{grad} \varphi \\ \operatorname{div} \vec{v} &= 0 \end{aligned}$$

where j^{\pm} - ionic bulk current, c^+, c^- - distribution of partial concentrations, z^+, z^- - valencies, \vec{v} - velocity field, φ - electric potential distribution, ε - dielectric constant, η - viscosity, P - pressure field, ρ - density of charges, F - Faraday constant. j^{\pm} - the ion flux density, contains three terms, each describing the possible mechanisms of ionic transport in the electrolyte: the migration in the electric field, the diffusion and the convective drag due to the motion of the medium:

$$2.4 \quad j^{\pm} = -D^{\pm} \text{grad } c^{\pm} \mp \frac{F}{RT} D^{\pm} z^{\pm} c^{\pm} \text{grad } \Psi + c^{\pm} \vec{v}$$

D^{\pm} - diffusion coefficients

The DL is in the quasi-equilibrium state. That enables to express the potential Ψ and the ion concentrations c as

$$2.5 \quad \Psi = \Psi_0 + \Psi_1' \quad c^{\pm} = c_0^{\pm} + (c_1^{\pm})'$$

we will omit primes from now on, $c_1' = c_1$, $\Psi_1' = \Psi_1$

The condition of the local neutrality

$$2.6 \quad z^+ c^+ - z^- c^- = 0 \quad c^+ / z^- = c^- / z^+ = c$$

allows to describe the ion concentrations by the one function:

$$2.7 \quad c = \frac{c^{\pm}}{z^{\mp}}$$

For the weak polarization we have the condition [13]:

$$2.8 \quad \frac{c_1 - c_0}{c_0} \ll 1$$

and the Peclet number Pe is

$$2.9 \quad Pe = \frac{av}{D} \ll 1$$

v - electroforetic rate of the particle.

With these assumptions the Navier - Stokes eqs. (2.3 c) and the convective component in the fluxes drop out and we are left

with the Laplace equations for c_1 and Ψ_1

$$2.10 \quad \Delta \Psi_1 = 0 \quad \Delta c_1 = 0$$

the terms c_1 and Ψ_1 vanish at the infinite distance from the particle

$$2.11 \quad \Psi_1 \Big|_{r \rightarrow \infty} = 0 \quad c_1 \Big|_{r \rightarrow \infty} = 0$$

The boundary conditions at the outer boundary of the DL express the continuity of the flows of cations and anions - the tangential ionic currents within the DL are fed by the normal components of the ionic currents from the bulk

$$2.12 \quad j_n^\pm = -D^\pm \text{grad } C^\pm \mp \frac{F}{RT} D^\pm z^\pm C^\pm \text{grad } \Psi = -\text{div } I_s^\pm$$

j_n^\pm is the normal flow from the bulk to the surface of the particle, and I_s^\pm is the excess tangential flow of the ions of the diffuse part of the DL, consisting of the diffusion term $I_s^\pm(D)$ and the electromigration term $I_s^\pm(E)$ - the convection term dropped out

$$2.13 \quad I_s^\pm \Big|_s = -D^\pm \frac{\Gamma_o^\pm}{C_o} \nabla_{\odot} C^\pm \mp \frac{F}{RT} D^\pm \Gamma_o^\pm \nabla_{\odot} \Psi$$

∇_{\odot} - tangential component of the gradient

$\Gamma_o^\pm = (2 C_o / z^\pm) [\exp(\pm F \Psi_o / 2 RT)]$ is the equilibrium adsorption of cations and anions in the diffuse part of the DL.

3. Longitudinal polarization of the particles.

Consider the system of long, ellipsoidal molecules, embedded in the solution. Let the external, constant electric field E applied to the system be parallel to the symmetry axis of the molecule / semimajor axis a / $E \parallel z \parallel a$, z - cartesian coordinate.

With the DL polarization established, we can represent the potential distribution outside the particle ψ^e and c as

$$3.1 \quad \psi^e = \psi_0^e + \psi_1^e \quad c = c_0 + c_1$$

where ψ_0^e is the potential distribution in the neighborhood of the uncharged particle, obeying the Laplace eq. and the boundary conditions

$$3.2 \quad \Delta \psi_0^e = 0 \quad \psi_0^e|_{\infty} = -E \cdot z \quad \nabla_n \psi_0^e|_s = 0$$

The set of equations, describing the potential distribution is based on the quasi-equilibrium DL model of Dukhin and Shilov, described in the previous section, eqs (2.10 - 2.13)

$$\Delta \psi_1^e = 0 \quad \Delta c_1 = 0 \quad \psi_0^e|_{\infty} = \psi_1^e|_{\infty} = -Ez \quad (a)$$

$$3.3 \quad c_1|_{\infty} = \psi_1^e|_{\infty} = 0 \quad (b)$$

$$\left(\pm \frac{F}{RT} c_0 \nabla_n \psi^e + \nabla_n c_1 \right)_s = \text{div}_s \left(\mp \frac{F}{RT} \Gamma_0^{\pm} \nabla_{\Theta} \psi^e + \frac{\Gamma_0^{\pm}}{c_0} \nabla_{\Theta} c_1 \right) \quad (c)$$

For the elongated spheroidal molecules in the shape of the ellipsoid of the revolution, the use of the prolate spheroidal coordinates is convenient [14, 15, 17]

$$\begin{aligned}
 x &= h \operatorname{sh} \omega \sin \Theta \cos \Psi & 0 \leq \Psi \leq 2\pi \\
 y &= h \operatorname{sh} \omega \sin \Theta \sin \Psi & 0 \leq \Theta \leq \pi \\
 z &= h \operatorname{ch} \omega \cos \Theta & 0 \leq \omega < \infty
 \end{aligned}$$

3.4

semiaxes a and b are

$$\begin{aligned}
 a &= h \operatorname{ch} \omega_0 \\
 b &= h \operatorname{sh} \omega_0 \\
 h &= \sqrt{a^2 - b^2}
 \end{aligned}$$

3.5

$\omega = \omega_0$ is the surface equation of an elongated ellipsoid of the revolution with foci lying on the z axis at a distance $2h$. The axial ratio is $e = \operatorname{ch} \omega_0 / \operatorname{sh} \omega_0$ and $\omega_0 \ll 1$ corresponds to a very elongated ellipsoid. Within these coordinate system φ_0^e is given [2]

$$\varphi_0^e = -h E C(\omega, \omega_0) \cos \Theta$$

3.6

$$C(\omega, \omega_0) = \operatorname{ch} \omega + 2 \left[\ln \frac{\operatorname{ch} \omega_0 + 1}{\operatorname{ch} \omega_0 - 1} - \frac{2 \operatorname{ch} \omega_0}{\operatorname{ch}^2 \omega_0 - 1} \right]^{-1} \left[1 - \frac{1}{2} \operatorname{ch} \omega \ln \frac{\operatorname{ch} \omega + 1}{\operatorname{ch} \omega - 1} \right]$$

For sufficiently charged particles / negative ones /, where $\Gamma_0^+ \gg \Gamma_0^-$, the boundary condition (3.3 c), expressed in the ellipsoidal coordinates takes the form:

$$3.7 \quad \frac{\partial \varphi_1^e}{\partial \omega} = -\frac{\Gamma_0^+}{c_0} \frac{1}{h\sqrt{ch^2\omega_0 - \cos^2\Theta}} \frac{1}{\sin\Theta} \frac{\partial}{\partial \Theta} \left[\sin\Theta \left(\frac{\partial \varphi_1^e}{\partial \Theta} + \frac{1}{2} \frac{\partial \varphi_0^e}{\partial \Theta} \right) \right]$$

$$\varphi_1^e = \frac{c_1}{c_0} \frac{RT}{F}$$

In that equation the basic concepts of the quasi-equilibrium DL are contained.

Eremova and Shilov [16]/ see also Dukhin [4]/ solved this equation for φ_1^e using the Legendre series expansion. They found

$$3.8 \quad \varphi_1^e = a_1 Q_1(ch\omega) P_1(\cos\Theta)$$

$$a_1 = \frac{1}{2} h E C(\omega_0, \omega_0) \left[Q_1(ch\omega_0) + \frac{1}{b_{11}} \left(\frac{\Gamma_0^+}{c_0 h} \right)^{-1} \frac{\partial Q_1(\omega)}{\partial \omega} \Big|_{\omega_0} \right]^{-1}$$

where $P_1(\cos\Theta)$ and $Q_1(ch\omega)$ are Legendre functions of the first and the second kind respectively and b_{11} is found as

$$3.9 \quad b_{11} = -\frac{3}{2} \int_{-1}^1 (1-x^2) \frac{\partial P_1(\Theta)}{\partial x} \cdot \frac{\partial}{\partial x} \left[P_1(\Theta) \frac{1}{\sqrt{ch^2\omega_0 - x^2}} \right] dx$$

$$x = \cos\Theta$$

In the formula (3.8) only the first term of the Legendre expansion appears, according to the calculations /Eremova, Dukhin/ the higher terms do not give the relevant contribution - less than 5%.

On the basis of these results we can calculate the potential distribution φ^i inside the molecule and the

internal field function $B_1 = B^{\parallel}$. Inside the molecule ψ^i must satisfy the Laplace equation, remain finite at the centre of the molecule and depend on the constant vector $E [1]$. We seek the potential ψ^i in the form satisfying these conditions and using the boundary conditions on the particle surface.

At the interface of two dielectric the following conditions must be fulfilled: the continuity of the potential through the interface

$$3.10 \quad \psi^i \Big|_S = \psi^e \Big|_S$$

and the continuity of the field induction vector D , which gives [1]

$$3.11 \quad \epsilon_1 \frac{\partial \psi^e}{\partial n} \Big|_S = \epsilon_2 \frac{\partial \psi^i}{\partial n} \Big|_S$$

ϵ_1 - dielectric constant of the electrolyte
 $\epsilon_2 = (\epsilon_a, \epsilon_b = \epsilon_c)$ - dielectric constant of the molecule

Applying the external uniform field E parallel to the symmetry axis of the particle we obtain the longitudinal polarization. For the weakly polarized DL case, we assume the internal potential ψ^i in the form

$$3.12 \quad \psi^i = \psi_0^i + \psi_1^i$$

where ψ_0^i is the potential distribution inside the un-

charged particle [1,2,3]

$$3.13 \quad \varphi_0^i = b_0 P_1(\cos \Theta) P_1(chw) = E_{\text{eff}} \cdot z = B_0 E \cdot z$$

$$E \parallel z \parallel a$$

B_0 are the internal field functions - the polarizability coefficients, denoted as B_a in sec.1.

For the ellipsoid of the revolution B_0 is

$$B_0 = [1 + \left\{ \frac{\epsilon_a}{\epsilon_1} - 1 \right\} A_a]^{-1}$$

$$3.14 \quad A_a = \frac{ab^2}{2} \int_0^\infty \frac{d\lambda}{(a^2 + \lambda)^{3/2} (b^2 + \lambda)}$$

φ_0^i fulfills the conditions

$$\varphi_0^e \Big|_s = \varphi_0^i \Big|_s \quad (a)$$

$$3.15 \quad \epsilon_1 \frac{\partial \varphi_0^e}{\partial n} \Big|_s = \epsilon_2 \frac{\partial \varphi_0^i}{\partial n} \Big|_s \quad (b)$$

We seek the potential distribution φ_1^i in the form of the Legendre expansion

$$3.16 \quad \varphi_1^i = \sum_{n=1}^{\infty} b_n P_n(\cos \Theta) P_n(chw)$$

then

$$3.17 \quad \varphi^i = \varphi_0^i + \varphi_1^i = b_0 P_1(\cos \Theta) P_1(chw) + \sum_{n=1}^{\infty} b_n P_n(\cos \Theta) P_n(chw)$$

To solve the problem of finding b_n and φ_1^i it is convenient to introduce the set of variables defined as

$$\begin{aligned}
 3.18 \quad \zeta_1 &= ch \omega & 1 \leq \zeta_1 < \infty \\
 \zeta_2 &= \cos \Theta & -1 \leq \zeta_2 \leq 1 \\
 \zeta_3 &= \Psi & 0 \leq \zeta_3 \leq 2\pi
 \end{aligned}$$

The equation of the particle surface is expressed now as

$$3.19 \quad \zeta_1 = \zeta_0 = ch \omega_0$$

In these coordinates the conditions (3.10-3.11) have the form

$$3.20 \quad \left. \varphi^e(\zeta_1, \zeta_2) \right|_{\zeta_1=\zeta_0} = \left. \varphi^i(\zeta_1, \zeta_2) \right|_{\zeta_1=\zeta_0} \quad (a)$$

$$\varepsilon_1 \frac{\partial}{\partial \zeta_1} \varphi^e(\zeta_1, \zeta_2) \Big|_{\zeta_1=\zeta_0} = \varepsilon_a \frac{\partial}{\partial \zeta_1} \varphi^i(\zeta_1, \zeta_2) \Big|_{\zeta_1=\zeta_0}$$

The distribution potentials φ^e and φ^i in the new coordinates are

$$\varphi^e = -hEC(\zeta_0, \zeta_1)\zeta_2 + a_1(\zeta_0, \Gamma_0^+, c_0)Q_1(\zeta_1)P_1(\zeta_2) \quad (a)$$

$$3.21 \quad a_1 = \frac{1}{2} E h C(\zeta_0, \zeta_0) \left[Q_1(\zeta_0) + \frac{1}{b_n} \left(\frac{\Gamma_0^+}{c_0 h} \right)^{-1} \frac{\partial Q_1(\zeta_1)}{\partial \zeta_1} \sqrt{\zeta_1^2 - 1} \right] \Big|_{\zeta_1=\zeta_0}^{-1} \quad (b)$$

$$C(\zeta_1, \zeta_0) = \zeta_1 - p(\zeta_0)Q_1(\zeta_1) \quad (c)$$

$$p(\zeta_0) = -2 \left[\frac{2\zeta_0}{\zeta_0^2 - 1} - \ln \frac{\zeta_0 + 1}{\zeta_0 - 1} \right]^{-1} \quad (d)$$

$$3.21 \quad \varphi_0^i = b_0 P_1(\zeta_1) P_1(\zeta_2) \quad (e)$$

$$\varphi_1^i = \sum_{n=1}^{\infty} b_n P_n(\zeta_1) P_n(\zeta_2) \quad (f)$$

Using the eq. (3.20) and the general solution form (3.21 f) we calculate the potential distribution φ_1^i inside the molecule. Substitution (3.21) into the boundary conditions (3.20) gives us the set of equations for b_n .

The truncation of the Legendre series in φ_1^e , eq. (3.3), to the first term only causes that all b_n vanish for $n \neq 1$. The calculated coefficient b_1 is then found as

$$3.22 \quad b_1 = \left[\left(\frac{\epsilon_a - \epsilon_1}{\epsilon_1} \right) (\zeta_0^2 - 1) \zeta_0 \right]^{-1} a_1 =$$

$$= \frac{1}{2} E h C(\zeta_0, \zeta_0) \left[Q_1(\zeta_0) + \frac{1}{b_{11}} \left(\frac{\Gamma_0^+}{\cos h} \right)^{-1} \left(\sqrt{\zeta_1^2 - 1} \frac{\partial Q_1(\zeta_1)}{\partial \zeta_1} \right) \right]^{-1} \left[\frac{\epsilon_a - \epsilon_1}{\epsilon_1} (\zeta_0^2 - 1) \zeta_0 \right]^{-1}$$

Then the total potential φ^i inside the molecule is

$$3.23 \quad \varphi^i = b_0 P_1(\zeta_1) P_1(\zeta_2) + b_1 P_1(\zeta_1) P_1(\zeta_2) = E_{\text{eff}}(\alpha) \cdot z =$$

$$= B^{\parallel} \cdot E \cdot z$$

Using the eqs. (3.13), (3.22), (3.23) we obtain the following formula for the longitudinal polarizability coefficient B^{\parallel} when the external field E is parallel to z axis, $E \parallel z \parallel a$

$$B^{II}(\zeta_0; \epsilon_1, \epsilon_a; c_0, \Gamma_0^+) = \left[1 + \left\{ \frac{\epsilon_a - \epsilon_1}{\epsilon_1} - 1 \right\} A_a \right]^{-1} +$$

3.24

$$+ \frac{1}{2} C(\zeta_0, \zeta_0) \left[Q_1(\zeta_0) + \frac{1}{b_H} \left(\frac{\Gamma_0^+}{c_0 h} \right)^{-1} \left(\sqrt{\zeta_0^2 - 1} \right) \frac{\partial Q_1(\zeta_1)}{\partial \zeta_1} \right] \Big|_{\zeta_1 = \zeta_0}^{-1} \left[\frac{\epsilon_a - \epsilon_1}{\epsilon_1} (\zeta_0^2 - 1) \zeta_0 \right]^{-1}$$

The calculated polarizability coefficients, or the internal field functions $B^{II}(c_0, \Gamma_0^+)$ show the dependence on c_0 , ion concentration of the electrolyte and Γ_0^+ , ion adsorption coefficient for the diffuse part of the DL. In the formula (3.24) the influence of the double layer polarization is contained. The coefficients $B^{II}(c_0, \Gamma_0^+; \epsilon_1, \epsilon_a)$ depend not only on the geometry of the system and the dielectric constants like in purely dielectric case / with both media nonconducting/ but are characterized by the parameters describing the properties of the weakly polarized DL.

Now if we consider the form of the polarized energy, found for the nonconductive particles in the dielectric case, eq.(1.6), we can calculate the energy of the polarization for the case of ellipsoid of revolution / following Peterlin & Stuart, Holcomb & Tinoco, O'Konski & Krause /

$$U = \frac{-\epsilon_1 V E^2}{8\pi} \left[\cos^2 \Theta \frac{(\epsilon_a - \epsilon_1)}{\epsilon_1} B^{II}(\zeta_0, c_0, \Gamma_0^+, \epsilon_1, \epsilon_a) + \sin^2 \Theta \cos^2 \Psi \cdot \right.$$

3.25

$$\left. \cdot \frac{(\epsilon_b - \epsilon_1)}{\epsilon_1} B^{\perp}(\zeta_0, c_0, \Gamma_0^+, \epsilon_b, \epsilon_1) + \sin^2 \Theta \sin^2 \Psi \frac{(\epsilon_b - \epsilon_1)}{\epsilon_1} B^{\perp}(\zeta_0, c_0, \Gamma_0^+, \epsilon_b, \epsilon_1) \right]$$

B^\perp - internal field functions for the lateral polarizability,
 $E \perp a$

For a macromolecule, represented as an ellipsoid of revolution, with semimajor axis a and semiminor axis b and whose principal axes for the refractive index and dielectric tensors are also a and b , one has [6,7,9,10,11]

$$3.26 \quad K_{sp} = \frac{2\pi}{15n^2} (g_a - g_b) (P_a - P_b + Q_{ab})$$

$(\epsilon_a - \epsilon_b)$ - optical anisotropy factor

P_a, P_b - permanent dipole terms

$Q_{ab} = (Q_a - Q_b)$ - total induced dipole moment

Assuming that the considered molecule has no permanent dipole moment and using the above calculated formula for the polarization energy U we obtain, after calculations

$$3.27 \quad K_{sp} = \frac{2\pi}{15n^2} (g_a - g_b) \frac{\epsilon_1 U \epsilon_0}{k_B T} \left[\frac{\epsilon_a - \epsilon_1}{\epsilon_1} B^\parallel(c_0, \Gamma_0^+; \epsilon_a, \epsilon_1) - \frac{\epsilon_b - \epsilon_1}{\epsilon_1} B^\perp(c_0, \Gamma_0^+; \epsilon_b, \epsilon_1) \right]$$

where the lateral polarizability and the internal field functions $B^\perp(c_0, \Gamma_0^+)$ are to be found. This problem will be solved in the part II of this work.

We obtained the formula for K_{sp} explicitly dependent on c_0^- ion concentration of the electrolyte and Γ_0^+ - ion adsorption coefficient in the double layer. In this formula the influence of the DL polarization on the electrooptic effect

is expressed through the form of coefficients B^{\parallel} and B^{\perp}

4. Conclusions

A weakly polarized, thin double layer is described by the set of equations consisting of Poisson-Boltzmann equation for the potential distribution, equations of convective diffusion of cations and anions and equations of hydrodynamics for viscous fluids.

The longitudinal polarization of the thin double layer is found for the negatively charged nonconductive molecule, having the shape of the ellipsoid of revolution. The effective field inside the molecule is found for the external electric field E parallel to the semimajor axis of the ellipsoid, $E_{\text{eff}}(a)$. The calculated polarizability coefficients $B^{\parallel}(\epsilon_1, \epsilon_2, c_0, \Gamma_0^+)$ depend on the ion concentration c_0 and Γ_0^+ - adsorption coefficients of the double layer, besides the dependence on the dielectric constants of the system and the geometry factor.

The formula for the induced dipole moment Q_{ab} and for the specific Kerr constant found in this model contains the explicit dependence on the parameters, characterizing the weakly polarized double layer. That expresses the fact that the polarization of the double layer plays an important role in the dielectric properties of macromolecules in the solution.

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DOUBLE LAYER POLARIZATION OF NONCONDUCTING SPHEROIDAL
PARTICLES AND ITS APPLICATION TO KERR EFFECT
II. LATERAL POLARIZATION IN A CONSTANT ELECTRIC FIELD .

Abstract

The double layer polarization of elongated spheroidal charged particles in an electrolyte solution for the electric field E perpendicular to the symmetry axis of the molecule is discussed. The Dukhin - Shilov model for the weakly polarized quasi-equilibrium double layer is used to calculate the internal electric potential distribution ψ_i inside the molecule. The lateral polarizability coefficient B^+ is found. The specific Kerr constant K_{sp} calculated using the polarization energy found for the discussed system is given, showing the explicit dependence on the double layer parameters, ion concentration c_0 and ion adsorption coefficient Γ_0 .

In the previous paper [14] we discussed the longitudinal polarization of elongated, spheroidal, nonconducting

charged particles embedded in an electrolyte solution, when the external field E was applied parallel to the symmetry axis of the molecule. We set up the diffuse double layer model, based on Dukhin and Shilov assumptions [3-5, 14], then found the electric potential distribution function φ inside the molecule and then the effective internal field E_{eff} and the polarizability coefficients B^{\parallel} . That enabled us to calculate the induced polarization energy associated with the induced polarization of the ellipsoidal molecule embedded in an electrolyte solution. The steady state specific Kerr constant was found for the discussed system.

Here we discuss the lateral polarization of the nonconducting charged spheroidal particles, embedded in the isotropic dielectric, conducting solvent, with the constant external field E applied perpendicular to the symmetry axis of the molecule. The molecule is supposed to have the shape of the ellipsoid of revolution, the semimajor axis directed along z -axis. The field E is applied perpendicular to z -axis, say along x -axis. When the molecule is placed in the solution, a double layer is formed. We develop the model of the double layer in quasi-equilibrium state, outlined in [14]. We consider the quasi-equilibrium double-layer of small thickness, $\kappa^{-1}a \gg 1$ where κ^{-1} is the reciprocal Debye radius, a is the particle radius. As before, the distribution of the electric potential φ and the electrolyte concentration c within the double layer give us the necessary information about the system. Both distributions fulfill the set of equations of continuity, Poisson equation and Navier - Stokes equation

for viscous fluids, [14]. The problem of finding the electric potential Ψ reduces to the solution of the Laplace equation for Ψ and c with the boundary conditions on the particle surface, which take into consideration the compensation of the divergence of surface fluxes in the double-layer by normal fluxes. When the external field E is applied perpendicular to the symmetry axis, there is no axial symmetry. That means, adopting the spheroidal coordinate system, that the surface fluxes will have not only

Θ - component I_{Θ} but also Ψ - component I_{Ψ}

We use the prolate spheroidal coordinate system

$$\begin{aligned}
 x &= h \operatorname{sh} \omega \sin \Theta \cos \Psi & 0 \leq \Psi \leq 2\pi \\
 y &= h \operatorname{sh} \omega \sin \Theta \sin \Psi & 0 \leq \Theta \leq \pi \\
 z &= h \operatorname{ch} \omega \cos \Theta & 0 \leq \omega < \infty
 \end{aligned}$$

where $\omega = \omega_0$ defines the particle surface and semiaxes a and b are

$$\begin{aligned}
 a &= h \operatorname{ch} \omega_0 & h &= \sqrt{a^2 - b^2} \\
 b &= h \operatorname{sh} \omega_0
 \end{aligned}$$

We find the boundary conditions on the particle surface by equating the incoming normal flux of ionic transport on the particle surface $\omega = \omega_0$ in a square bounded by the lines $\Theta, \Theta + d\Theta; \Psi, \Psi + d\Psi$ to the total surface ionic flux outgoing through the sides of the square.

That gives us

$$3 \quad j_n^\pm = -\text{div}_s [I_s^\pm]$$

where the ion flux density j_n^\pm is [3,4,14]

$$4 \quad j_n^\pm = \frac{D^\pm}{h\sqrt{ch^2\omega_0 - \cos^2\Theta}} \frac{\partial}{\partial \omega} \left[\mp \frac{F}{RT} c_0 \varphi - c_1 \right]$$

F - Faraday constant, R - universal gas constant
and the surface fluxes $I_\Theta^\pm, I_\gamma^\pm$ are

$$I_\Theta^\pm = \frac{\Gamma_0^\pm}{c_0 h} \frac{D^\pm}{\sqrt{ch^2\omega_0 - \cos^2\Theta}} \frac{\partial}{\partial \Theta} \left[\mp \frac{F}{RT} c_0 \varphi - c_1 \right]$$

5

$$I_\gamma^\pm = \frac{\Gamma_0^\pm}{c_0 h} \frac{D^\pm}{\sin\Theta \text{sh}\omega_0} \frac{\partial}{\partial \gamma} \left[\mp \frac{F}{RT} c_0 \varphi - c_1 \right]$$

here c_0 is the equilibrium concentration of the electrolyte outside the double layer, c_1 is the change in the electrolyte concentration upon the polarization, D^\pm are the diffusion coefficients of cations and anions, Γ_0^\pm is the equilibrium adsorption coefficient in the diffuse part of the double layer for cations and anions.

Assuming the weak polarization of the double layer, we can express the electric potential φ^e outside the particle

as

$$6 \quad \varphi^e = \varphi_0^e + \varphi_1^e$$

φ_0^e is the distribution potential describing the polarization of an uncharged particle, for which [2,4,13]

$$\left. \frac{\partial \varphi_0^e}{\partial \omega} \right|_{\omega=\omega_0} = 0 \quad \left. \frac{\partial \varphi_0^e}{\partial x} \right|_{\omega} = -E \quad E \parallel x$$

7

$$\varphi_0^e = E h C(\omega, \omega_0) P_1^1(\cos \Theta) \cos \Psi$$

$$C(\omega, \omega_0) = \text{sh} \omega - Q_1^1(\text{ch} \omega) \left[\frac{1}{2} \text{th} \frac{\text{ch} \omega_0 + 1}{\text{ch} \omega_0 - 1} - \frac{\text{ch}^2 \omega_0 - 2}{\text{ch} \omega_0 (\text{ch}^2 \omega_0 - 1)} \right]^{-1}$$

$Q_1^1(\text{ch} \omega)$, $P_1^1(\cos \Theta)$ are associated Legendre functions of the second and the first kind, respectively. φ_1^e is the perturbation term due to the polarization of the formed double layer. Assuming that for strongly charged particles $\Gamma_0^+ \gg \Gamma_0^-$, we get the boundary condition equation, incorporating all the phenomena occurring within the polarized double layer, from eqs. (3-5), (6)

$$\left. \frac{\partial \varphi_1^e}{\partial \omega} \right|_{\omega=\omega_0} = \left(-\frac{\Gamma_0^+}{C_0 h} \right) \left\{ \frac{1}{h \sqrt{\text{ch}^2 \omega_0 - \cos^2 \Theta}} \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \left[\sin \Theta \left(\frac{\partial \varphi_1^e}{\partial \Theta} + \frac{1}{2} \frac{\partial \varphi_0^e}{\partial \Theta} \right) \right] \right\} +$$

$$+ \left. \frac{\sqrt{\text{ch}^2 \omega_0 - \cos^2 \Theta}}{\sin^2 \Theta \text{sh}^2 \omega_0} \frac{\partial^2}{\partial \Psi^2} \left(\varphi_1^e + \frac{1}{2} \varphi_0^e \right) \right\} \Big|_{\omega=\omega_0}$$

$$F/RT \cdot \varphi_1^e = C_1 / C_0$$

Using the Legendre series expansion

$$9 \quad \varphi_1^e = \sum_{n=1}^{\infty} a_n Q_n^1(\text{ch} \omega) P_n^1(\cos \Theta) \cos \Psi$$

where $Q_n^1(\text{ch} \omega)$ and $P_n^1(\cos \Theta)$ are associated Legendre functions of the second and first kind respectively, one gets

the solution for Ψ_1^e [4,13]

$$10 \quad \Psi_1^e = a_1 Q_1'(chw) P_1^1(\cos \Theta) \cos \Psi$$

where

$$11 \quad a_1 = \frac{1}{2} E h C(\omega_0, \omega_0) \left[Q_1'(chw_0) + \frac{1}{b_{11}} \left(\frac{\Gamma_0^+}{c_0 h} \right)^{-1} \frac{\partial Q_1'(chw)}{\partial w} \right] \Big|_{w=\omega_0}^{-1}$$

and

$$12 \quad b_{11} = \frac{3}{2} \frac{1}{\text{sh}^2 \omega_0} \int_{-1}^1 \left\{ \frac{\text{sh}^2 \omega_0 (x^2 - x \sqrt{1-x^2} + (ch^2 \omega_0 - x^2))}{\sqrt{ch^2 \omega_0 - x^2}} \right\} dx$$

In eqs. (10) only the first term of the Legendre expansion appears, because for all values of the axial ratio and charge of the particle, a_1^n differs from a_1^1 by not more than 1% [4,13].

Having found the potential distribution Ψ^e outside the molecule, surrounded by the polarized double layer, we can calculate the potential distribution Ψ^i inside the molecule. The potential Ψ^i inside the molecule must satisfy the Laplace equation, remain finite at the centre of the molecule and depend on the constant vector E . We will seek the potential Ψ^i in the form satisfying these conditions and using the boundary conditions on the particle surface.

The condition of the continuity of the potential

through the interface and the continuity of the field induction vector D at the interface of two dielectric give us [1,3]

$$\varphi^i \Big|_s = \varphi^e \Big|_s$$

$$13 \quad \varepsilon_1 \frac{\partial \varphi^e}{\partial n} \Big|_s = \varepsilon_2 \frac{\partial \varphi^i}{\partial n} \Big|_s$$

ε_1 - dielectric constant of the electrolyte

$\varepsilon_2 = (\varepsilon_a, \varepsilon_\theta = \varepsilon_c)$ - dielectric constant of the molecule

For the weakly polarized double layer we seek the internal potential φ^i in the form

$$14 \quad \varphi^i = \varphi_0^i + \varphi_1^i$$

where φ_0^i is the potential distribution inside the uncharged particle [2]

$$15 \quad \varphi_0^i = b_0 P_1'(chw) P_1'(\cos \theta) \cos \psi = E_{\text{eff}} \cdot x = B_0(b) E \cdot x$$

$$b \parallel x \parallel E \perp z$$

$B_0(b)$ are the internal field functions - the polarizability coefficients for the field perpendicular to the long axis of the molecule.

For the ellipsoid of revolution, B_0 is [1,10,12]

$$16 \quad B_0(b) = \left[1 + \left\{ \frac{\varepsilon_b}{\varepsilon_1} - 1 \right\} A_b \right]^{-1}$$

$$16 \text{ a } A_b = \frac{ab^2}{2} \int_0^{\infty} \frac{d\lambda}{(b^2 + \lambda)^2 (a^2 + \lambda)^{1/2}}$$

a , b - semimajor and semiminor axes of the ellipsoid

ϵ_b - the principal value of the dielectric constant of the ellipsoid along the semiminor axis b

ϵ_1 - dielectric constant of the solvent

ψ_0^i fulfils the conditions for the uncharged molecule with no double layer

$$\psi_0^e \Big|_s = \psi_0^i \Big|_s$$

17

$$\epsilon_1 \frac{\partial \psi_0^e}{\partial n} \Big|_s = \epsilon_2 \frac{\partial \psi_0^i}{\partial n} \Big|_s$$

We seek the potential ψ_1^i inside the molecule in the form of the Legendre expansion

$$18 \quad \psi_1^i = \sum_{n=1}^{\infty} b_n P_n'(ch\omega) P_n'(\cos \Theta) \cos \Psi$$

and

$$19 \quad \psi^i = \psi_0^i + \psi_1^i = b_0 P_0'(ch\omega) P_0'(\cos \Theta) \cos \Psi + \sum_{n=1}^{\infty} b_n P_n'(ch\omega) P_n'(\cos \Theta) \cos \Psi$$

Substituting (19) and (10) into the boundary conditions (13) gives us the set of equations for b_n . All b_n for $n \neq 1$ vanish, because of the truncation of the Legendre series in

eqs. (9 - 10) to the first term only, With this condition we obtain

$$b_1 = \frac{a_1}{\left(\frac{\epsilon_0 - \epsilon_1}{\epsilon_1}\right)} \cdot \frac{sh\omega_0}{ch\omega_0} \left. \frac{\partial K(ch\omega)}{\partial \omega} \right|_{\omega=\omega_0}$$

$$20 \quad K(ch\omega) = \left[\frac{1}{2} h \frac{ch\omega+1}{ch\omega-1} - \frac{ch\omega}{ch^2\omega-1} \right] = \frac{\partial Q_1(ch\omega)}{\partial ch\omega}$$

a_1 is defined in eq. (17)

The total potential ψ^i inside the molecule is now

$$1 \quad \psi^i = \psi_o^i + \psi_e^i = b_o P_1'(ch\omega) P_1'(\cos\theta) \cos\psi + b_1 P_1'(ch\omega) P_1'(\theta) \cos\psi =$$

$$21 \quad = E_{eff}(\theta) \cdot x = B^+ E \cdot x$$

$$E \parallel B \parallel x$$

Here B^+ are the lateral polarizability coefficients for the external field applied perpendicular to the symmetry axis of the molecule, $E \perp a$

From eqs. (20-21) and (16) we get

$$B^+ (\omega_0, \epsilon_1, \epsilon_0, c_0, \Gamma_o^+) =$$

$$22 \quad = \left[1 + \left\{ \frac{\epsilon_0}{\epsilon_1} - 1 \right\} A_0 \right]^{-1} + \frac{1}{2} C(\omega_0, \omega_c) \left[Q_1'(ch\omega_c) + \frac{1}{b_{11}} \left(\frac{\Gamma_o^+}{c_0 h} \right)^{-1} \frac{\partial Q_1'(ch\omega)}{\partial \omega} \right]^{-1} \Bigg|_{\omega=\omega_0}^*$$

$$* \frac{sh\omega_0}{ch\omega_0} \left. \frac{\partial K(ch\omega)}{\partial \omega} \right|_{\omega=\omega_0} * \left[\frac{\epsilon_0 - \epsilon_1}{\epsilon_1} \right]^{-1}$$

where A_0 , $C(\omega_0, \omega_c)$ and b_{11} , $K(ch\omega)$ are defined in eqs. (16), (7), (12), (20).

Now the obtained general formula for the lateral polarizability coefficients B^\perp contains the dependence on the physical parameters, describing the polarized double layer: ion concentration of the electrolyte c_0 and ion adsorption coefficient of the diffuse part of the double layer Γ_0^+ . B^\perp also depend on the shape of the molecule through A_0 and ω_0 and on dielectric constants of the molecule and the solvent.

The polarization energy of the ellipsoidal, charged macromolecule in the dielectric conducting solvent can be found as [3, 9, 11, 12]

$$\begin{aligned}
 U = & \frac{-\epsilon_1 v E^2}{8\pi} \left[\cos^2 \Theta \frac{\epsilon_a - \epsilon_1}{\epsilon_1} B^{\parallel}(\omega_0, c_0, \Gamma_0^+, \epsilon_1, \epsilon_a) + \right. \\
 23 \quad & + \sin^2 \Theta \cos^2 \Psi \frac{\epsilon_b - \epsilon_1}{\epsilon_1} B^{\perp}(\omega_0, c_0, \Gamma_0^+, \epsilon_1, \epsilon_b) + \\
 & \left. + \sin^2 \Theta \sin^2 \Psi \frac{\epsilon_b - \epsilon_1}{\epsilon_1} B^{\perp}(\omega_0, c_0, \Gamma_0^+, \epsilon_1, \epsilon_b) \right]
 \end{aligned}$$

v - the volume of the molecule

where $B^{\parallel}(\omega_0, c_0, \Gamma_0^+)$ is the longitudinal polarization coefficient / or the internal field function / found in [14] as

$$\begin{aligned}
 B^{\parallel}(\omega_0, c_0, \Gamma_0^+, \epsilon_a, \epsilon_1) = & \left[1 + \left\{ \frac{\epsilon_a - \epsilon_1}{\epsilon_1} - 1 \right\} A_a \right]^{-1} + \\
 24 \quad & + \frac{1}{2} C^{\parallel}(\omega_0, \omega) \left[Q_1(\omega_0) + \frac{1}{b_{11}'} \left(\frac{\Gamma_0^+}{c_0 h} \right)^{-1} \frac{\partial Q_1(\omega)}{\partial \omega} \Big|_{\omega=\omega_0} \right]^{-1} * \\
 & * \left[\frac{\epsilon_a - \epsilon_1}{\epsilon_1} (ch^2 \omega_0 - 1) ch \omega_0 \right]^{-1}
 \end{aligned}$$

$$b_{11}' = -\frac{3}{2} \int_{-1}^1 (1-x^2) \frac{\partial P_1(x)}{\partial x} \frac{\partial}{\partial x} \left[P_1(x) \frac{1}{\sqrt{ch^2 \omega_0 - x^2}} \right] dx$$

24 a

$$A_a = \frac{ab^2}{2} \int_0^{\infty} \frac{d\lambda}{(a^2 + \lambda)^{3/2} (b^2 + \lambda)}$$

$$C'(\omega_0, \omega_0) = ch\omega_0 + 2 \left[\ln \frac{ch\omega_0 + 1}{ch\omega_0 - 1} - \frac{2ch\omega_0}{ch^2\omega_0 - 1} \right]^{-1} \left[1 - \frac{1}{2} ch\omega_0 \ln \frac{ch\omega_0 + 1}{ch\omega_0 - 1} \right]$$

The specific Kerr constant for the discussed system can be found as [6,7,9,10,11]

$$25 \quad K_{sp} = \frac{2\pi}{15n^2} (g_a - g_b)(P_a - P_b + Q_{ab})$$

$(g_a - g_b)$ - optical anisotropy factor

P_a, P_b - permanent dipole terms

n - refractive index of the solution

Q_{ab} - total induced dipole moment

For the molecules with no permanent dipole moments we can obtain, using eqs. (23), (25)

$$26 \quad K_{sp} = \frac{2\pi}{15n^2} (g_a - g_b) \frac{\epsilon_1 \nu \epsilon_0}{k_B T} \left[\frac{\epsilon_a - \epsilon_1}{\epsilon_1} B^{\parallel}(\omega_0, \omega_0, T_0^+, \epsilon_a, \epsilon_1) - \frac{\epsilon_b - \epsilon_1}{\epsilon_1} * B^{\perp}(\omega_0, \omega_0, T_0^+, \epsilon_b, \epsilon_1) \right]$$

B^{\parallel} and B^{\perp} are the longitudinal and lateral polarizability coefficients, defined in eqs (22), (24),

The specific Kerr constant, characterizing the electrooptic effect, expressed by eq. (26) depends essentially on the parameters of the polarized double layer surrounding the particle

in the solution.

Discussion.

We discussed the system of nonconducting, charged molecules of ellipsoidal shape in the electrolyte solution. The formed double layer is assumed to be in quasi-equilibrium state and described by the Dukhin - Shilov model [3 - 5, 14]. The external constant electric field E applied to the system is perpendicular to the molecule symmetry axis. We found the distribution potential ψ_c inside the molecule, effective field E_{eff} inside the molecule and the lateral polarizability coefficient $B^+(w_0, c_0, \Gamma_0^+, \epsilon_2, \epsilon_1)$ for the molecule with ^{the} weakly polarized double layer. We found the specific Kerr constant K_{sp} using the polarization energy of the molecule surrounded by the double layer. The electrooptic effect now is directly associated with the properties of the polarized double layer and depends on its parameters, ion concentration c_0 and the ion adsorption coefficient Γ_0^+ . The numerical calculations based on the outlined theory are under the preparation and will be published soon.

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