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**Statistical description of the many-body effects in classical
ion-molecular systems**

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Introduction

Relevance of a thesis work and degree of the problem development. Up to date ion-molecular systems (such as ionic liquids, zwitterions, polyelectrolytes, dielectric polymers, etc.) are very perspective for the field of the so-called smart materials development, that are materials, which physical-chemical properties could be controlled by the change of the different physical stimuli (such as temperature, pH, electric field, etc.) within some narrow intervals. Recently, coarse-grained modelling (CGM) methods have been widely used for the modelling of the equilibrium properties of the ion-molecular systems. CGM is based on the idea that separate atomic (molecular) groups are combined into large particles, interactions between which are described by the effective potentials. Despite of the certain success, achieved in reduction of the computational working time while using MD simulation with coarsening of the real structure of the molecules in comparison with their full-atomistic representation, modelling of the systems of a large number of particles (even with the coarsened structure) under the conditions of the condensed phase is still a sufficiently computational expensive. On the other side, for the modern chemical engineering it is necessary to possess such computational tools, which allow one to predict behavior of the thermodynamic parameters in the fast and effective way. Methods of modern statistical physics, such as field-theoretic methods, classical density functional theory, mean-field theory, etc., well-proven at the description of the thermodynamic properties of simple liquids and synthetic polymers, could, in principle, take on the role of such tools. However, for application of such approaches for the description of the ion-molecular systems at the equilibrium in the bulk and at the phase boundaries, it is necessary to take into account not only the universal intermolecular interactions (dispersion and excluded volume interactions), but also a peculiarity of the molecular structure of components, such as multipole moments, electronic polarizability, hydrophobicity/hydrophilicity, configurational asymmetry of the molecule, etc. Still, at the moment only first steps have been made in that direction. It is worth noting, that statistical methods, based on the concept of self-consistent field, in comparison with the coarse-grained MD simulation methods, are highly underestimated among modern physic-chemists and material scientists because of their mathematical complexity, on the one side, and the lack of the accessible software for the general public users, on the other side. There is a lump of problems down this road waiting for solution, some of them are presented in this work.

Lately in different electrochemical applications it has become necessary to study the influence of small impurities (co-solvents) in the electrolyte solutions on the properties of the electrical double layer, occurring at the metal electrode/liquid electrolyte interface. The main question, which bothers researches is: "How do properties of the molecules of impurities (dipole moment, polarizability, effective size, etc.) affect on the most important electrochemical characteristic – differential capacitance of the electrical double layer?" From general considerations it is clear, that presence of the electric field gradient, appearing due to the screening of the electrode charge by counterions, leads to the attraction of the polar/polarizable particles of the impurity from the bulk solution to the electrode surface, driven by dielectrophoretic force, which, in turn, leads to the increase in the local dielectric permittivity and, consequently, to the increase in differential capacitance. To investigate raised question, it is necessary to formulate self-consistent field theory, taking into account explicitly presence of the co-solvent molecules in the solution with constant dipole moments and/or electronic polarizability. On the other hand, latest experimental research of the electrical double layer properties, occurring at the ionic liquid/metal electrode interface, show that even small impurities of the polar solvents in the bulk of ionic liquid, such as acetonitrile and water, could affect on the value of the differential capacitance. As opposed to electrolyte solutions, for correct description of the electrical double layer properties in ionic liquids with small impurities of the polar solvents, it is necessary to consider, besides electrostatic interactions and excluded volume interactions between ions and polar molecules, short-range specific interactions (which range is about several effective molecular sizes), associated, for example, with the hydrogen bonding, $\pi - \pi$ stacking, asymmetry effect of ions, their hydrophobic/hydrophilic properties, etc. However, until recently, there have not been made even any efforts in development of the phenomenological theory of the electrical double layer for ionic liquids, taking into account presence of the polar molecules of the impurity in the bulk solution with account for the short-range specific interactions between the mixture components.

Recent advances in experimental studies of the different organic compounds, such as proteins, betaines, zwitterionic liquids, etc., consisting simultaneously of the positively and negatively charged ionic groups, located at rather long distances (~ 10 nm), offer a challenge to statistical physics to develop analytical approaches to describe their thermodynamic properties. The fundamental difference of such systems from classical polar small molecules, such as water and aliphatic alcohols, is that they should not be modelled as particles, carrying point-like dipoles. Instead, they must be considered as pairs of bonded oppositely charged ionic groups, located at the fixed or fluctuating distances between each other, incorporating to the theory another length scale, associated with the effective distance between ionic groups. Moreover, since in practice such systems are located in the polar solvent (primary in water) with the addition of different electrolytes, it is necessary to develop a model of the electrolyte solution with the additive of the polar particles, described as ionic pairs with fluctuating distances between charged centers. Such an "nonlocal" theory could allow one to solve a range of the fundamental problems, existing in the polar fluids theory. Firstly, such model allows one to describe behavior of the point charge potential in the medium of the electrolyte solution with the addition of polar particles at the scale of their effective size. Secondly, this theory must be devoid of the "ultraviolet" divergences of the electrostatic free energy of the pure polar fluid, happening in the existing "local" theories.

Nowadays statistical thermodynamics of the dielectric polymers, i.e. polymers, carrying permanent dipole moments on their monomers or having sufficiently large polarizability (such as ionomers, polymeric ionic liquids, weak polyelectrolytes, etc.) is a poorly developed area of the polymer physics. One of the underexplored, but, at the same time, extremely important for applications problems of dielectric polymer physics is connected with the investigation of the conformational behavior of the weak polyelectrolytes chains in the dilute solutions. In the dilute solutions of weak polyelectrolytes it is thermodynamically favorable for charged monomers and counterions to form solvent-separated ionic pairs, so the latter could be considered as dipoles, freely rotating around the macromolecular backbone. If macromolecule is in the coil conformation, then dipoles, located in average at sufficiently large distance between each other, suffer the effective Keesom attraction. Thus, under temperature decrease polymer chain must shrink due to the Keesom attraction of monomers and, ultimately, undergo a transition from the conformation of expanded coil to the conformation of sufficiently compact globule. However, it is worth noting that mechanism of the dipole-dipole interactions for the sufficiently dense globule can not be restricted to the representation of the pair-wise Keesom interaction. Instead, one must account for the dipole correlations at the many-body level. Whereas there are models, describing mentioned collapse of macromolecule qualitatively, all of them consider the dipole correlations as pair-wise, i.e. at the level of Keesom interaction. Thus, there is a fundamental problem of the consideration of the dipole correlations of macromolecule monomers of the weak polyelectrolytes at the many-body level. On the other side, when a polymer chain adopts conformation of sufficiently dense globule, dipole moments on monomers can not be described as point-like dipolar particles, as for the case of the coil conformation. On the contrary, in that case, it is necessary to take into account presence of the ionic groups on the monomer, located at some distance. This description, obviously, must lead to the new regimes of the conformational behavior of the weak polyelectrolytes macromolecules relative those, predicted by previously formulated local theories.

Another important problem of statistical physics of dielectric polymers is related to the investigation of the external electric field influence on the conformational behavior of the dielectric macromolecules in dilute solutions. Indeed, possibility to control the conformational state of the macromolecules in solutions by the change of the electric field strength is very attractive for modern technological applications, considering relative simplicity of its technical implementation. As is well known, conformations of fixed in space polyelectrolytes, carrying electric charges on their monomers, are strongly sensitive to the external electric field. However, as it was mentioned above, there is a wide class of pointed above dielectric polymers, which monomers are electrically neutral, but able to obtain dipole moment in the external electric field due to the different mechanisms of polarizability. Due to the chain connectivity of the polarizable monomers in flexible polymer chain, application of the electric field must lead to not only macroscopic polarisation of the polymer, as in the case of

liquid dielectrics, consisting of chemically unbounded polarizable particles, but also to the substantial change of its conformational condition due to the electrostriction effect. However, unlike the polyelectrolytes, carrying electric charge on the monomers, change of the conformational state of the dielectric polymers in the external electric field must be sufficiently weaker. Nevertheless, this opens pretty wide range of perspectives for applications: pharmacology (control of the drug compounds concentration in the polymer volume by the change of the field strength), robotics (polymer materials for the production of the artificial muscles), textile industry (increase of the effectiveness of the polymeric fiber dyeing in the electric field) and so on. From fundamental point of view, it is interesting to theoretically investigate the conformational behavior of a single dielectric polymer chain in constant uniform electric field, which monomers are isotropically polarizable molecules. It is important to note, that till recently in the world literature there have not been made any efforts to theoretically analyse such system even at the level of primitive Flory-de Gennes mean-field type models. From the fundamental point of view the following questions must be answered.

- Is it possible to de-collapse a dielectric polymer globule with isotropic polarizable monomers by the electrostriction effect?
- How does a polarizability value of the monomer influence on the behavior of such transition?
- Is it possible to control concentration of polarizable particles of some low-molecular target compound within the volume of polarizable polymer chain in dilute solutions by the electric field change?

To answer the raised questions, one has to formulate the simplest theoretical Flory-de Gennes type model of the polarizable polymer chain in the medium of the liquid solvent in the constant uniform electric field and generalize it in the case of the polarizable molecules of target compound presence in the bulk phase.

Goal of the work. To develop approaches for the description of the thermodynamic and structural properties of ion-molecular systems (such as electrolyte solutions, ionic liquids, zwitterions and dielectric polymers) in the bulk and at the interfaces, accounting for characteristics of their molecular structure (dipole moment, polarizability, effective size, parameters of specific interactions, etc.) from the first principles of classical statistical mechanics.

For the achievement of the goal following **problems** were posed.

- To develop formalism, based on the classical density functional theory and functional integrals, allowing one to obtain self-consistent field equations, which reflect presence of the solvent molecules in the electrolyte solution, carrying constant dipole moment and/or polarizability.
- To formulate, using obtained self-consistent field equation, theory of the electrical double layer at the metal electrode/liquid electrolyte interface with account for polar or polarizable molecules of the co-solvent. To study, basing on the developed theory, a behavior of the differential electric capacitance of the electrical double layer, depending on the values of dipole moment, polarizability of co-solvent molecules and its concentration, and also on the specific interactions between the components of the mixture.
- To develop a nonlocal field-theoretic model of the electrolyte solution with a small additives of the polar particles with polar groups, located at sufficiently large fluctuating distances between each other. To derive, within formulated model, the self-consistent field equation, generalizing well-known Poisson-Boltzmann-Langevin equation, for electrostatic potential, created by external charges in the electrolyte solution in presence of the particles with sufficiently large dipole moments. To obtain a general expression for the electrostatic free energy of the electrolyte solution with the additive of the considerably long polar particles within the framework of Gaussian approximation.
- To construct a Flory-de Gennes type model of the weak polyelectrolyte macromolecule with account for the many-body dipole correlations of the monomers. To investigate, within the

developed model, a coil-globule transition of the weak polyelectrolyte chain, induced by dipole-dipole interactions of the monomers, including many-body effects. To compare theoretical and MD simulation results.

- To develop a Flory-de Gennes type model of the flexible dielectric polymer chain with an isotropically polarizable monomers, dissolved in the liquid dielectric in the uniform electric field. To investigate conformational behavior of the flexible dielectric polymer chain in the constant uniform electric field in the regimes of good and poor solvents.
- To develop a model of the dielectric polymer chain with the isotropically polarizable monomers in the medium of the dielectric solvent with a small additive of polarizable particles of the low-molecular target compound in the constant uniform electric field. To investigate, in the framework of developed model, behavior of the local concentration of the low-molecular particles within the polymer volume depending on the relation between the polarizabilities of the monomers and molecules of target compounds.

Research methodology. During the execution of thesis, modern methods of equilibrium statistical mechanics have been utilised, such as methods of functional integration, classical density functional theory and self-consistent field theory.

Main results, carried out to defence and their scientific novelty.

- Generalizations of the well-known theories of the electrical double layer at the metal/electrolyte solution interface have been formulated **for the first time**, taking into account presence of the polar/polarizable particles of the co-solvent in the solution. **For the first time** the behavior of the differential capacitance of the electrical double layer with the increase of the dipole moment and/or polarizability of the co-solvent molecules has been investigated.
- A **new** formalism has been formulated, based on the classical density functional theory, allowing one to obtain the self-consistent field equations for the electrostatic potential, considering presence of the polarizable/polar particles of the impurity (co-solvent) in the electrolyte solution.
- A **new** formalism has been represented, based on the classical density functional theory, describing the electrical double layer at the metal/ionic liquid interface with a small additive of the polar solvent with account for the short-range specific interactions between the compounds of the mixture. **For the first time** an explanation has been offered of the differential capacitance behavior at the ionic liquid/charged electrode interface with increase of the water concentration within the volume of the ionic liquid, observed experimentally. The influence of the short-range specific interactions between the ions and molecules of polar solvent on the differential capacitance of the electrical double layer has been systematically investigated **for the first time**.
- **For the first time** a self-consistent field theory of the electrolyte solutions with an admixture of the particles with fluctuating distance between polar groups has been formulated, generalizing the well-known Poisson-Boltzmann-Langevin theory. **For the first time** the self-consistent field equation for the electrostatic field potential, formed by external charges in the electrolyte solutions with the addition of polar particles, has been obtained. Within the Gaussian approximation **for the first time** the general expression for the electrostatic free energy of the electrolyte solution, defined by the thermal fluctuations of the local electrostatic potential near its zero value, with the addition of the polar particles has been obtained. It has been shown, that in the presence of the electrolyte ions in the solution, electrostatic free energy of polar particles, defined as an integral over vectors of the reciprocal space, converges at the ultraviolet limit.
- **For the first time** the Flory-de Gennes type model of the flexible polymer chain with monomers, carrying constant dipole moments, accounting for the dipole correlations at the

many-body level, has been developed. Within the developed model **new** regimes of the conformational behavior of the dipolar polymer chain have been discovered. **For the first time** a good agreement between the theoretical predictions and the results of the MD simulations has been achieved.

- A **new** model of the dielectric polymer chain with isotropically polarizable monomers in the constant uniform electric field has been developed. Within the elaborated model the globule-coil transition, induced by the external electric field, has been predicted **for the first time**.
- **For the first time** the model of the dielectric polymer chain with isotropically polarizable monomers in the medium of liquid-phase dielectric solvent in the presence of the isotropically polarizable molecules of the target compound has been developed. **For the first time** it has been shown the possibility to control the conformational state of the dielectric polymer by the change of the electric field strength. **For the first time** the possibility of impregnation of the polarizable polymer chain with the particles of the target compound in the medium of the liquid dielectric has been theoretically justified.

Theoretical significance of the work consists in the development of the new approaches for the description of the thermodynamical properties of ion-molecular systems in the bulk and phase boundary with the account for their molecular structure specifics from the first principles of statistical physics.

Practical significance of the work consists in the fact that developed approaches could be used for the fast and effective analysis of the thermodynamical properties behavior of the real ion-molecular systems in different fields, such as electrochemistry, colloid chemistry, pharmacology, industry of the smart materials production, etc.

Individual contribution of the author consists of the formulation of the problems, models development, performance of the analytical and numerical calculations, analysis of the obtained results and completion of the publications.

The main content of thesis

In **Introduction** relevance of the thesis and authenticity of the obtained results are claimed, goal and problems of the project, main results, carried out to defence, scientific novelty, practical and theoretical importance were formulated, and also research methods were described.

Chapter 1

Part 1.1

Poisson-Boltzmann (PB) equation, being one of the simplest and, at the same time, the most effective theoretical tools for the determination of the equilibrium distributions of the charged particles concentrations near the charged surfaces, nowadays found a wide range of applications in such areas, as colloid chemistry, electrochemistry, biophysics, etc. However, PB equation contains several assumptions, which do not allow one to apply it for a quantitative description of the ionic equilibria in the real physical-chemical systems. Indeed, PB equation, while based on the mean-field approximation, does not take into account effects of the ionic correlations, and at the same time, simulation of the solvent as a continuous medium makes it impossible to consider effects, associated with its molecular structure. These two main restrictions motivated theorists over the last couple of decades to discover new statistical-mechanical approaches to modify the PB equation. It is worth noting, that achieved modifications have sufficiently pushed forward the theory of electrolytes, which, in turn, allowed one to calculate physical-chemical characteristics of the real solutions, such as solution dielectric permittivity and activity coefficient.

Most of the theoretical research are devoted to the investigation of the dependence of the different microscopic parameters of ions on the macroscopic quantities of the electrical double layer

(EDL), such as profiles of the ionic concentrations near the charged electrodes, disjoining pressure and differential capacitance (DC). The latest is the most important characteristic for the modern electrochemical applications, in particular, for the designing of the electrochemical capacitors. For the present moment it is well enough studied how characteristics of the ions (charge, size, polarizability, dipole moment) influence on the properties of the EDL, appearing at the metal/liquid electrolyte interface. However, until recently, it has been unexplored, how properties of the molecules of co-solvent impurity in the electrolyte solution have impact on the behavior of the DC. This question is one of the most important for the modern electrochemical technologies, where one of the main problems is to achieve the maximum DC at the minimum applied voltage. In this regard, from the fundamental point of view, two natural questions arise:

- How will DC change with the addition of the impurity molecules (co-solvent), having electronic polarizability or permanent dipole moment, to the solution?
- How much is the quantitative difference between the effects of the dipole moment and polarizability of the co-solvent molecules on the DC value?

Answering the raised questions, in the first part of the Chapter 1 field-theoretical approach, allowing one to obtain the self-consistent field equation, taking into account explicitly co-solvent molecules with nonzero dipole moments and/or polarizability tensor, has been formulated. Using obtained equation, the classical Gouy-Chapman EDL theory at the metal/electrolyte solution interface was generalized for the case, when the polar/polarizable co-solvent is added to the bulk solution.

Electrolyte solution is examined, containing N_+ point ions with a charge q_+ ($q_+ > 0$), N_- ions with a charge q_- ($q_- < 0$), and solvent, described as a continuous dielectric medium with a constant dielectric permittivity ε . Besides, it is supposed that solution contains N_0 co-solvent molecules, having dipole moment, equivalent to p and polarizability tensor $\hat{\gamma}_c$. It is also supposed, that solution is in the equilibrium in the volume V with the temperature T . For simplicity, all of the interactions, except electrostatic ones, are neglected.

Then, bearing in mind all stated above model assumptions and using standard Hubbard-Stratonovich transformation, the representation of the configuration integral of the system at the thermodynamic limit in the form of the functional integral has been obtained. Further, within the mean-field approximation, i.e. equaling variational derivative of the integrand functional to zero, the following self-consistent field equation in $\psi(\mathbf{r})$, generalizing classical PB equation in the case of the presence of the polarizable/polar solvent molecules in the electrolyte solution, has been obtained

$$\nabla(\hat{\varepsilon}(\mathbf{r})\nabla\psi(\mathbf{r})) = -4\pi\rho_{ext}(\mathbf{r}) - 4\pi\left(q_-c_-e^{-\frac{q_-\psi(\mathbf{r})}{k_B T}} + q_+c_+e^{-\frac{q_+\psi(\mathbf{r})}{k_B T}}\right), \quad (1)$$

where the tensor of the local dielectric permittivity is introduced

$$\hat{\varepsilon}(\mathbf{r}) = \varepsilon\mathbf{I} + 4\pi c_0 e^{\frac{\nabla\psi(\mathbf{r})\hat{\gamma}_c\nabla\psi(\mathbf{r})}{2k_B T}} \frac{\sinh\beta p|\nabla\psi(\mathbf{r})|}{\beta p|\nabla\psi(\mathbf{r})|} \left(\hat{\gamma}_c + \mathbf{I}\frac{p^2}{k_B T} \frac{L(\beta p|\nabla\psi(\mathbf{r})|)}{\beta p|\nabla\psi(\mathbf{r})|}\right) \quad (2)$$

with the Langevin function $L(x) = \coth x - 1/x$; \mathbf{I} is the unity tensor. Besides this, the general expression for the electrostatic free energy of the mixture within the mean-field approximation has been obtained.

As an application of the obtained self-consistent field equation (1), a generalization of the classical Gouy-Chapman theory of the EDL, appearing at the metal/electrolyte solution interface, was formulated. Considering the system, containing charged electrode, described by a flat surface with a surface charge density σ , point ions of 1 : 1 electrolyte ($q_+ = -q_- = e$, e is the elementary charge) and point isotropically polarizable co-solvent molecules with dipole moment p and scalar polarizability tensor $\hat{\gamma}_c = \gamma_c\mathbf{I}$, choosing axis z being normal to the electrode and placing there origin, one can write a self-consistent field equation

$$\frac{d}{dz}(\varepsilon(z)\psi'(z)) = 8\pi ce \sinh(\beta e\psi(z)), \quad (3)$$

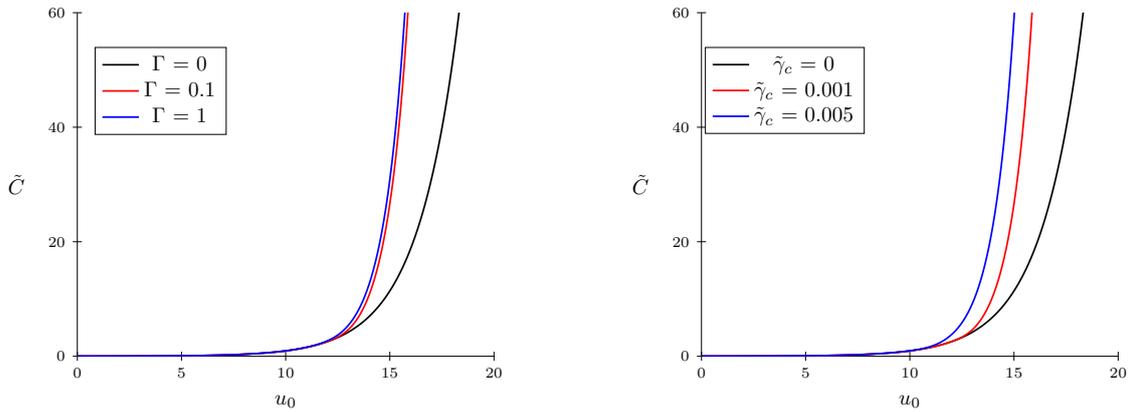


Figure 1: Differential capacitance \tilde{C} as a function of the electrode potential u_0 at different Γ and fixed parameters $\tilde{\gamma}_c = 10^{-3}$, $\theta = 10^{-3}$ и $\tilde{p} = 0$ (on the left). Differential capacitance \tilde{C} as a function of the electrode potential u_0 at different $\tilde{\gamma}_c$ and fixed parameters $\Gamma = 0.1$, $\theta = 10^{-3}$ and $\tilde{p} = 0$ (on the right).

where the local dielectric permittivity is introduced

$$\epsilon(z) = \epsilon + 4\pi c_0 \exp\left\{\frac{\gamma_c(\psi'(z))^2}{2k_B T}\right\} \frac{\sinh(\beta p \psi'(z))}{\beta p \psi'(z)} \left(\gamma_c + \frac{p^2}{k_B T} \frac{L(\beta p \psi'(z))}{\beta p \psi'(z)}\right), \quad (4)$$

and it has been assumed that far from the electrode (in the bulk solution) the average concentrations of the ions are the same, i.e. $c_+ = c_- = c$.

Then, using the boundary condition $\psi'(\infty) = 0$, the first integral of the equation (3) can be obtained, which defines the condition of the mechanical equilibrium of the solution and allows us, in turn, to obtain an electrostatic potential profile $\psi(z)$. Further, using the boundary condition

$$-\epsilon(0)\psi'(0) = 4\pi\sigma, \quad (5)$$

first integral of the equation (3) at $z = 0$ and definition of the DC

$$C = \frac{d\sigma}{d\psi_0}, \quad (6)$$

where $\psi_0 = \psi(0)$ is the electrode potential, following analytical expression

$$C = \frac{ec \cosh(\beta e \psi_0)}{2\pi\sigma} \epsilon_{el} \quad (7)$$

is obtained. The latter relation determines that within the self-consistent field approximation the DC of the flat EDL is proportional to the local dielectric permittivity $\epsilon_{el} = \epsilon(0)$ on the electrode.

Before turning to the numerical results, the following dimensionless parameters were introduced $\tilde{p} = p/el_B$, $\tilde{\gamma}_c = \gamma_c/l_B^3\epsilon$, $\theta = l_B^3 c$, $\Gamma = l_B^3 c_0$, где $l_B = e^2/\epsilon k_B T$ is the Bjerrum length. Apart from that, the dimensionless potential $u = \beta e \psi$, electric field strength $\tilde{\mathcal{E}} = \mathcal{E} \beta e l_B$, surface charge density $\tilde{\sigma} = \sigma \beta e l_B / \epsilon$, DC $\tilde{C} = d\tilde{\sigma}/du_0$ ($u_0 = u(0)$), and distance from the electrode $\tilde{z} = z/l_B$ were introduced. Then, it is established, that in the case of non-polar co-solvent ($\tilde{p} = 0$) with nonzero polarizability ($\tilde{\gamma}_c \neq 0$) increase in both the co-solvent concentration Γ and the polarizability $\tilde{\gamma}_c$ leads to the sufficient increase in DC at rather big electrode potentials (fig. 1a,b). In the case of the polar co-solvent at the zero electronic polarizability, in contrast, in the region of physically realizable parameters, increase of the dipole moment leads to the slight increase in DC. Finally, influence of the polarizable co-solvent on the electrostatic potential profile $u(\tilde{z})$ is discussed. It is determined, that increase of the polarizable particles concentration leads to the slowdown of the electrostatic potential decrease when moving away from the electrode. It is noted, that the effect of the polarizable co-solvent additive to the solution on the electrostatic potential profile is quite weak and becomes noticeable at sufficiently big values of the parameter Γ , that physically corresponds to the case of big co-solvent concentrations or low enough temperatures.

Part 1.2

As it was clearly shown by Kornyshev [Kornyshev, J. Phys. Chem. B., 2007] within the lattice gas model and later by him and coauthors using the MD simulations, the effects of the excluded volume of ions must have a strong impact on the DC behavior at the large electrode potentials. Therefore, consideration of the excluded volume effects are extremely important for the correct description of the DC behavior at sufficiently high electrode potentials. As one can understand from the general considerations, at large enough polarizability and electrode potentials ($e\psi_0/k_B T \gg 1$), a significant amount of co-solvent molecules could accumulate near its surface. Thereby, accumulation of the excess amount of the co-solvent molecules near the electrode surface would take place due to the dielectrophoretic force. So, even if the co-solvent concentration is low far from electrode, near its surface co-solvent concentration might become significant, so that the excluded volume effect will play an important role. Apart from that, also from the general considerations, it is clear that at rather big polarizabilities, co-solvent molecules would compete with the ions for the "space" near the charged electrode. So, the natural question arises: "How will simultaneous account for both the polarizability and excluded volume of the co-solvent molecules affect on DC behavior at the high electrode potentials?"

As such, in the second part of Chapter 1 classical density functional theory (DFT) of the electrolyte solution, mixed with the polarizable molecules of the co-solvent, allowing one to consider both the polarizability of the co-solvent molecules and excluded volume of the mixture particles, is formulated. Using the local Legendre transformation, the grand potential of the mixture as a functional of the electrostatic potential $\psi(\mathbf{r})$ has been obtained:

$$\Omega[\psi] = \int \left(-\frac{\varepsilon (\nabla\psi)^2}{8\pi} + \rho_{ext}\psi - P(\mu_+ - q_+\psi, \mu_- - q_-\psi, \mu_0 + \frac{\gamma_c}{2} (\nabla\psi)^2) \right) d\mathbf{r}. \quad (8)$$

It is noted, that if the dependence of the particles pressure on the chemical potential is known $P = P(\mu_+, \mu_-, \mu_0)$, then one can obtain the self-consistent field equation, varying the functional (8) over the potential $\psi(\mathbf{r})$. Then, for the consideration of the excluded volume effect of the species, a three-component symmetric lattice gas was chosen as a reference system, for which the mentioned dependence is well-known. Then, varying the functional (8) over the potential ψ , and using the expressions for the chemical potentials of the lattice gas species and equation of state of the lattice gas, the following self-consistent field equation with accounting for the polarizability of the co-solvent molecules, their excluded volume and excluded volume of ions has been obtained:

$$\nabla(\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})) = -4\pi\bar{\rho}_c(\mathbf{r}), \quad (9)$$

where the equilibrium charge densities are introduced

$$\bar{\rho}_c(\mathbf{r}) = \rho_{ext}(\mathbf{r}) + q_+\bar{c}_+(\mathbf{r}) + q_-\bar{c}_-(\mathbf{r}), \quad (10)$$

local ions concentrations

$$\bar{c}_{\pm}(\mathbf{r}) = \frac{c_{\pm,b} \exp[-\beta q_{\pm}\psi(\mathbf{r})]}{1 + v \left(c_{+,b} (e^{-\beta q_+\psi(\mathbf{r})} - 1) + c_{-,b} (e^{-\beta q_-\psi(\mathbf{r})} - 1) + c_{0,b} \left(e^{\frac{\beta\gamma_c}{2} (\nabla\psi(\mathbf{r}))^2} - 1 \right) \right)} \quad (11)$$

and local dielectric permittivity

$$\varepsilon(\mathbf{r}) = \varepsilon + 4\pi\gamma_c\bar{c}_0(\mathbf{r}), \quad (12)$$

where

$$\bar{c}_0(\mathbf{r}) = \frac{c_{0,b} \exp\left[\frac{\beta\gamma_c(\nabla\psi(\mathbf{r}))^2}{2}\right]}{1 + v \left(c_{+,b} (e^{-\beta q_+\psi(\mathbf{r})} - 1) + c_{-,b} (e^{-\beta q_-\psi(\mathbf{r})} - 1) + c_{0,b} \left(e^{\frac{\beta\gamma_c}{2} (\nabla\psi(\mathbf{r}))^2} - 1 \right) \right)} \quad (13)$$

is the local concentration of the co-solvent molecules and $c_{\pm,b}$ and $c_{0,b}$ are the concentrations of ions and co-solvent molecules in the bulk solution, respectively, v is a volume of the lattice gas cell.

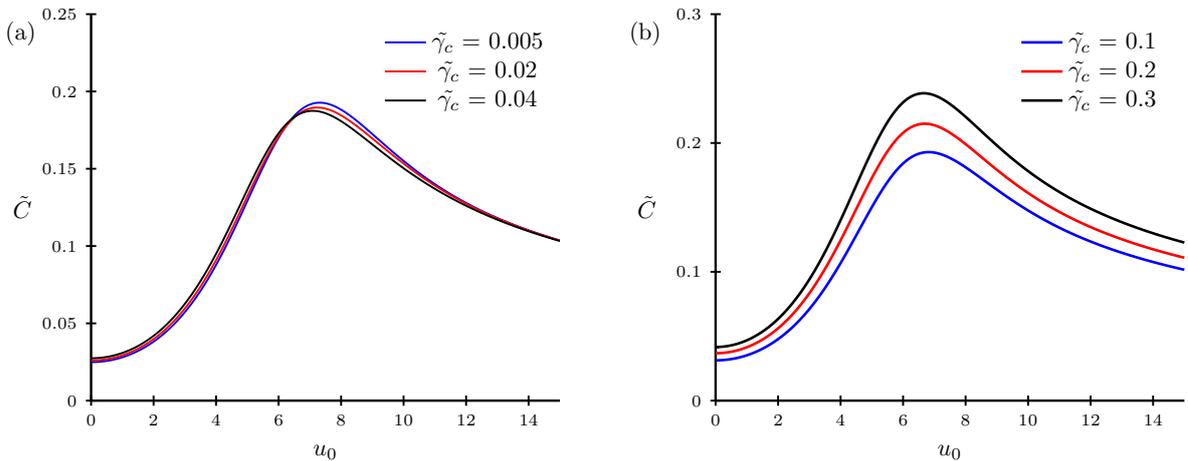


Figure 2: Differential electric capacitance at different polarizabilities: (a) $\tilde{\gamma}_c = 0.005, 0.02, 0.04$ and (b) $\tilde{\gamma}_c = 0.1, 0.2, 0.3$. The data is shown for $\tilde{c} = 1.63 \times 10^{-3}$, $\tilde{c}_{0,b} = 0.5$, $\xi = 2.32$.

Then, much as in the first part of the Chapter 1, a theory of the flat EDL at the metal/electrolyte solution interface was constructed. As in the previous part an 1:1 electrolyte was considered, i.e. $q_+ = -q_- = e$. As in the first part, using the first integral of the self-consistent field equation and the boundary condition, relating the induction on the electrode and its surface charge density, an analytical expression for the DC has been obtained, taking into account effects of the excluded volume of the solution particles, and, in addition, the polarizability of the co-solvent

$$C = \frac{e(\bar{c}_{+,s} - \bar{c}_{-,s})}{4\pi\sigma} \epsilon_{el}, \quad (14)$$

where $\bar{c}_{\pm,s} = \bar{c}_{\pm}(0)$ is the local concentrations of the ions on the electrode;

$$\epsilon_{el} = \varepsilon + 4\pi\gamma_c\bar{c}_{0,s} \quad (15)$$

is local dielectric permittivity on the electrode, $\bar{c}_{0,s} = \bar{c}_0(0)$ is the local co-solvent concentration on the electrode.

Turning to the numerical results, the following dimensionless parameters were introduced: $\tilde{c}_{0,b} = c_{0,b}v$, $\tilde{c} = cv$, $\tilde{\gamma}_c = \gamma_c/v\varepsilon$, $\tilde{\mathcal{E}} = \beta ev^{1/3}\mathcal{E}$, $u = \beta e\psi$, $\tilde{z} = z/v^{1/3}$, $\tilde{\sigma} = \sigma\beta ev^{1/3}/\varepsilon$, $\xi = l_B/v^{1/3}$ ($l_B = e^2/\varepsilon k_B T$ is the Bjerrum length). Effective linear size $v^{1/3}$ of the lattice gas cell has been chosen as a length scale. To perform the numerical calculations, following values of the physical parameters were taken $\varepsilon = 80$, $T = 300 \text{ K}$, $c = 0.1 \text{ mol/L}$, $v^{1/3} = 0.3 \text{ nm}$, which result in the following dimensionless parameters: $\tilde{c} = 1.63 \times 10^{-3}$, $\xi = 2.32$.

During the analysis of the DC behavior it was determined that increase in the co-solvent molecules polarizability leads to the increase in the DC in the region of the potentials, which values are lower than certain threshold value, close to the "saturation" potential u_{sat} (potential, at which the maximum of DC is realised). However, if the potential on the electrode exceeds that threshold value, then the increase in the polarizability, oppositely, causes a decrease in the DC (fig. 2a). On the contrary, when the polarizability becomes big enough, its increase leads to the continuous growth of the DC for all values of the electrode potential (fig. 2b). Such a behavior of the DC is determined by the fact that at the small values of the polarizability $\tilde{\gamma}_c$, the increase in the electrode potential results in expelling the co-solvent molecules from the double layer by the ions, which are attracted from the bulk solution. However, when the polarizability is large enough, the co-solvent molecules start to compete with the ions for the "space" in the vicinity of the electrode, so there is an excess of the co-solvent molecules in the double layer in comparison to the bulk solution. In addition, it is worth noting, that attraction of the co-solvent molecules, possessing induced dipole moments, from the bulk solution to the charged electrode happens due to the presence of the electric field gradient, which, in turn, appears due to the electrode charge screening by the oppositely charged ions. Analysis showed that increase in the bulk co-solvent concentration may lead to the

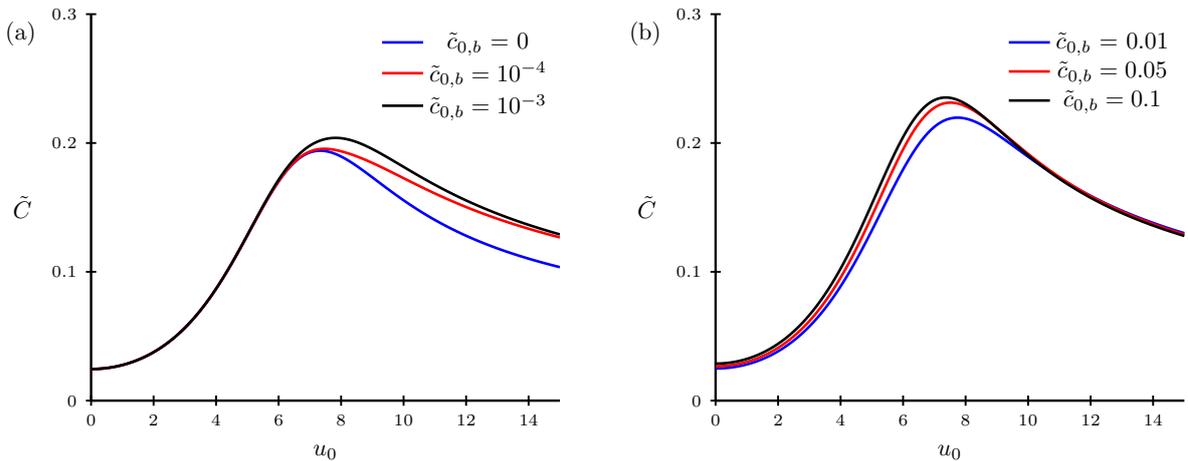


Figure 3: Differential electric capacitance $\tilde{C} = \tilde{C}(u_0)$ at different co-solvent concentrations in the bulk phase: (a) $\tilde{c}_{0,b} = 0, 10^{-4}, 10^{-3}$ and (b) $\tilde{c}_{0,b} = 0.01, 0.05, 0.1$. The data is shown for $\tilde{c} = 1.63 \times 10^{-3}$, $\xi = 2.32$, $\tilde{\gamma}_c = 0.3$.

shift of the saturation potential in two different ways. Namely, when the bulk co-solvent concentration is small enough, its increase leads to the shift of the maximum of $\tilde{C} = \tilde{C}(u_0)$ to the region of larger values of the electrode potential (fig. 3a). That means, that additive of the small amount of the polarizable co-solvent prevents DC from saturation. In the case of large enough co-solvent concentrations maximum of the DC profile shifts, alternatively, to the region of smaller potential values (fig. 3b). Then, the dependence of the saturation potential on the co-solvent concentration at the different polarizabilities has been studied. It was established, that non-monotonic behavior of the saturation potential with the co-solvent concentration in the bulk solution appears only when the polarizability is big enough. However, additive of the co-solvent with rather small polarizability leads to the monotonic decrease in the saturation potential.

Then, the comparison of the DC behavior, predicted by the theory without account for the excluded volume effect (formulated in the first part of the Chapter 1) and theory, based on the lattice gas model, was made. It was shown, that account for the excluded volume leads to the appearance of the maximum in the DC dependance on the electrode potential, which is in agreement with the Kornyshev theory [Kornyshev, J. Phys. Chem. B, 2007].

Finally, it was discussed how the additive of the polarizable co-solvent molecules and change of their polarizability affects on the profile of the electrostatic potential $u(\tilde{z})$. It was shown, that increase in the co-solvent polarizability leads to the slowdown of the decrement of the electrostatic potential. As in the theory without accounting for the excluded volume effect, this behavior could be explained by the continuous increase of the local dielectric permittivity on the electrode and, as follows, weakening of the screening effect of the electrode charge by the oppositely charged ions. Nevertheless, the increase of the co-solvent concentration could lead to the distinction in the behavior of the electrostatic potential profile from that obtained by the theory without excluded volume effect. That is, a small additive of the co-solvent to the bulk solution leads to the slowdown of the electrostatic potential decrease. However, if the co-solvent concentration is bigger than certain threshold value, then its further increase will lead to the decrease in the electrostatic potential, starting from a certain distance from the electrode. It was noted, that non-monotonic behavior of the potential profile with increase in the co-solvent concentration has a clear physical interpretation. Indeed, when the co-solvent concentration is small, its increase leads to the continuous growth of the local co-solvent concentration in the EDL, and, as a consequence, to the reduction of the electrode charge screening by the ions. However, at the big enough bulk co-solvent concentrations, from the certain distance from the electrode, attractive force between the electrode and polarizable molecules becomes smaller than repulsion force between these molecules and ions due to the excluded volume effect that leads to the decrease in the electrostatic potential values. Note that existence of the non-monotonic behavior of the potential profile with the co-solvent concentration is a new observation

as against to the simplified theory without account for the excluded volume effect (where the monotonic increase in the potential with the increase in the co-solvent concentration is realized), and is determined, as is easily seen, by the competition between the polarizability and the excluded volume effect.

In the conclusion of the Chapter 1 restrictions of the offered EDL models and their potential improvements are discussed, and also possible physical-chemical systems, which one can apply these models to, are mentioned. It was pointed out that the predicted effects of the co-solvent electronic polarizability are waiting for their experimental confirmation. In addition, it is noted that the proposed theory can be used as a theoretical framework for the modelling of the solubilization of the aromatic compounds (for instance, benzene) in aqueous solution by the charged micellar aggregates, formed by the ions of the amphiphilic imidasole ionic liquids.

Chapter 2

The situation with the liquid electrolytes – ionic liquids (IL) with a small addition of polar solvent molecules is of a great interest for the modern electrochemical applications. The importance of this problem determines by the fact, that IL, which in their pure state represent liquid electrolytes without solvent, are universal absorbents of the small molecules of any compounds. Addition of the small amount of polar organic solvent in IL is a conventional procedure, leading to the increase of the ionic mobility, increasing electric conductivity. On the other side, IL themselves can easily sorb different molecules from atmosphere, first of all, water molecules from the air. For chemical engineers the effect of the water absorption from the atmosphere is highly unfavorable, as it leads to the uncontrolled physical-chemical properties of IL, associated with the air humidity fluctuations. This problem is the most important for the electrochemistry. Indeed, one of the IL advantages is connected with the wide electrochemical window (range of the electrode potential values, where the solvent molecules are stable). It is assumed, that IL, confined in the area between two electrodes, does not participate in the electrochemical reactions, if it is used as an inert electrolyte for the initiation of the electrocatalytic reactions of the dissolved in it molecules. However, if there are water molecules in the form of impurity, they can participate in extraneous electrolysis reactions, which can interfere one in the investigation of the main electrochemical processes, proceeding on the electrodes. Such processes would take place in supercapacitors. In such a manner, researches, oriented at the practical use of IL, in the first place would like to know how the water molecules, absorbed by IL, would be distributed in the vicinity of the charged electrode. Thus, two fundamental questions arise:

- Will the water molecules, located in the IL volume, be adsorbed to the surface of the charged electrode?
- How will adsorption (electrosorption) be influenced by the electrode potential?

With the reference to the above mentioned, a classical density functional theory (DFT) of the IL with a small amount of the molecules of polar solvent is formulated in the Chapter 2. In contrast to the existing theories, in addition to the electrostatic interactions between the species, the short-range specific interactions have been taken into account. Formulated theory has been applied to the description of the flat EDL at the metal/IL interface. It has been shown, that unlike the classical self-consistent field theories for EDL without accounting for the specific short-range interactions, current theory allows one to describe DC behavior with the increase of the water concentration in the IL, recently discovered experimentally.

It is assumed that ions have charges $\pm e$ (e is the elementary charge), whereas the molecules of the polar solvent carry the permanent dipole moment p . Then, the grand thermodynamic potential of the system is written in the form

$$\Omega = - \int \frac{\varepsilon (\nabla\psi(\mathbf{r}))^2}{8\pi} d\mathbf{r} + \int \rho_c(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} - k_B T \int d\mathbf{r} c_0(\mathbf{r}) \ln \left(\frac{\sinh \beta p |\nabla\psi(\mathbf{r})|}{\beta p |\nabla\psi(\mathbf{r})|} \right)$$

$$\begin{aligned}
& -\frac{1}{2} \int d\mathbf{r} \sum_{i,j} A_{ij}^{-1} \phi_i(\mathbf{r}) \phi_j(\mathbf{r}) + \int d\mathbf{r} \sum_i c_i(\mathbf{r}) \phi_i(\mathbf{r}) + \int d\mathbf{r} \sum_i c_i(\mathbf{r}) W_i(\mathbf{r}) \\
& + \int (f(c_+(\mathbf{r}), c_-(\mathbf{r}), c_0(\mathbf{r})) - \mu_+ c_+(\mathbf{r}) - \mu_- c_-(\mathbf{r}) - \mu_0 c_0(\mathbf{r})) d\mathbf{r}, \tag{16}
\end{aligned}$$

where ε is the dielectric permittivity of the pure ionic liquid, $c_{\pm}(\mathbf{r})$ are the local ionic concentrations, $\rho_c(\mathbf{r}) = e(c_+(\mathbf{r}) - c_-(\mathbf{r})) + \rho_{ext}(\mathbf{r})$ is the local charge density, $c_0(\mathbf{r})$ is the local concentration of the polar solvent. First two terms determine the electrostatic energy of the ionic liquid. Third one is a free energy of the ideal gas of the dipolar molecules in the electric field with the strength $-\nabla\psi(\mathbf{r})$ according to the Langevin theory, $\beta = 1/k_B T$, k_B is the Boltzmann constant, T is the absolute temperature; the fourth and fifth terms describe the free energy of the short-range specific interactions between the components of the mixture, described by the "interaction matrix" A_{ij} ($i, j = \pm, 0$) and fictitious "potentials" $\phi_j(\mathbf{r})$ of the specific interactions ($j = \pm, 0$). The sixth term describes the energy of the mixture particles interactions with the external fields with potential energies $W_i(\mathbf{r})$. In the seventh term f determines the free energy density of the reference system, which in our case is the ternary mixture of the particles without specific and electrostatic interactions. Then, using local Legendre transformation as in the chapter 1 and varying the grand thermodynamic potential over the potentials ψ and ϕ_i , the following system of the self-consistent equations has been obtained:

$$\nabla(\varepsilon(\mathbf{r})\nabla\psi(\mathbf{r})) = -4\pi e (\bar{c}_+(\mathbf{r}) - \bar{c}_-(\mathbf{r})), \tag{17}$$

and

$$\phi_i(\mathbf{r}) = \sum_j A_{ij} \bar{c}_j(\mathbf{r}), \tag{18}$$

where

$$\varepsilon(\mathbf{r}) = \varepsilon + \frac{4\pi p^2}{k_B T} \bar{c}_0(\mathbf{r}) \frac{L(\beta p |\nabla\psi(\mathbf{r})|)}{\beta p |\nabla\psi(\mathbf{r})|} \tag{19}$$

is the local dielectric permittivity; $L(x) = \coth x - 1/x$ is the standard Langevin function;

$$\bar{c}_{\pm} = \frac{\partial P}{\partial \mu_{\pm}}, \quad \bar{c}_0 = \frac{\partial P}{\partial \mu_0} \tag{20}$$

are the local concentrations of the ions and solvent molecules. Potentials of the specific interactions $\phi_{i,b}$ in the bulk phase are calculated with the aid of the expression (18) for the concentrations of the mixture components in the bulk phase $c_{j,b}$.

Then, the case of the flat electrode is considered. For the basis system two independent lattice gases with equal effective cell volume v are chosen, so the mentioned above dependence of the pressure on the chemical potentials of species can be written in the form:

$$P(\mu_+, \mu_-, \mu_0) = \frac{k_B T}{v} \left(\ln \left(1 + e^{\beta \mu_+} + e^{\beta \mu_-} \right) + \ln \left(1 + e^{\beta \mu_0} \right) \right). \tag{21}$$

It has been noted, that such selection of the reference system is due to the fact that, generally, size of the molecules of the polar solvents (such as water or acetonitrile), added to the IL, have effective size much less than the size of the ions. This allows one to simulate solvent molecules as the particles of the lattice gas, lattice sites of which are located in the space between the IL ions. It has been also noted, that presence of the large space between the ions in IL is indirectly confirmed by the data of the small molecules solubility in them, such as carbon dioxide.

Parameters of the specific interactions are introduced using next expressions: $A_{++} = vA_c$, $A_{--} = vA_a$, $A_{+-} = A_{-+} = vA_{ca}$, and $A_{00} = vA_s$, $A_{0+} = A_{+0} = vB_{cs}$ и $A_{0-} = A_{-0} = vB_{as}$. It is noted, that the solution of the equation system (18) allows one to obtain potentials of the specific interactions as the functions of the local electrostatic potential $\psi(z)$ and electric field strength $\mathcal{E} = -\psi'(z)$, i.e. $\phi_i = \phi_i(\psi, \mathcal{E})$. Knowing these dependencies, one can calculate the component concentrations, using expressions (20). Then, the self-consistent field equation could be written in the following form:

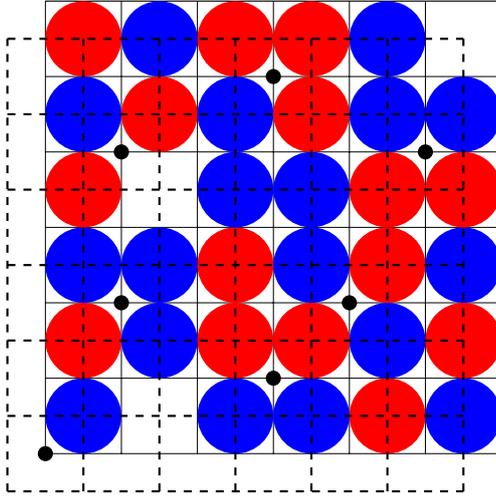


Figure 4: Schematic illustration of the ionic liquid model with a small addition of the polar solvent.

$$\frac{d}{dz} (\epsilon(z)\psi'(z)) = -\frac{2\pi e\gamma}{v} \frac{e^{\beta(\phi_{+,b}-\phi_{+}-e\psi-W_{+})} - e^{\beta(\phi_{-,b}-\phi_{-}+e\psi-W_{-})}}{1 - \gamma + \frac{\gamma}{2}[e^{\beta(\phi_{+,b}-\phi_{+}-e\psi-W_{+})} + e^{\beta(\phi_{-,b}-\phi_{-}+e\psi-W_{-})}]}, \quad (22)$$

where the following local dielectric permittivity

$$\epsilon(z) = \epsilon + \frac{4\pi p^2 \gamma_s}{k_B T v} \frac{\mathcal{G}(\beta p \mathcal{E}) e^{\beta(\phi_{0,b}-\phi_0-W_0)}}{1 - \gamma_s \left(1 - \frac{\sinh(\beta p \mathcal{E})}{\beta p \mathcal{E}} e^{\beta(\phi_{0,b}-\phi_0-W_0)}\right)} \quad (23)$$

is introduced, containing the auxiliary function $\mathcal{G}(x) = (\sinh(x)L(x))/x^2$; $\gamma = 2cv$ is the ion packing parameter [Kornyshev, J. Phys. Chem. B, 2007], $\gamma_s = c_{0,b}v$ is the packing parameter of the polar solvent molecules [Budkov, et al., Electrochimica Acta, 2018]. Equations (22) are complemented with the following boundary conditions:

$$\psi(0) = \psi_0, \quad \psi(\infty) = 0, \quad (24)$$

where ψ_0 is the electrode potential.

Surface charge density of the electrode is determined by the standard relation: $\sigma = \epsilon_{el}\mathcal{E}_s/4\pi$, where $\epsilon_{el} = \epsilon(0)$ и $\mathcal{E}_s = \mathcal{E}(0)$ – are values of the dielectric permittivity and the electric field at the electrode, respectively. DC is calculated by the conventional approach: $C = d\sigma/d\psi_0$. For the numerical calculations it is assumed that $W_{\pm}(z) = W_{c/a}H(l-z)$ and $W_0(z) = W_0H(l-z)$, where $H(z)$ is the Heaviside step-function and $W_{c/a} \leq 0$ are energies of the specific adsorption of the ions to the electrode; W_0 is solvophobicity of the electrode, if $W_0 > 0$ or the solvophilicity, if, on the opposite, $W_0 < 0$; l is the characteristic thickness, in the range of which the specific interactions of the ions and molecules with the electrode are relevant. For the simplicity we neglect specific interactions between the molecules of the polar solvent, i.e. consider $A_s = 0$. The latter condition is motivated by the fact that at small enough concentrations of the polar solvent, which are realizable in practice, specific interactions (such as hydrogen bonding in the case of water or alcohols) have a little effect on the DC.

Turning to the discussion of the numerical results, it is considered that the thickness, within which the specific interactions of the particles with the electrode are significant, is approximately equal to $l \simeq v^{1/3}$, i.e. is of the molecular size order. For numerical calculations, following physical parameters are chosen $\epsilon = 3.5$, $p = 1.8 D$, $T = 338 K$, $v^{1/3} = 0.7 nm$, $\gamma = 0.8$, $\gamma_s = 0.025$, $A_c = A_a = 50 k_B T$ and $A_{ca} = 0$, which are roughly equal to the parameters of the real IL with water addition. It is mentioned, that the values of the parameters of the cation-cation and anion-anion specific interactions are chosen in virtue of the adjusting theoretical values of the DC with experimental ones for the pure ionic liquid [Goodwin et al., Electrochimica Acta, 2017].

Three physically interesting cases are investigated (fig. 5): (1) IL without specific interactions ($B_{cs} = B_{as} = 0$), (2) hydrophobic IL ($B_{cs} > 0, B_{as} = 0$) and (3) hydrophillic IL ($B_{cs} = 0, B_{as} < 0$). It is shown, that in the absence of the specific ion-water interactions, the electrosorption curve is symmetric. In that case, an electric field gradient, occurring due to the screening of the electrode charge by the oppositely charged ions, leads to the attraction of the polar molecules to the electrode (so called dielectrophoretic force), so the increase in the electrode potential always leads to the continuous growth of the water concentration. However, the hydrophobic properties of the cation and hydrophillic properties of the anion result in strongly asymmetrical behavior of the DC. Indeed, at the positive electrode potentials, water concentration on the electrode increases in both cases, whereas at the negative potentials water concentration decreases, attains minimum and, then, begins to slowly grow.

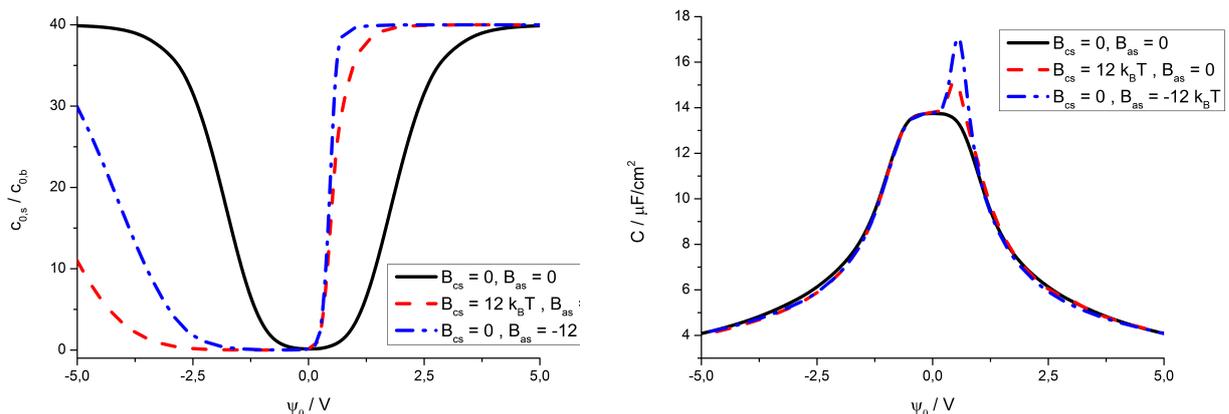


Figure 5: Dependence of the normalized water concentration (on the left) $c_{0,s}/c_{0,b}$ at electrode (electrosorption curves) and differential electric capacitance (on the right) on the electrode potential for three different cases: (1) ionic liquid without specific interactions (red line), (2) hydrophobic ionic liquid (black line) and (3) hydrophillic ionic liquid (blue line). The data is shown for $\gamma = 0.8$, $\gamma_s = 0.025$, $A_c = A_a = 50 k_B T$, $A_{cs} = 0$, $A_s = 0$, $W_0 = 2 k_B T$.

Then, it is described, how behavior of the local water concentration influences on the DC. In the case, when anion-water and cation-water specific interactions are absent, the graph for the DC dependence on the electrode potential presents a standard bell-shaped form (fig. 5). However, inclusion of the strong short-range specific interactions of the ions with the water molecules changes the behavior of the DC qualitatively. In both cases of the hydrophobic and the hydrophillic IL there is a pronounced satellite maximum on DC in the region of the positive electrode potentials. However, at the negative electrode potentials, presence of the specific interactions between the ions and water molecules does not lead to new effects. Occurrence of the satellite maximum at the positive electrode potentials is determined by the fact, that in the case of both hydrophillic and hydrophobic IL, increase of the electrode potential leads to the abrupt increase in the local concentration of the water molecules. However, significantly lower value of the water concentration on the electrode in comparison to the concentration in the bulk phase at small negative potentials and slow growth of the water concentration at large enough potentials in its absolute value leads to the standard bell-shaped profile of the DEC.

It is established, that increase of the water concentration in the bulk phase leads to the continuous growth of the water concentration on the electrode and more pronounced satellite maximum on the DC curves. It is noted that such behavior of DC is in qualitative agreement with the experimental behavior for the IL with small additive of water, presented in recent works [Wippermann et al., Phys. Chem. Chem. Phys., 2017; Friedl et al, ChemElectroChem, 2017].

Then, it has been shown that increase in the electrode hydrophobicity W_0 leads to the quite expected electrosorption curves behavior: continuous decrease of the water concentration on the

electrode at all values of the electrode potential. The same trends are seen for hydrophobic IL. Finally, it has been discussed how specific adsorption of the ions to the electrode influences on the DEC. For simplicity a case of the IL without impurities is investigated, with account of the specific adsorption of the cations to the electrode. It has been established that increase (in absolute value) of the energy of the specific adsorption of ions to the electrode ($W_c < 0$) leads to the shift of the DC maximum into the region of the positive potential values. It can be explained by the fact that specific adsorption of the cations to the electrode leads to the fact, that, even at zero potential, the electrode charge will not be equal to zero. Such a behavior of the DC is in the full agreement with the results of self-consistent field theory, proposed recently in the paper [Uematsu, et al. J. Phys.: Condens. Matter, 2018].

In the conclusion of the Chapter 2 it is noted that formulated phenomenological theory will serve as a foundation for the following experimental and theoretical investigations of the ILs, mixed with polar solvents, located on the charged electrodes, and will be useful for the interpretations of the future experimental and numerical results.

Chapter 3

The existing statistical theories of polar fluids describe molecules as the point dipoles [Abrashkin et al., Phys. Rev. Lett., Coalson, Duncan, J. Phys. Chem., 1996] or hard spheres with the point dipole in its center [Levin, Phys. Rev. Lett., 1999]. As is well known, disregard of the details of the internal electrical structure of the polar molecules in the calculations of the electrostatic free energy of the polar fluid from the first principles of statistical mechanics leads to its "ultraviolet divergence", which makes researches resort to the artificial "ultraviolet cut-off", while integrating over the vectors of the reciprocal space [Levy, et al., Phys. Rev. Lett., 2012; Budkov et al., Eur. Phys. J. E, 2017]. On the other hand, a "local" theory without consideration of the charge distribution inside the polar molecule, does not allow one to describe the behavior of the point charge potential, surrounded by the polar molecules, at the distances of its linear size order. One can expect that "non-local" statistical theory, taking such details into account, will be spared from the ultraviolet divergence of the free energy, taking place in the local theories, and will allow one to investigate the behavior of the electrostatic potential at the distances from the test point charge, that are comparable with the characteristic distances between charged centers of the polar particles. On the other side, the latest achievements in the experimental studies of the different organic compounds (such as proteins, betains, zwitterionic liquids, etc.), containing long enough polar groups ($\sim 5 - 20$ nm), challenge statistical physics to develop analytical approaches for the modelling of the polar particles not as point ones, but as a combination of the charge centers with fixed or fluctuating distances between them.

With reference to the above mentioned, a non-local statistical theory of the polar molecules, located in the electrolyte solution medium is formulated in the Chapter 3. The electrolyte solution (further, for simplicity, salt) is investigated with N_+ point cations with charges $q_+ > 0$, N_- point anions with charges $q_- < 0$ and N_d dipolar particles with point ionic groups with charges $\pm e$ (e is the elementary charge), confined in the volume V at temperature T . Let the number of ions N_{\pm} satisfy condition of the electrical neutrality $q_+ N_+ + q_- N_- = 0$. It is considered, that particles are located in solvent, which is modelled as a continuous dielectric medium with the constant dielectric permittivity ε . It is postulated, that there is a probability distribution function $g(\mathbf{r})$, associated with each dipolar particle, of the distance between charge centres. Taking into account mentioned model assumptions, a configurational integral of the mixture is written in the following form:

$$Q = \int d\Gamma_d \int d\Gamma_s \exp[-\beta H], \quad (25)$$

where

$$\int d\Gamma_d(\cdot) = \int \prod_{j=1}^{N_d} \frac{d\mathbf{r}_j^{(+)} d\mathbf{r}_j^{(-)}}{V} g(\mathbf{r}_j^{(+)} - \mathbf{r}_j^{(-)})(\cdot) \quad (26)$$

is the measure of integration over the coordinates $\mathbf{r}_j^{(\pm)}$ of the ionic groups with the mentioned above probability distribution function $g(\mathbf{r})$, which, from its definition, must satisfy the normalization condition:

$$\int g(\mathbf{r})d\mathbf{r} = 1, \quad (27)$$

and

$$\int d\Gamma_s(\cdot) = \frac{1}{V^{N_++N_-}} \int \prod_{l=1}^{N_+} d\mathbf{r}_l^{(+)} \int \prod_{k=1}^{N_-} d\mathbf{r}_k^{(-)}(\cdot) \quad (28)$$

is the integration measure over the coordinates of the salt ions; $\beta = 1/k_B T$, k_B is the Boltzmann constant. Energy of the electrostatic interactions is written in the form:

$$H = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \hat{\rho}(\mathbf{r}) G_0(\mathbf{r} - \mathbf{r}') \hat{\rho}(\mathbf{r}') = \frac{1}{2} (\hat{\rho} G_0 \hat{\rho}), \quad (29)$$

where $G_0(\mathbf{r} - \mathbf{r}') = 1/(\varepsilon|\mathbf{r} - \mathbf{r}'|)$ is the Green function of the Poisson equation and

$$\hat{\rho}(\mathbf{r}) = e \sum_{j=1}^{N_d} (\delta(\mathbf{r} - \mathbf{r}_j^{(+)})) - \delta(\mathbf{r} - \mathbf{r}_j^{(-)}) + q_+ \sum_{k=1}^{N_+} \delta(\mathbf{r} - \mathbf{r}_k^{(+)}) + q_- \sum_{l=1}^{N_-} \delta(\mathbf{r} - \mathbf{r}_l^{(-)}) + \rho_{ext}(\mathbf{r}) \quad (30)$$

is the full charge density of the system, consisting of the microscopic charge density of the polar particles and ions (first, second and third terms) and charge density of the external charges (forth term). Also note, that in the work the contribution of the repulsion forces between the particles is neglected. It can be justified by the rather small concentrations of salt and polar particles. Using the standard Hubbard-Stratonovich transformation, in the thermodynamical limit

$$V \rightarrow \infty, N_{d,\pm} \rightarrow \infty, N_{d,\pm}/V \rightarrow n_{d,\pm},$$

the following representation of the configurational integral in the form of the functional integral has been obtained:

$$Q = \int \frac{\mathcal{D}\varphi}{C} \exp \{-S[\varphi]\}, \quad (31)$$

where the following functional is introduced:

$$S[\varphi] = \frac{\beta}{2} (\varphi G_0^{-1} \varphi) - i\beta (\rho_{ext} \varphi) - n_d \int d\mathbf{r} \int d\mathbf{r}' g(\mathbf{r} - \mathbf{r}') (\exp [i\beta e(\varphi(\mathbf{r}) - \varphi(\mathbf{r}'))] - 1) - n_+ \int d\mathbf{r} (\exp [i\beta q_+ \varphi(\mathbf{r})] - 1) - n_- \int d\mathbf{r} (\exp [i\beta q_- \varphi(\mathbf{r})] - 1). \quad (32)$$

Further, it is shown, that obtained integrand functional $S[\varphi]$ in the case of the polar particles with hard geometrical structure passes into the well-known Poisson-Boltzmann-Langevin functional [refer to Abrashkin et al., PRL, 2007; Coalson, et al., J. Phys. Chem., 1996].

Then, in the mean field approximation the self-consistent field equation

$$-\frac{\varepsilon}{4\pi} \Delta \psi(\mathbf{r}) = 2n_d e \int d\mathbf{r}' g(\mathbf{r} - \mathbf{r}') \sinh \frac{e(\psi(\mathbf{r}') - \psi(\mathbf{r}))}{k_B T} + q_+ n_+ \exp [-\beta q_+ \psi(\mathbf{r})] + q_- n_- \exp [-\beta q_- \psi(\mathbf{r})] + \rho_{ext}(\mathbf{r}) \quad (33)$$

for the electrostatic potential $\psi(\mathbf{r})$ and the expression for the electrostatic free energy

$$F_{el}^{(MF)} = k_B T S[i\psi] \quad (34)$$

have been obtained.

Then, within the approximation of the weak electrostatic interactions $e\psi(\mathbf{r})/k_B T \ll 1$, solving the self-consistent field equation (33), the expression for the electrostatic potential of the test point ion with the charge q was obtained

$$\psi(\mathbf{r}) = \frac{4\pi q}{\varepsilon} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{e^{i\mathbf{k}\mathbf{r}}}{k^2 + \varkappa^2(\mathbf{k})}, \quad (35)$$

where

$$\kappa^2(\mathbf{k}) = \kappa_s^2 + \frac{8\pi n_d e^2}{\varepsilon k_B T} (1 - g(\mathbf{k})) \quad (36)$$

is a screening function, and

$$g(\mathbf{k}) = \int d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} g(\mathbf{r}) \quad (37)$$

is the characteristic function of the distribution; $I = (q_+^2 n_+ + q_-^2 n_-) / 2e^2$ is the ionic strength of the solution. For the model characteristic function

$$g(\mathbf{k}) = \frac{1}{1 + \frac{k^2 l^2}{6}}, \quad (38)$$

determining the following distribution function

$$g(\mathbf{r}) = \frac{3}{2\pi l^2 r} \exp\left(-\frac{\sqrt{6}r}{l}\right), \quad (39)$$

where $r = |\mathbf{r}|$, in the absence of the ions ($n_{\pm} = 0$), following expression for the electrostatic potential of the point charge was obtained:

$$\psi(\mathbf{r}) = \frac{q}{\varepsilon_{loc} r}, \quad (40)$$

where

$$\varepsilon_{loc}(r) = \frac{\varepsilon(1 + y_d)}{1 + y_d \exp\left(-\frac{r}{l_s}\right)} \quad (41)$$

is the local dielectric permittivity; $y_d = 4\pi n_d e^2 l^2 / (3\varepsilon k_B T) = l^2 / 6r_D^2$ is the dimensionless parameter, determining a "strength" of the dipole-dipole electrostatic interaction and $l_s = l / \sqrt{6\varepsilon(1 + y_d)}$; $r_D = (8\pi n_d e^2 / \varepsilon k_B T)^{-1/2}$ is the effective Debye screening length, associated with the charged centers of the polar particles. Thus, the length l_s determines a radius of the sphere around the point charge, within which the dielectric permittivity is smaller than its bulk value, determined by the relation

$$\varepsilon_b = \varepsilon(1 + y_d) = \varepsilon + \frac{4\pi n_d e^2 l^2}{3k_B T}. \quad (42)$$

Thus, it is found, that length l_s can be interpreted as the effective solvation radius of the point charge, surrounded by the dipoles, within the linear response theory.

With the presence of the salt ions in the bulk phase of the solution following expression for the electrostatic potential has been obtained

$$\psi(\mathbf{r}) = \frac{q}{\varepsilon r} \left(u(y_d, y_s) e^{-\kappa_1(y_d, y_s)r} + (1 - u(y_d, y_s)) e^{-\kappa_2(y_d, y_s)r} \right), \quad (43)$$

where

$$\kappa_{1,2}(y_d, y_s) = \frac{\sqrt{3}}{l} \left(1 + y_s + y_d \pm \sqrt{(1 + y_s + y_d)^2 - 4y_s} \right)^{1/2}, \quad y_s = \frac{\kappa_s^2 l^2}{6}, \quad (44)$$

$$u(y_d, y_s) = \frac{y_s + y_d + \sqrt{(1 + y_s + y_d)^2 - 4y_s} - 1}{2\sqrt{(1 + y_s + y_d)^2 - 4y_s}}, \quad (45)$$

which transforms into the expression (40) at $y_s = 0$. In the absence of the polar particles ($y_d = 0$) we obtain standard Debye-Huckel (DH) potential:

$$\psi(\mathbf{r}) = \frac{q}{\varepsilon r} e^{-\kappa_s r}. \quad (46)$$

Then, after simple algebraic transformations it has been shown that mean-field electrostatic free energy within the linear approximation takes the form:

$$F_{el}^{(MF)} = \frac{1}{2} \int d\mathbf{r} \rho_{ext}(\mathbf{r}) \psi(\mathbf{r}). \quad (47)$$

To obtain the expression for the solvation free energy of the test ion, one has to subtract its self-energy from the electrostatic free energy, i.e.

$$\Delta F_{solv} = \frac{1}{2} \int d\mathbf{r} \rho_{ext}(\mathbf{r}) (\psi(\mathbf{r}) - \psi_{ext}(\mathbf{r})) = -\frac{q^2}{2\varepsilon} (u(y_d, y_s)(\kappa_1(y_d, y_s) - \kappa_2(y_d, y_s)) + \kappa_2(y_d, y_s)). \quad (48)$$

It has been shown, that in the absence of the salt ions ($y_s = 0$) in the solution, the expression for the solvation free energy (48) of the test charge takes the form

$$\Delta F_{solv} = -\frac{q^2}{2\varepsilon R} \frac{y_d}{\sqrt{1 + y_d}}, \quad (49)$$

where $R = l/\sqrt{6}$ is the mean-square distance between the ionic groups of the dipolar particles.

Basing on the obtained analytical results, the numerical analysis of the point charge potential, surrounded by the dipolar particles only, and with the presence of the salt ions in the bulk solution has been carried. It has been shown, that presence of the long enough dipolar particles in the solution leads to the significant deviation of the electrostatic potential from the Coulomb (in the absence of salt) and DH (in the presence of salt) laws. It has been shown, that in both cases increase of the dipolar particles concentration leads to the shift of the potential profile to the region of the smaller distances. The latter is associated with the occurrence of the additional screening of the test ion charge due to the presence of the charged centers of dipolar particles in its vicinity. Besides that, the behavior of the electrostatic potential of the test point ion in the aqueous salt-free solution of the dipolar particles with dipole moments, corresponding to those of the protein molecules ($p \approx 1000 D$), was investigated. It has been found, that effects of non-locality become significant at the distances of $r \sim 1 - 2 nm$, which are much smaller than dipole length $l = 20 nm$, but, nevertheless, are big enough in the comparison with the characteristic sizes of the solvent molecules.

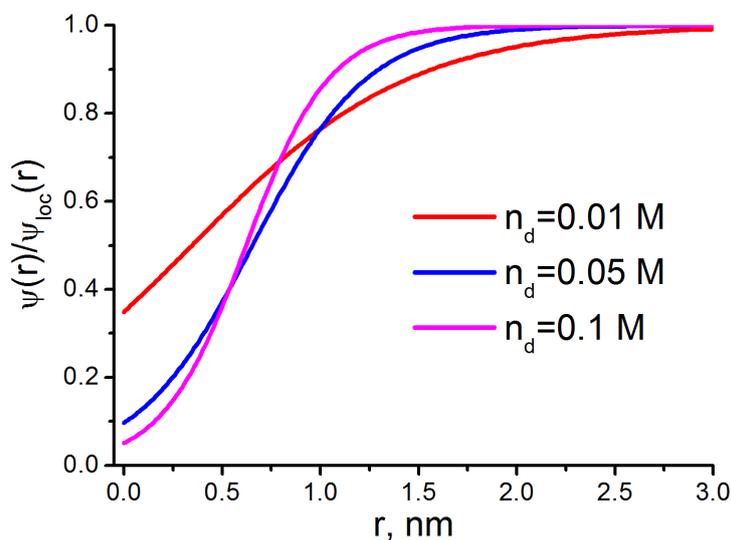


Figure 6: Ratio of the electrostatic potential $\psi(\mathbf{r})$ of the point charge in the dipolar particles surrounding, obtained within the non-local theory, to the potential $\psi_{loc}(\mathbf{r})$, obtained within the local theory, as a function of the distance, at different concentrations n_d of the dipolar particles. The data is shown for $l = 20 nm$, $\varepsilon = 80$, $T = 300 K$.

Then, the evaluation of the electrostatic free energy of the ion-dipole mixture within the Gaussian approximation (GA) was formulated. Expanding the functional $S[\varphi]$ in (31) into a power series near a mean-field $\varphi(\mathbf{r}) = i\psi(\mathbf{r})$ and truncating it at the quadratic term over the potential φ , following

expression has been obtained:

$$Q \approx \exp \{-S[i\psi]\} \int \frac{\mathcal{D}\varphi}{C} \exp \left[-\frac{\beta}{2} (\varphi \mathcal{G}^{-1} \varphi) \right], \quad (50)$$

where

$$\mathcal{G}^{-1}(\mathbf{r}, \mathbf{r}' | \psi) = k_B T \frac{\delta^2 S[i\psi]}{\delta \varphi(\mathbf{r}) \delta \varphi(\mathbf{r}')}$$

is the renormalized reciprocal Green function with the mean-field electrostatic potential $\psi(\mathbf{r})$, satisfying the equation (33). Thus, evaluating the Gaussian functional integral using the standard methods, the following general relation for the configuration integral within GA has been obtained:

$$Q \approx \exp \left\{ -S[i\psi] + \frac{1}{2} \text{tr} (\ln \mathcal{G} - \ln G_0) \right\}, \quad (51)$$

where symbol $\text{tr}(\dots)$ means the trace of the integral operator. In the absence of the external charges (i.e., $\rho_{ext}(\mathbf{r}) = 0$), electrostatic potential $\psi(\mathbf{r}) = 0$, so the mean-field contribution to the electrostatic free energy $F_{el}^{(MF)} = k_B T S[0] = 0$. Thus, in this case the electrostatic free energy is fully determined by the thermal fluctuations of the electrostatic potential near its zero value and adopts the following form:

$$F_{el} = \frac{V k_B T}{2} \int \frac{d\mathbf{k}}{(2\pi)^3} \left(\ln \left(1 + \frac{\varkappa^2(\mathbf{k})}{k^2} \right) - \frac{\varkappa^2(\mathbf{k})}{k^2} \right), \quad (52)$$

where screening function $\varkappa^2(\mathbf{k})$ is determined by the expression (36). For the distribution function, defined by the relation (38), in the absence of the ions in system, the integral in (52) is calculated analytically:

$$F_{el} = -\frac{V k_B T}{l^3} \sigma(y_d), \quad (53)$$

where the following auxiliary dimensionless function is introduced:

$$\sigma(y_d) = \frac{\sqrt{6}}{4\pi} (2(1 + y_d)^{3/2} - 2 - 3y_d). \quad (54)$$

Electrostatic free energy of the solution of the dipolar particles has been analysed in two limiting regimes, resulting from (53-54), that is:

$$\frac{F_{el}}{V k_B T} = \begin{cases} -\frac{\sqrt{6}\pi e^4 \ln_d^2}{3(\epsilon k_B T)^2}, y_d \ll 1 \\ -\frac{1}{12\pi r_D^3}, y_d \gg 1. \end{cases} \quad (55)$$

It is noted, that in the first regime the gas of the dipolar particles, interacting via the Keesom potential, is realized, whereas in the second regime the charged groups of the dipolar particles can be considered as unbound ions, so the electrostatic free energy is described by the DH limiting law.

Then the limiting regimes of the electrostatic free energy behavior in the presence of the salt ions at $y_d \ll 1$ and $y_d \gg 1$ have been analysed. At $y_d \ll 1$ the result is

$$\frac{F_{el}}{V k_B T} = -\frac{\kappa_s^3}{12\pi} - \frac{3\sqrt{6}}{2\pi l^3} \frac{y_s}{1 + \sqrt{y_s}} y_d - \frac{3\sqrt{6}}{16\pi l^3} \frac{1 + 3\sqrt{y_s} + y_s}{(1 + \sqrt{y_s})^3} y_d^2 + O(y_d^3), \quad (56)$$

where the first term in the right-hand side describes the contribution of the ionic species to the electrostatic free energy within the DH approximation. The second and third terms describe the contributions of the ion-dipole and dipole-dipole pair correlations, respectively. In the opposite regime, when the $y_d \gg 1$, we arrive to the DH limiting law:

$$\frac{F_{el}}{V k_B T} \simeq -\frac{1}{12\pi} \left(\frac{8\pi(n_d + I)e^2}{\epsilon k_B T} \right)^{3/2}. \quad (57)$$

It is worth noting, that in this case the charged groups of the polar particles behave as unbounded ions, participating in the screening of the charge along with the salt ions.

In the conclusion of the Chapter 3 it is noted, that developed formalism is unclosed, as it contains undefined probability distribution function $g(\mathbf{r})$ of the distance between ionic groups of the dipolar particles. Thus, for the applications of the obtained relations for the thermodynamic description of the real polar fluids, it is necessary to independently determine the distribution function $g(\mathbf{r})$. It is noted, that for this purpose it is necessary to solve a quantum-mechanical problem on the determination of the orbitals of the ionic groups of the isolated dipolar particle (for example, using the Hartree-Fock method), which, in their turn, will allow one to evaluate desired distribution function. Besides that, possibilities of the applications of the developed formalism is discussed. It is noted, that current formalism could be applied to the description of the phase behavior of the polar fluids with the consideration of the formation of the chain clusters of the polar particles, their dispersion and excluded volume interactions. Finally, it is mentioned that the theory can be easily generalized for the description of the polar particles mixtures, and also for the particles with arbitrary electrical structure.

Chapter 4

It is well known from the experimental research (for reference [Mel'nikov, et al. J. Am. Chem. Soc., 1999]) and molecular dynamic simulations [Gavrilov et al., *Macromolecules*, 2016], that in the dilute salt-free solutions of the flexible polyelectrolytes in the regime of good solvent a coil-globule (CG) transition can take place. Such unconventional conformational transition is usually accompanied by the counterion condensation onto the backbone of the polyelectrolyte macromolecule, which reflects its electrostatic nature. Besides, considering that transition takes place in the regime of good solvent, i.e. when polyelectrolyte is highly soluble, we can not apply classical models of the CG transition, based on the concept of theta-temperature, for its description.

Nowadays, there are two possible mechanisms of the CG transition in the dilute polyelectrolyte solutions are proposed. The first one, "coulomb" mechanism (ref. [Brilliantov et al., *Phys. Rev. Lett.*, 1998]) is based on the idea, that this transition is caused by strong electrostatic correlations of the counterions. In more details, when characteristic electrostatic energy becomes much larger than thermal energy $k_B T$, it becomes thermodynamically profitable for the counterions to "adsorb" onto the polymer "surface", neutralizing its charge. Within this mechanism, counterions are not localised on the monomers, but can freely move along the polymer backbone. Despite full neutralization of the macromolecule charge due to the counterion condensation, the thermal fluctuations of the charge density near its zero value have to take place due to the thermal motion of the counterions. These fluctuations of the charge density, in their turn, lead to the cooperative mutual attraction of the monomers (so-called Kirkwood-Shumakher interaction [Kirkwood, Shumakher, *Proc. Natl. Acad. Sci. USA.*, 1952]), resulting in the CG transition. Because of the fact, that this transition takes place in the region of the strong electrostatic interactions, electrostatic contribution to the total free energy of the system must be taken into account beyond the Debye-Huckel (DH) theory, which is valid, as it is well known, in the region of the weak electrostatic interactions. A successful attempt to describe such electrostatic CG transition beyond the DH theory for the first time was made in the paper [Brilliantov et al., *Phys. Rev. Lett.*, 1998], where a Flory-de Gennes type theory of the strongly charged polyelectrolyte chain was formulated. It is worth noting, that accounting for the electrostatic correlations of the counterions within the one-component plasm (OCP) model allowed one to understand the scaling laws for the gyration radius of the polyelectrolyte chain, obtained recently within the MD simulation [Tom et al., *Phys. Rev. Lett.*, 2016].

The second, "dipole" mechanism is based on the assumption, that CG transition happens due to the attraction of the thermally fluctuating dipole moments, appearing along the polymer chain backbone due to the counterion condensation. This mechanism was for the first time proposed in the paper [Schiessel and Pincus, *Macromolecules*, 1998] and was studied timorously in the following papers. However, in all existing theoretical models the dipole correlations are considered at the pairwise approximation level: through the renormalization of the second virial coefficient of the volume interactions of the monomers due to the existence of the effective Keesom attraction, occurring between the polar particles at the long distances, or with the aid of the addition of the effective Keesom pair potential to the potential of the volume interactions. However, as is well known from

the theory of polar molecules, the dipole correlations could be described at the Keesom attraction level only when the average distance between the dipoles are much bigger than the dipole length (the case of the dipole gas or dilute solution of the polar molecules). For the polymer solutions this condition, obviously, can be realized only for the case of the coil conformation of the macromolecule. Though, approaching the globule conformation of the polymer, it is crucial to consider the many-body dipole correlations, leading to, strictly speaking, renormalization of each virial coefficient. Beyond that, in all of the available theoretical works, related to the dipole mechanism of the collapse, a presence of the constant dipole moments on the monomers has been taken into account only in the electrostatic free energy of the polymer chain, although the dipole structure of the monomers, formally, must also influence on the excluded volume contribution. Indeed, for example, varying the counterion diameter in the solutions of weak polyelectrolytes, we will affect not only the electrostatic interactions of the monomers (due to the change of the dipole moment), but also the value of the effective excluded volume of the monomer. Hereby, the equilibrium conformation of the dipolar polymer chain must be defined mostly by the competition between the contributions of the electrostatic interactions and excluded volume interactions. Physically, in the real polyelectrolyte solutions both mechanisms of collapse may be realized.

Which mechanism will be implemented in the real polyelectrolyte solutions is dependent on the chemical specifics of the monomers and counterions. From the general considerations it is clear, that coulomb mechanism can take place in the strong polyelectrolyte solutions, where the complete dissociation of the monomers takes place, whereas the dipole mechanism – in the weak polyelectrolyte solutions, where the counterions are localized on the monomers, forming solvent-separated ionic pairs (dipolar particles). Thus, both mechanisms must be closely investigated using the methods of the statistical physics. However, statistical theory of the CG transition of the polymer chain, induced by the dipole-dipole interactions of the monomers, with regard to the many-body dipole correlations, has not been developed until recently in contrast to the theory of coulomb collapse. As such, in the Chapter 4 the statistical theory of the conformational behavior of the flexible polymer chain, carrying on its monomers constant dipole moments, with accounting for the many-body dipole correlations, has been developed.

A flexible polymer chain is considered, consisting of N monomers, representing a hard sphere of the diameter σ_p and charge e , connected with the spherical counterion of the diameter σ_c and charge $-e$. Herewith, counterion can freely rotate around the polymer backbone, keeping the fixed distance $d = (\sigma_p + \sigma_c)/2$ from the monomer. Thus, all monomers of the polymer chain contain freely rotating dipoles with constant dipole moments ed . It was assumed, that polymer chain is located in the low-molecular solvent, which is modeled as a continuous dielectric medium with a constant dielectric permittivity ε . To describe conformational behavior of the dipolar polymer chain, following the methodology, proposed in the papers by Flory and de Gennes, the free energy of the polymer chain as a function of its gyration radius R_g was constructed:

$$F(R_g) = F_{conf}(R_g) + F_{ev}(R_g) + F_{el}(R_g), \quad (58)$$

where

$$F_{conf}(R_g) = \frac{9}{4}k_B T \left(\frac{6R_g^2}{Nb^2} + \frac{Nb^2}{6R_g^2} \right) \quad (59)$$

is interpolation formula for the conformational free energy of the gaussian polymer chain with the fixed gyration radius (ref. [Fixman, J. Chem. Phys., 1962; Budkov, Kolesnikov, J. Stat. Mech., 2016]). The chain bond length is fixed and set to $b = \sigma_p$. The contribution of the excluded volume interactions is estimated by the virial expansion, truncated at the third term:

$$F_{ev}(R_g) = Nk_B T \left(\frac{NB}{V_g} + \frac{N^2C}{V_g^2} \right), \quad (60)$$

where $V_g = 4\pi R_g^3/3$ is the gyration volume, B and C are the second and third virial coefficients of the excluded volume interactions, respectively. The last ones are estimated as the coefficients of the hard dumbbells [Boublik et al., J. Chem. Phys., 1990]:

$$B = v(1 + 3\alpha_c), \quad C = v^2(3\alpha_c^2 + 6\alpha_c + 1)/2, \quad (61)$$

where $v = \pi(\sigma_c^3 + \sigma_p^3)/6$ is the dumbbell volume and $\alpha_c = R_c S_c / 3V_c$ is the non-sphericity parameter of the convex body. Geometrical parameters R_c , S_c and V_c , characterising every convex body, for the dumbbells take the following form [Boublik et al., J. Chem. Phys., 1990]:

$$R_c = \frac{\sigma_p^2 + \sigma_c^2 + \sigma_p \sigma_c}{2(\sigma_p + \sigma_c)}, \quad S_c = \frac{\pi}{2} (\sigma_p + \sigma_c)^2, \quad V_c = \frac{\pi}{24} (\sigma_p + \sigma_c)^3. \quad (62)$$

For estimation of the electrostatic interactions contribution to the total free energy the mutual influence of the connectivity effect of the monomers and their electrostatic correlations is neglected. Electrostatic free energy $F_{el}(R_g)$ is calculated within the modified gaussian approximation (MGA) [Gordievskaya, et al., Soft Matter, 2018] for the unbound dipole particles:

$$F_{el}(R_g) \simeq \frac{V_g k_B T}{2} \int_{|\mathbf{k}| < \Lambda} \frac{d\mathbf{k}}{(2\pi)^3} \left(\ln \left(1 + \frac{\chi^2(\mathbf{k})}{k^2} \right) - \frac{\chi^2(\mathbf{k})}{k^2} \right), \quad (63)$$

where the screening function takes the form (ref. to description of the Chapter 3)

$$\chi^2(\mathbf{k}) = \kappa_D^2 (1 - g(\mathbf{k})), \quad (64)$$

where the square of the reciprocal Debye screening length $\kappa_D^2 = 8\pi l_B \rho_p$ is introduced; $l_B = e^2 / \epsilon k_B T$ is the Bjerrum length; k_B is the Boltzmann constant; T is the absolute temperature, ϵ is the solvent dielectric permittivity. For the exception of the nonphysical modes from the summation (integration) over the wave vectors \mathbf{k} , corresponding to the small distances between the mass centers of the dipolar particles, the ultraviolet cut-off is introduced, i.e. maximal wave vector $\Lambda = 2\pi/r_s = (6\pi^2 \rho_p)^{1/3}$, where $r_s = (3/4\pi \rho_p)^{1/3}$ is the radius of the sphere, containing exactly one monomer (Wigner-Seitz radius) and $\rho_p = N/V_g$ is the average concentration of the monomers. It is noted, that introducing the ultraviolet cut-off, associated with the average distance between particles, substantially widens the region of the GA application, including region of the strong electrostatic interactions [Brilliantov, Contrib. Plasma Phys., 1998; Gordievskaya, et al., Soft Matter, 2018]. Then, using the model characteristic function of the distribution over the distance between ionic groups of the dipolar monomers, such as in the Chapter 3, i.e. $g(\mathbf{k}) = 1/(1 + k^2 d^2/6)$ and taking into account, that $\Lambda = (6\pi^2 \rho_p)^{1/3}$, the following analytical expression has been obtained:

$$F_{el} = \frac{k_B T V_g}{d^3} \sigma(y_d, \theta), \quad (65)$$

where

$$\sigma(y_d, \theta) = \frac{\sqrt{6}}{2\pi^2} \theta^3 \ln \left(1 + \frac{y_d}{1 + \theta^2} \right) + \frac{\sqrt{6}}{2\pi^2} \left((2 + 3y_d) \arctan \theta - 2(1 + y_d)^{3/2} \arctan \left(\frac{\theta}{\sqrt{1 + y_d}} \right) - \theta y_d \right), \quad (66)$$

with $y_d = \kappa_D^2 d^2 / 6 = l_B d^2 N / R_g^3$ and $\theta = \Lambda d / \sqrt{6} = (9\pi/2)^{1/3} N^{1/3} d / (\sqrt{6} R_g)$.

Then, the limiting regimes, following from the interpolation formula (65), are discussed:

$$\frac{F_{el}}{V_g k_B T} \simeq \begin{cases} - \left(\frac{48}{\pi} \right)^{1/3} l_B \rho_p^{4/3}, & 1 \ll \theta^2 \ll y_d \\ - \frac{1}{12\pi r_D^3}, & 1 \ll y_d \ll \theta^2 \\ - \frac{\sqrt{6}\pi}{3} l_B^2 d \rho_p^2, & y_d \ll 1. \end{cases} \quad (67)$$

It is noted that in the first regime ($r_D \ll r_s \ll d$) the amorphous structure of the densely packed polar groups, which act as unbounded ions, is realized. In the second regime ($r_s \ll r_D \ll d$), as in the first one, the polar groups also can be considered as the free ions. However, here polar groups must be organized as in the dilute electrolyte solution, so the electrostatic free energy is described by the DH limiting law. Finally, the third regime occurs at the condition $r_D \gg d$, at which there is no screening of the charge at all in the system, and the electrostatic correlations of the monomers are reduced to the effective pairwise-additive Keesom attraction of the dipolar particles, which leads to

the renormalization (decrease) of the second virial coefficient of the monomer-monomer interaction. Then, it is shown that for the globular conformation the first two regimes, mentioned in (67), can be implemented. For the case, when $r_D \ll r_s \ll d$, the following scaling law for the gyration radius takes place

$$R_g \sim B^{1/2} l_B^{-1/2} N^{1/3}. \quad (68)$$

In the second regime ($r_s \ll r_D \ll d$) the result is:

$$R_g \sim B^{2/3} l_B^{-1} N^{1/3}. \quad (69)$$

For the coil conformation following relation, up to the numerical prefactor, takes place:

$$R_g \sim b^{2/5} B_r^{1/5} N^{3/5}, \quad (70)$$

where

$$B_r = B - \frac{\sqrt{6\pi}}{3} d l_B^2 \quad (71)$$

is renormalized second virial coefficient.

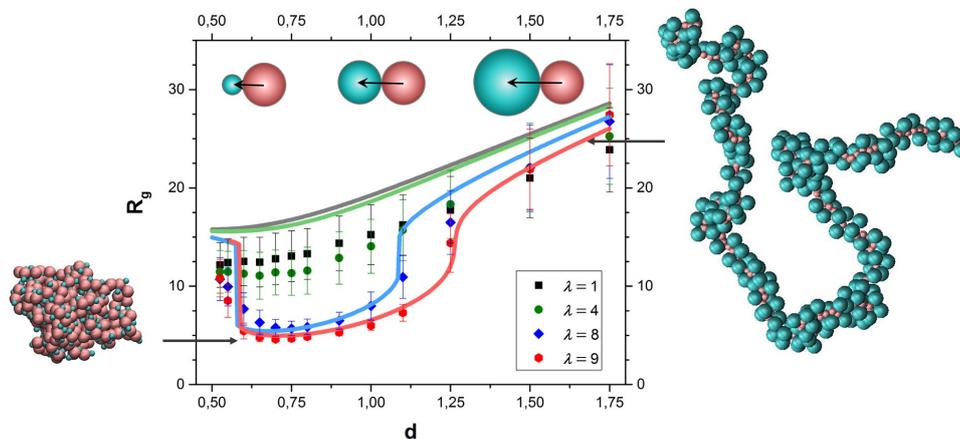


Figure 7: The dependencies of the gyration radius of the polymer chain with $N = 256$ on the dipole length $d = (\sigma_p + \sigma_c)/2$ at fixed monomer diameter $\sigma_p = 1$ and different counterion diameters σ_c , plotted at different $\lambda = l_B/\sigma_p$. Theoretical curves are plotted as solid lines, and the MD simulation data as points. There are also screenshots of the globular (on the left) and coil (on the right) conformations, obtained by the MD simulation [Gordievskaya, et al., *Soft Matter*, 2018].

For the investigation of the conformational behavior of the polymer chain it is considered, that all lengths are expressed in the units of the monomer diameter, i.e. $\sigma_p = 1$. Besides that, the dimensionless parameter $\lambda = l_B/\sigma_p$ is introduced, defining how much the energy of the electrostatic interactions differs from the thermal energy $k_B T$. To show how the counterion size affect on the conformational behavior of the dipolar polymer chain, the dependencies of the gyration radius of the dipolar polymer chain on the dipole length d (fig. 7), varying by the change of the counterion diameter σ_c , have been plotted at the different values of the parameter λ , obtained from the minimization of the total free energy and from the MD simulation [Gordievskaya, et al., *Soft Matter*, 2018]. Predicted within the theory and confirmed by the MD simulation conformational behavior of the dipolar polymer chain was interpreted in the following way. At the small electrostatic interaction (small λ), which takes place in the strongly polar solvents or at the high enough temperatures, the contribution of the excluded volume interactions always dominates over the electrostatic contribution. Hereby, the increase in the counterion diameter leads to the swelling of the polymer coil due to the increase in the steric repulsion of the monomers. However, electrostatic interactions intensify with the increase in the parameter λ and, starting from certain threshold value, they begin to dominate over the excluded volume interactions, that, in such manner, leads to the collapse of the polymer chain. As a result, the presence of even small dipole moments on the monomers will

lead to its shrinkage. Nevertheless, the growth of the dipole length d is accompanied by the simultaneous growth of the counterion diameter and, as a result, the excluded volume interactions begin to dominate again, leading to the expansion of the polymer chain. It is noted, that the results of the theory are in the good agreement with the findings of the computer simulations.

In the conclusion of the Chapter 4 the assumptions of the potential applications of the formulated theoretical model are stated. It is noted, that the model could be applied to the qualitative description of the conformational behavior of the polyelectrolytes and weak polyelectrolytes.

Chapter 5

Part 5.1

As is known, electric field is one of the potential external stimuli on the conformations of the macromolecules in solutions, which are used in practice. The change of the external electric field strength could be used, for example, to control the release of the molecules of the drug compound, captured by the polymer coil (globule), serving as the capsule for the targeted delivery. In the case of the macromolecules, which monomers carry constant dipole moments or have a large enough polarizability, the application of the electric field may lead to such effects, as electrostriction (deformation of the polymer material in the external field) and dielectrophoresis (movement of the polarizable macromolecule in the nonhomogeneous field).

Currently, influence of the electric field on the conformational properties was studied in depth within the statistical models of the strong polyelectrolytes. Conformational properties of the strong polyelectrolytes are fairly sensitive to the external electric field (due to the presence of the ionic groups on the monomers), that makes them perfect systems for the implementation of the targeted delivery of the drug compounds or for the creation of the artificial muscles. However, there is a wide variety of the so-called dielectric polymers, which monomers possess constant in magnitude dipole moment and/or polarizability, which are also susceptible to the influence of the electric field. Though, in comparison with the strong polyelectrolytes, effect of the electric field on the conformational condition of the macromolecule of the dielectric polymer have to be much weaker. Yet, it has to be noted, that theoretical investigations of the dielectric polymers in the electric field are not presented in the literature as extensively as the ones for the polyelectrolyte macromolecule systems. Despite the immense practical importance of the studying of the electric field influence on the conformational state of the dielectric polymer chains in dilute solutions (first of all, for the pharmacology tasks, related to the targeted delivery of the drug compounds), until quite recently there were no attempts of the systematic investigation of this problem using the methods of the statistical physics even at the level of the simplest mean-field Flory-de Gennes type theory. Therefore, in the first part of the Chapter 5 the Flory-de Gennes type theory of the conformational behavior of the flexible polymer chain with the isotropically polarizable monomers in the constant uniform electric field in the medium of the liquid-phase solvent is presented.

Flexible polymer chain is considered with the polymerization degree N with the isotropically polarizable monomers with the polarizability γ_p , located in the solvent, which is modeled as a continuous dielectric medium with the constant dielectric permittivity ε . It is considered, that polymer chain is in the homogeneous electric field with the strength \mathbf{E} . To describe the conformational behavior of the polymer chain in the external electric field, the simplest Flory-de Gennes type model was formulated, considering the gyration radius of the polymer chain R_g as the single order parameter. It is also set, that polymer chain on average occupies a volume in space, which can be estimated by the gyration volume $V_g = 4\pi R_g^3/3$. Thus, the total free energy of the polymer chain is written in the following form:

$$F(R_g) = F_{conf}(R_g) + F_{vol}(R_g) + F_{el}(R_g), \quad (72)$$

where $F_{conf}(R_g)$ is the conformational free energy of the polymer chain, which can be estimated with the aid of the following interpolation formula

$$F_{conf}(R_g) = \frac{9}{4}k_B T \left(\alpha^2 + \frac{1}{\alpha^2} \right), \quad (73)$$

where $\alpha = R_g/R_{0g}$ is the expansion factor, $R_{0g}^2 = Nb^2/6$ is the mean-square gyration radius of the Gaussian polymer chain, b is the Kuhn length of the polymer chain, k_B is the Boltzmann constant, T is the absolute temperature; the contribution of the volume interactions to the total free energy is estimated with the use of the virial expansion, truncated at the third order (which is acceptable for the consideration of not so dense globules)

$$F_{vol}(R_g) = k_B T \left(\frac{N^2 B}{V_g} + \frac{N^3 C}{V_g^2} \right), \quad (74)$$

where B and C are the second and third virial coefficients of the monomer-monomer volume interactions, respectively; electrostatic contribution to the free energy is estimated as the free energy of the dielectric sphere with the dielectric permittivity ε_p , inserted into the medium with the dielectric permittivity ε in the constant uniform electric field

$$F_{el}(R_g) = -\frac{V_g E^2}{8\pi} \frac{3\varepsilon(\varepsilon_p - \varepsilon)}{2\varepsilon + \varepsilon_p} = -\frac{3N\varepsilon\gamma_p E^2}{2\left(3\varepsilon + \frac{4\pi\gamma_p N}{V_g}\right)}, \quad (75)$$

where the dielectric permittivity within the polymer volume ε_p is estimated within the mean-field approximation

$$\varepsilon_p = \varepsilon + \frac{4\pi\gamma_p N}{V_g}. \quad (76)$$

Then, basing on the minimization of the total free energy, the influence of the electrostatic field on the conformational behavior of the polarizable polymer chain in the regimes of good and poor solvents has been investigated.

In the regime of good solvent ($B > 0$), i.e. when the polymer chain, in the absence of the external electric field, is in the conformation of the swollen coil, i.e. $\alpha \gg 1$, the minimization of the free energy provides the following algebraic equation for the expansion factor

$$\alpha^5 - \alpha = \frac{3\sqrt{6}}{\pi b^3} \sqrt{N} \left(B + \frac{2\pi\gamma_p^2 E^2}{3k_B T \varepsilon} \right). \quad (77)$$

As is seen from the equation (77), the presence of the electric field leads to the effective increase in the second virial coefficient and, consequently, to the additional expansion of the coil. In the region of the strong enough electric field near the theta-temperature $T \simeq \theta$ (where $B \approx 0$), one can obtain the following estimation (up to the numerical prefactor) for the gyration radius: $R_g/b \sim (\gamma_p^2 E^2 / k_B \theta \varepsilon b^3)^{1/5} N^{3/5}$.

In the region of the poor solvent ($B < 0$), when in the absence of the electric field the polymer chain is in the globular conformation, it is necessary to take into account triple correlations of the monomers, so the minimization of the free energy yields the following estimation for the average density of the globule at weak enough fields

$$\rho_p = \frac{N}{V_g} = \frac{|B|}{2C} - \frac{6\pi\gamma_p^2 E^2}{C k_B T \left(1 + \frac{2\pi\gamma_p |B|}{3\varepsilon C}\right)^2} + O(E^4). \quad (78)$$

The first term in the right-hand side of the relation (78) defines the density of the globule at zero electric field. The second term is the first term of the expansion in the square over the field E . It is mentioned that at the further increase of the field strength, the globule-coil transition of the polymer chain will take place.

Before turning to the analysis of the numerical results, the following dimensionless parameters were introduced: $\tilde{E} = E\sqrt{\varepsilon b^3/k_B T}$, $\tilde{B} = Bb^{-3}$, $\tilde{C} = Cb^{-6}$ and $\tilde{\gamma}_p = \gamma_p b^{-3}/\varepsilon$, so the equation in the expansion factor is written as:

$$\alpha^5 - \alpha = \frac{3\sqrt{6}}{\pi} \sqrt{N} \left(\tilde{B} + \frac{2\pi\tilde{\gamma}_p^2 \tilde{E}^2}{3\left(1 + \frac{6\sqrt{6}\tilde{\gamma}_p}{\alpha^3 \sqrt{N}}\right)^2} \right) + \frac{162\tilde{C}}{\pi^2 \alpha^3}. \quad (79)$$

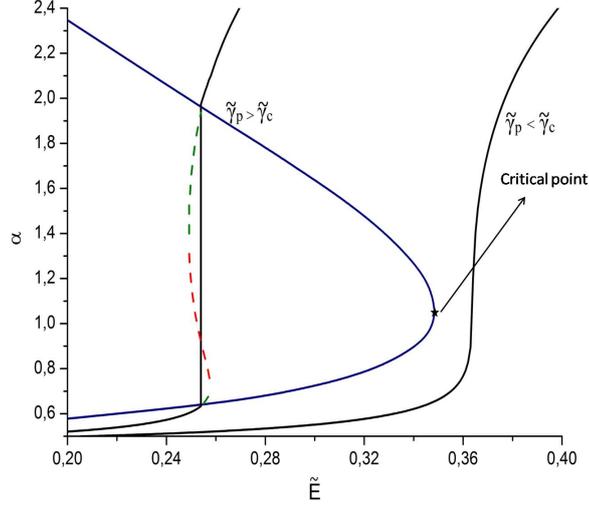


Figure 8: Phase diagram of the polarizable polymer chain, plotted in the coordinates α - \tilde{E} . Green dashed lines are metastable states; red dashed line is the absolutely unstable states. The data is shown for $\tilde{B} = -0.5$, $\tilde{C} = 2.4$, $N = 10^5$.

Then, basing on the obtained equation, the conformational behavior of the polymer chain in the electric field at different polarizabilities of the monomers have been obtained (fig. 8). At the small enough polarizabilities of the monomers, increase in the electric field leads to the smooth increase in the expansion factor. In that case, at the infinite chain length limit ($N \rightarrow \infty$) at small enough polarizabilities of the monomers, the globule-coil transition of the macromolecule proceeds as the second-order phase transition. However, if the polarizability exceeds the certain critical value $\tilde{\gamma}_c$, the globule-coil transition proceeds abruptly. It is noted that the globule-coil transition points form a binodal with the critical point.

Part 5.2

In the previous part of the Chapter 5 within the mean field Flory-de Gennes type theory it was established that in presence of the polarizability on the monomers of the flexible polymer chain, the electric field application to the dilute polymer solution always leads to its electrostrictive expansion. In other words, polarization of the macromolecule under the field leads to the occurrence of the additional effective repulsion between monomers. The appearance of the electrostrictive expansion of the polymer coil in the constant uniform electric field makes the next question reasonable: how the electrostriction will influence on the polarizable molecules concentration of some target compound (TC) within the dielectric polymer volume? In other words, can one influence on the number of TC molecules, captured by the polymer macromolecule, by the change of the electric field strength? As far as is known, until recently this question has not been theoretically studied in the world literature, even at the level of the mean-field theory. Thus, in the second part of the Chapter 5 the theoretical research of the concentration behavior of the polarizable TC molecules in the volume of the polarizable polymer in the constant uniform electric field within the mean-field theory has been performed.

The isolated flexible polymer chain is considered with N isotropically polarizable monomers, situated in the solvent medium with a small addition of the isotropically polarizable molecules of the TC. As in the first part of the Chapter 5, the solvent is modeled as a continuous dielectric medium with the constant dielectric permittivity ε . It is considered that solution is confined between two oppositely charged membranes with the surface charge densities $\pm\sigma$, generating the external electric field, impenetrable for the TC molecules, but permeable for the solvent. It is established, that the system is in the thermodynamical equilibrium at the temperature T and osmotic pressure

Π , produced by the TC molecules. The problem consists in the exploration of the number of the sorbed TC molecules by the polymer chain volume alongside its conformational behavior depending on the membranes surface charge density. It is noted that presence of the TC molecules in the bulk solution does not allow one to apply a simple Flory-de Gennes type theory, presented in the previous part of the Chapter 5. To solve assigned problem, it is necessary to construct a thermodynamic potential of the system, taking into account that not only the temperature is fixed in the system, but also the osmotic pressure. For simplicity it is assumed that total volume of the system is divided into two parts: internal polymer volume (estimated, as above, by the gyration volume of the polymer chain) and the bulk phase.

Using the mean-field approximation (80) for the dielectric permittivity

$$\varepsilon_b = \varepsilon + 4\pi\gamma_c\rho, \quad (80)$$

standard thermodynamic relations, the expressions for the free energy ϕ per particle, chemical potential μ , and osmotic pressure Π

$$\phi = k_B T (\ln(\Lambda^3 \rho) - 1) + \frac{1}{2} k_B T B_c \rho - \frac{8\pi^2 \gamma_c \sigma^2}{\varepsilon \varepsilon_b}, \quad (81)$$

$$\mu(\rho, T) = \frac{\partial(\rho\phi)}{\partial\rho} = k_B T (\ln(\rho\Lambda^3) + 2B_c\rho) - \frac{8\pi^2 \gamma_c \sigma^2}{\varepsilon_b^2}, \quad (82)$$

$$\Pi(\rho, T) = \rho(\mu - \phi) = k_B T (\rho + B_c\rho^2) + \frac{32\pi^3 \gamma_c^2 \rho^2 \sigma^2}{\varepsilon \varepsilon_b^2}, \quad (83)$$

where γ_c is the polarizability of the TC molecules, ρ is the TC concentration, T is the temperature, k_B is the Boltzmann constant. The first term in the right-hand side of the expression (81) defines the free energy of ideal gas, the second term is the contribution of the TC molecules interactions to the free energy at the level of the second term of the virial expansion (considered only pair correlations of the particles) and the third is the free energy of the dielectric body, confined between two semipermeable membranes with the fixed surface charge densities $\pm\sigma$; Λ is the thermal de Broglie wavelength, B_c is the second virial coefficient of the interactions between TC molecules.

Then, model of the solution in the presence of the polarizable polymer chain was formulated. It is mentioned, that, as against the situation described in the first part, in this case it is insufficient to just write the free energy of the polymer chain as a function of its gyration radius. Instead, it is necessary to construct the thermodynamic potential, considering the equilibrium of the target compound in the bulk phase and within the polymer volume at the temperature T and osmotic pressure Π . Thus, two order parameters are chosen: the gyration radius R_g of the polymer chain and number of TC molecules N_c , located in the polymer volume. In such manner, thermodynamic potential of the solution is written in the following form

$$\Phi(N_c, R_g) = F_{id}(R_g, N_c) + F_{vol}(R_g, N_c) + F_{el} + \Pi V_g - \mu N_c, \quad (84)$$

where

$$F_{id} = \frac{9}{4} k_B T (\alpha^2 + \alpha^{-2}) + N_c k_B T \left[\ln \left(\frac{N_c \Lambda^3}{V_g} \right) - 1 \right] \quad (85)$$

is the free energy of the ideal Gaussian chain, surrounded by the gas of the TC molecules, located in the gyration volume $V_g = 4\pi R_g^3/3$; $\alpha = R_g/R_{0g}$ is the expansion factor of the polymer chain ($R_{0g}^2 = Nb^2/6$ is the mean-square gyration radius of the ideal polymer chain, b is the Kuhn length of the polymer chain). Free energy of the ideal polymer chain is estimated in the same manner as in the previous part with the use of the Fixman interpolation formula. Chemical potential μ and osmotic pressure Π of the TC are defined by the relations (82) and (83), respectively. Contribution F_{vol} of the polymer-TC, TC-TC and polymer-polymer interactions to the total free energy is described within the virial expansion at the level of the first nonzero terms over the TC and monomers concentrations

$$F_{vol} = k_B T \left(\frac{B_p N^2}{V_g} + \frac{B_c N_c^2}{V_g} + \frac{2B_{pc} N_c N}{V_g} \right), \quad (86)$$

where B_p , B_c and B_{pc} are corresponding second virial coefficients. Electrostatic free energy of the mixture, confined in the gyration volume, can be presented as

$$F_{el} = F_{ex,p} + F_{ex,c}, \quad (87)$$

where $F_{ex,p}$ is the excess electrostatic free energy of the mixture, confined in the gyration volume, in comparison with the bulk phase of the solution, and $F_{ex,c}$ is the excess electrostatic free energy of the TC solution, confined in the gyration volume, as relative to the pure solvent. Within the mean-field approximation these contributions can be estimated in the following way:

$$F_{ex,p} = -\frac{6\pi V_g \sigma^2}{\varepsilon_b} \frac{\varepsilon_p - \varepsilon_b}{2\varepsilon_b + \varepsilon_p} \quad (88)$$

and

$$F_{ex,c} = 2\pi\sigma^2 V_g \frac{\varepsilon - \varepsilon_b}{\varepsilon_b}. \quad (89)$$

It is noted, that polymer coil together with the sorbed TC molecules is described by the dielectric sphere of the radius R_g with the dielectric permittivity

$$\varepsilon_p = \varepsilon + 4\pi\gamma_c\rho_c + 4\pi\gamma_p\rho_p \quad (90)$$

(γ_p is the polarizability of the monomer, $\rho_c = N_c/V_g$ is the average concentration of the TC in the gyration volume, $\rho_p = N/V_g$ is the average concentration of monomers), immersed in the dielectric medium with the dielectric permittivity ε_b . Thus, total electrostatic free energy is determined as the excess electrostatic free energy of the polymer chain and TC molecules, located in the gyration volume, as compared to the pure solvent, occupying the same volume. The minimization of the thermodynamic potential over the order parameters leads to the system of the transcendent equations in expansion parameter α and average TC concentration within the polymer volume.

Before the analysis of the numerical results, the following dimensionless parameters have been introduced: $\tilde{B}_p = B_p/b^3$, $\tilde{B}_c = B_c/b^3$, $\tilde{B}_{pc} = B_{pc}/b^3$, $\tilde{\gamma}_p = \gamma_p/(b^3\varepsilon)$, $\tilde{\gamma}_c = \gamma_c/(b^3\varepsilon)$, $\tilde{\sigma} = 4\pi\sigma\sqrt{b^3/\varepsilon k_B T}$. It is noted, that all calculations are accomplished for the polymer chain with the polymer-polymer and polymer-TC interactions, being repulsive, so that $\tilde{B}_{pc} > 0$. Then, the numerical results for two qualitatively different regimes were analysed: $\tilde{\gamma}_p > \tilde{\gamma}_c$ and $\tilde{\gamma}_p < \tilde{\gamma}_c$.

Regime I: $\tilde{\gamma}_p > \tilde{\gamma}_c$. The parameters values are fixed: $N = 10^2$, $\tilde{B}_p = 0.25$, $\tilde{B}_c = 0.25$, $\tilde{B}_{pc} = 0.75$, $\tilde{\rho} = 0.15$, which allow one to obtain the conformation of the condensed coil at $\sigma \rightarrow 0$ due to the "solvophobic" properties of the polymer chain relative to the TC molecules.

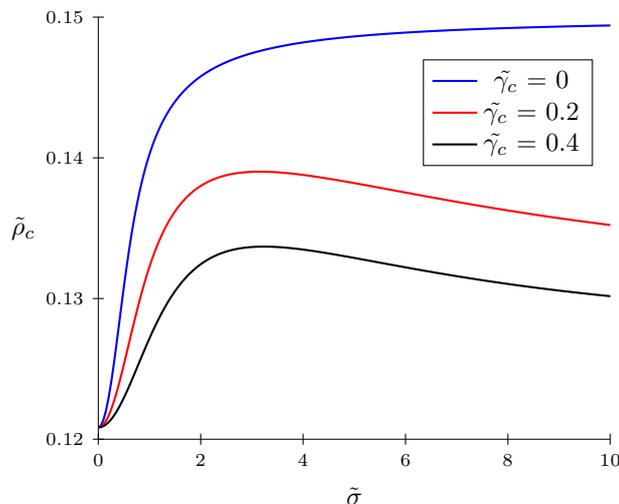


Figure 9: Dependence of the TC concentration $\tilde{\rho}_c$ within the polymer volume on the surface charge density of the membranes $\tilde{\sigma}$ at fixed polarizability of the monomers $\tilde{\gamma}_p = 0.8$ and different polarizabilities of the TC molecules.

At zero electric field polymer coil is sufficiently shrunk due to its solvophobicity in relation to the TC molecules, whereas the inclusion of the field leads to the coil expansion due to the electrostriction effect. If the TC molecules are not polarizable ($\tilde{\gamma}_c = 0$), then with the increase of the surface charge density of the membranes, the local concentration $\tilde{\rho}_c$ tends to the concentration $\tilde{\rho}$, settled in the bulk phase. However, in the case of the polarizable TC molecules ($\tilde{\gamma}_c \neq 0$) at the increase in $\tilde{\gamma}_c$, the TC concentration in the gyration volume monotonically grows. In fact, at the non-zero TC polarizability, the dependence of the local concentration $\tilde{\rho}_c$ on the field strength \tilde{E} has a pronounced maximum (fig. 9). Then, the behavior of the dependence $\tilde{\rho}_c(\tilde{\sigma})$ at the increase in the polymerization degree N of the polymer coil has been examined. It is shown that going of the polymerization degree to the infinity ($N \rightarrow \infty$) leads to the fact that $\rho_c \rightarrow \rho$. It is established, that at the increase in the polymerization degree the mentioned above non-monotonic dependence $\tilde{\rho}_c(\tilde{\sigma})$ becomes less pronounced and disappears in the limit of the infinitely long coil.

Regime II: $\tilde{\gamma}_p < \tilde{\gamma}_c$. In the second regime the dependencies of the expansion factor α and local concentration of the TC molecules $\tilde{\rho}_c$ on the monomers polarizability at the fixed surface charge densities $\tilde{\sigma}$ and other parameters of the model have been examined. An interesting feature – graphics of the functions, corresponding to the different values of $\tilde{\sigma}$, have a common intersection point. The common intersection point corresponds to the equality of the dielectric permittivities within the polymer volume and in the bulk phase.

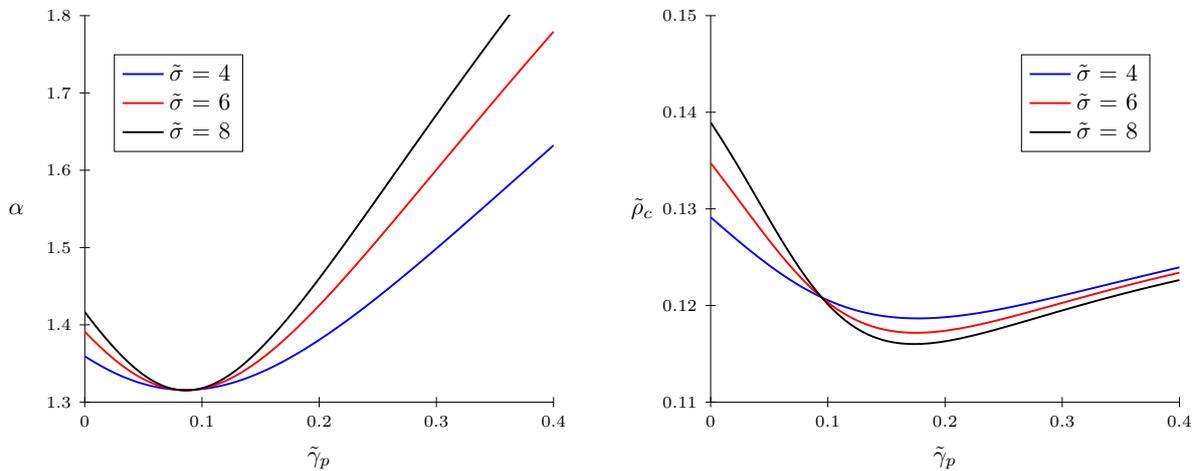


Figure 10: Expansion factor α (on the left) and TC concentration $\tilde{\rho}_c$ in the polymer coil volume (on the right) as a function of the polarizability $\tilde{\gamma}_p$ of monomers for the solvophobic polymer at the fixed surface charge densities of the membranes $\tilde{\sigma}$. Polarizability of the TC molecules is $\tilde{\gamma}_c = 0.5$.

Finally, within the second regime the case of the non-polarizable ($\tilde{\gamma}_p = 0$), solvophobic, relatively to the polarizable ($\tilde{\gamma}_c \neq 0$) TC molecules, polymer chain has been examined. The following values of the second virial coefficients are adopted: $\tilde{B}_p = 0.125$, $\tilde{B}_c = 0.125$, $\tilde{B}_{pc} = 0.75$. The dependence of the expansion factor and the local TC molecules concentration on the surface charge density of the membranes $\tilde{\sigma}$ at the different TC polarizabilities $\tilde{\gamma}_c$ has been investigated. It is shown that at sufficiently small surface charge densities of the membranes, the expansion factor remains almost constant and, further, monotonically increases. It is mentioned, that due to the large enough solvophobicity of the polymer at zero charge of the membranes, the TC molecules concentration within the gyration volume is much smaller, than in the bulk phase of the solution ($\tilde{\rho}_c \ll \tilde{\rho}$), that leads to the shrinkage of the polymer coil (due to the osmotic pressure difference). However, at the large enough charge density on the membranes, its increase will lead to the increase in the TC concentration within the polymer volume, that, in turn, will lead to the expansion of the polymer coil.

In the conclusion of the Chapter 5 it is noted that both presented theoretical models have obvious restrictions. They could be applied to the description of the conformational behavior of the polymer chains with isotropically polarizable monomers. In other words, non-diagonal components of the polarizability tensor of the monomer unit must be much smaller than diagonal ones. As

is known, for the flexible synthetic polymers this assumption appears quite reasonable [Gurovich, *Macromolecules*,1994; Gurovich, *Macromolecules*, 1995]. Second restriction of the proposed models is related to the fact that for the description of the conformational behavior of the polymer chain in the electric field only one order parameter is used, that is the gyration radius of the chain, which allows one to control the change of the polymer volume, but does not allow one to understand anything about the change of its form. Nevertheless, from the general considerations it is clear, that this restriction is not that serious at the electric field strengths, at which only a slight swelling of the polymer happens, i.e. which do not lead to the sufficiently strong extension of the polymer chain along the field direction due to the mechanical orientation of the monomers. Moreover, these fields must not lead to the electrolysis of the solvent molecules. Apparently, such fields must have strength much smaller than the strengths of the intermolecular fields ($\sim 10^8 - 10^9$ V/m). Besides that, it is mentioned, that within the examined models the dipole correlations of the monomers, related to the fluctuations of the dipole moments of the monomers, have not been taken into account. It can be shown [Budkov and Kolesnikov, *Eur. Phys. J. E.*, 2016], that the consideration of the dipole correlations will not qualitatively change eventual results, but only shift parameters regions (polarizability and field strength), where the discussed effects are presented.

Conclusion

In chapter **Conclusion** the following outcomes were summarized:

- It was developed a formalism, based on the classical density functional theory, allowing one to obtain self-consistent field equations, taking into account presence of the solvent molecules in the electrolyte solution, possessing constant dipole moment and/or polarizability.
- Basing on the developed formalism, theory of the electrical double layer at the metal electrode/liquid electrolyte interface was formulated with account for the polar or polarizable impurity molecules, present in the bulk phase. On the basis of the developed theory the behavior of the differential capacitance of the electrical double layer as a function of the dipole moment, polarizability of the co-solvent molecules and its concentration, and also specific interactions between the components of the mixture was investigated.
- A non-local field-theoretic model of the electrolyte solution with a small additive of the dipolar particles with polar groups, located at the long enough fluctuating distances between each other, was developed. In terms of formulated model the self-consistent field equation, generalizing the well-known Poisson-Boltzmann-Langevin equation, for the electrostatic potential, created by the external charges in the electrolyte solution in the presence of the particles with sufficiently long dipole moments, was obtained. A general relation for the electrostatic free energy of the electrolyte solution with the additive of the long enough dipolar particles within the Gaussian approximation was obtained.
- It was formulated a Flory-de Gennes type model of the weak polyelectrolyte macromolecule with account for the many-body dipole correlations of the monomers. A coil-globule transition of the weak polyelectrolyte macromolecule, induced by the dipole-dipole interactions of the monomers with the many-body effects consideration, was investigated within developed model. A good agreement between the theoretical and MD simulations results was achieved.
- A Flory-de Gennes type model of the flexible dielectric polymer chain, dissolved in the liquid dielectric under the constant uniform electric field with isotropically polarizable monomers was formulated. A conformational behavior of the flexible dielectric polymer chain in the constant uniform electric field in the regimes of good and poor solvents was investigated. A new conformational coil-globule transition, induced by the electrostrictive swelling of the polymer in the electric field was predicted. An essential possibility of the control of the conformational state of the polymer by the change of the electric field strength has been presented.

- Model of the dielectric polymer chain with isotropically polarizable monomers in the medium of the dielectric solvent with a small additive of the isotropically polarizable particles of the low-molecular target compound in the external electric field was developed. Within the developed model the behavior of the local concentration of the low-molecular particles of the target compound within the polymer volume as a function of the relation between the polarizabilities of the monomer units and particles of the target compound was investigated.

Appendix

In the **Appendix** the appliance of the path integration to the calculation of the distribution function over the gyration radius of the Gaussian polymer chain in d -dimensional space has been shown. Basing on the obtained asymptotic relations for the distribution function at large and small gyration radii, the interpolation formula for the configuration entropy as a function of the gyration radius of the Gaussian polymer chain in d -dimensional space has been constructed, used in the Chapters 4-5 for the description of the conformational entropy contribution of the polymer chain in the case of $d = 3$.

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