

## **AUTHOR'S REFERENCE**

### **of the scientific contributions in all works of Assistant Prof. Dr. Kamelia Kamburova**

The author's reference covers 21 scientific papers (referred to the Scopus database) and 6 papers in conference proceedings published in the period 2006-2021. The total number of noticed citations of all publications is 176.

My research activity is focused on two areas:

- 1) electrical properties of colloidal particles in aqueous suspensions with added polyelectrolytes and stability of the suspensions;
- 2) design, preparation and characterization of multilayer films of polyelectrolytes on colloidal particles.

The main results were obtained using electro-optical methods, which provide information on the electrical polarizability and size of non-spherical colloidal particles. This information is necessary in connection with the widespread use of polyelectrolytes as stabilizers or flocculants of colloidal suspensions, as well as for the controlled preparation of polymeric multilayer coatings for encapsulation of active substances with applications in medicine and corrosion protection of metals.

#### **1. Electrical properties of colloid-polyelectrolyte suspensions**

The electrical properties and the resistance against aggregation of aqueous suspensions of model oxide particles have been studied ( $\beta$ -FeOOH -  $\beta$ -ferric oxyhydroxide, positively charged in a slightly acidic medium) in dependence on the charge of the adsorbed polymers (magnitude and distribution of charge along the chains) and the characteristics of the dispersed medium (ionic strength, pH, presence and type of low molecular weight salt) [№2,5,7,9,10,11,12]. The studies were performed with electro-optical methods - light scattering in electric field and electric birefringence, in addition microelectrophoresis was used. It has been shown that the amount of polymer adsorbed on oppositely charged oxide particles, which causes aggregation in the suspension, decreases with increasing charge density of the polymer [№9]. An exception is a highly charged polymer, which assumes partial condensation of intrinsic counterions on the polymer chains (due to strong electrostatic attraction), leading to a decrease in the effective charge of the polymer [№ 9]. Condensation of intrinsic counterions on the chains of polymers with different (high) charge density also explains the coincidence of the concentrations of the polymers, causing maximum instability of the oxide suspensions [№ 2]. The fraction of condensed counterions onto highly charged free polyelectrolytes in solution (Manning's theory) was evaluated and compared with that for polyelectrolytes adsorbed on weakly charged particles (Sens and Joanny's theory) and it was shown that the influence of the particles on the electrical properties of the adsorbed polymers is negligible [№ 2]. Experimentally, a decrease in the mobility of the counterions of adsorbed polymers in an electric field compared to the mobility of free ions in solution [№ 2,5,7,9,12] was found, as well as a coincidence of the relaxation frequency of the electro-optical effect of adsorbed and free highly charged polyelectrolyte [№ 5], which proves the contribution of the polarization of the condensed counterions of the adsorbed polyelectrolytes to the electrical polarizability of overcharged colloidal particles.

It has been shown experimentally that enhancement of the charge of a weak polyelectrolyte (with pH-dependent charge) leads to the increase of the length of its chains [№ 10]. A theoretical model is proposed that explains this result in terms of the counterion condensation phenomenon. The influence of the charge distribution of the polyelectrolyte (ordered or random) on the electrical properties and stability of a suspension of oxide particles has been established, which is interpreted as a demonstration of counterion condensation in the case of the polymer with ordered distribution of charge areas exceeding a certain critical value of the charge density [№ 12]. It is shown that the electrical polarizability and the thickness of layers of strongly charged polyelectrolytes adsorbed on weakly charged colloidal particles increase with increasing of the amount of low molecular salt in the medium due to an increase in the number of polymer chains adsorbed in the increasingly folded conformation [№ 11]. In this case, the small ions that form the electro-optical effect are mainly in the polymer matrix, and the contribution of the ionic atmosphere outside the polymer layer remains practically constant.

## **2. Multilayer films on colloidal particles obtained via layer-by-layer adsorption of polymers**

Polyelectrolyte multilayer films were obtained by depositing alternating layers of oppositely charged polymers on model (non-spherical) colloidal particles of  $\beta$ -FeOOH [№ 3,4,6,8,14]. Weak polyelectrolytes (biopolymers) whose charge density depends on the pH of the medium [№ 3,4,6,8] and synthetic polymers [№ 14] were used, applying the layer-by-layer technique described in the literature (with small corrections that make it applicable to electro-optical measurements). The electrical properties and the thickness of the films were determined by the methods of light scattering in an electric field and microelectrophoresis. New information has been obtained on the growth mechanism of weak polyelectrolyte films, according to which the thickness of the films and their electrical properties can be adjusted in a wide range only by changing the pH of the medium.

It was found that the thickness of the films of two strongly dissociated biopolymers increases linearly with the layer number and the formed films are thin (with 3-4 nm thickness of one bilayer), while when combining strongly with weakly dissociated polymer, half to one order of magnitude thicker films are obtained [№ 3,4,6,8]. The growth of thick films becomes linear or exponential. The exponential growth is explained by a diffusion mechanism, according to which part of the chains of the strongly dissociated polymer enter the volume of the film, causing additional dissociation of the less charged polymer in the formation of each bilayer [№ 4,6,14]. The linear growth in the thick films is associated with partial desorption from the film surface of semi-soluble complexes obtained from polyelectrolytes with different concentrations and chain lengths [№ 3,8,14].

A correlation was found between the charge of the polyelectrolytes involved in the formation of the films and the value of the electrical polarizability of the colloidal particles coated with multilayer films [№ 3,4,6,8,14]. It has been found that the amount and mobility of the small counterions in the last adsorbed polymer layer determine the electro-optical behavior of the whole films. It has been shown that condensed counterions of the polyelectrolyte, whose mobility is reduced compared to the mobility of free ions in solution, have a major contribution to the electrical polarizability of films with last layer of highly charged (dissociated) polyelectrolyte. This is confirmed by a comparative study of the frequency behavior of the electrical

polarizability of highly charged carboxymethyl cellulose before and after its adsorption on model colloidal particles [№ 5].

## **2.1. Encapsulation of drugs and corrosion inhibitors with polyelectrolytes**

### **Encapsulation of drugs**

The purpose of drugs encapsulation is to improve their biocompatibility, to control the rate of release and to target the active agent to a specific organ in order to increase its effectiveness and reduce side effects. A procedure for encapsulation of nanoparticles from the anti-inflammatory drug indomethacin (IMC) has been developed, which includes pre-treatment with ultrasound of an aqueous suspension of IMC microcrystals (average sizes of the obtained particles as a flat elliptical disks are  $200 \pm 70$  nm and  $140 \pm 50$  nm on both axes) and subsequent encapsulation of the drug with a multilayer film of two natural polysaccharides - pectin and chitosan [№13,18]. Coating of four polymer layers was found to cause a decrease in the release rate of indomethacin at physiological pH 7. The addition of NaCl was found to reduce the rate of drug release due to an increase in coating thickness. The addition of  $\text{CaCl}_2$  further slows the rate of drug release due to reduced permeability of the multilayer coating.

### **Encapsulation of corrosion inhibitors**

Polymer-based nanocontainers of the "core-shell" type are obtained by a layer-by-layer technique of two highly charged polyelectrolytes adsorbed successively on nanoparticles of hematite [№15] or kaolinite [№ 22]. Steel corrosion inhibitor benzotriazole (BTA) is trapped in polymer shells that contain a polyelectrolyte with pH-dependent charge and can release it when the pH changes during the corrosion process. In nanocontainers with a hematite core, it has been found that the amount of inhibitor retained in the shell depends on the charge of the last adsorbed polymer layer. The pH of the medium and the concentration of NaCl have been shown to influence the formation of stable nanocontainers with BTA in nanocontainers with a kaolinite core, with a higher amount of BTA being measured in nanocontainers prepared in the presence of NaCl. The amount of BTA measured by UV spectroscopy in both types of nanocontainers is high enough and can have a positive effect on the corrosion protection of steel.

## **2.2 Stabilization of colloidal suspensions for preparation of anticorrosive zinc coatings on steel**

### ***Zinc coatings with incorporated polymer-based nanocontainers impregnated with corrosion inhibitors of steel***

The design, preparation and incorporation of "smart" polymer nanocontainers containing corrosion inhibitors in standard zinc coatings on steel, as well as the anticorrosive characteristics of the obtained hybrid coatings, are described in papers № 17,19,23 and 26. The effect of two inhibitors with pH-dependent charge was studied: benzotriazole [№ 17,19,23] and safranin [№ 26]. Both inhibitors are captured by adsorption (as a separate layer) in the "core-shell" type polymer-based nanocontainers, obtained by layer adsorption of oppositely charged poly(acrylic)acid and poly(diallyldimethyl) ammonium chloride [№ 17,19,23] or poly(acrylic)acid and poly(ethyleneimine) [№ 26] on nanoparticles of hematite [№ 17, 23], kaolinite [№ 19,23] and zinc oxide [№ 26]. The optimal conditions have been found for obtaining stable suspensions from

nanocontainers (pH, ionic strength of the medium, concentration of polyelectrolytes and inhibitors) suitable for incorporation into a zinc coating by simultaneous [№ 17,19,23] or sequential [№ 26] electrodeposition with zinc from a weakly acidic solution of zinc sulphate. The main interaction forces that cause the formation of polymer-based nanocontainers and the encapsulation of inhibitors in these shells are electrostatic. The degree of dissociation of the negatively charged poly(acrylic)acid decreases with decreasing pH of the medium, which implies a decrease in the strength of interaction of its chains with those of positively (highly) charged polymers and the ability to release inhibitors trapped in the nanocontainers. Since the beginning of the corrosion process is accompanied by a change in the pH around the defects on the metal surface, the "smart" nanocontainers with a corrosion inhibitor release it when the pH of the medium changes and thus slow down the rate of the corrosion process. The comparison between the anticorrosive behavior of steel with pure zinc coating and with hybrid zinc coatings (tested in neutral aqueous medium with 5% NaCl) demonstrates the positive effect of nanocontainers with inhibitor in all studied systems [№ 17,19,23,26]. Active protection ensured by "smart" nanocontainers is added to the passive protection of steel from corrosion, the contribution of which has both zinc (sacrificial) coating and the presence in the hybrid coatings of oxide nanoparticles (cores) and polymers from the shells of nanocontainers.

#### ***Zinc coatings with embedded nanoparticles - steel corrosion inhibitors***

Direct incorporation of metal corrosion inhibitors into an anti-corrosion coating can cause an interaction with the coating and thus compromise its structure or deactivate the inhibitor. The isolation of colloidal-sized particles, which are corrosion inhibitors of steel, from the rest of the standard zinc coatings is achieved by coating them with polymers [№ 20,21,24,25,27]. Optimal conditions were found for obtaining anti-aggregation stabilized suspensions of particles of the conductive polymer polyaniline [№ 20,21,24,27] and carbon spheres [№ 25], by adsorption on the particles of suitable for this purpose charged [№ 20,21,27] and uncharged polymers [№ 24,25]. The preliminary adsorption of polymers on the particles embedded in the zinc coatings and the stabilization of their suspensions against aggregation allowed the production of relatively homogeneous coatings with good corrosion resistance. It has been established that stabilization of suspensions is registered at concentrations of the charged polymer, which cause a change in the sign of the charge of the particles [№ 20,21,27], and in case of uncharged polymers- at concentrations close to or higher than the critical micelle concentration [ № 24.25]. The electrochemical and corrosion behavior of hybrid zinc coatings on steel containing conductive [№ 20,21,24] or non-conductive [№ 27] polyaniline particles has been studied and it has been shown that non-conductive polyaniline particles (coated with polyethyleneimine) have better protective ability against corrosion of steel in a neutral model environment (5% aqueous NaCl solution).

#### **Other contributions**

The reflection spectra of a healthy tooth, the spectra of different carious conditions and of two pathologies - fluorosis and tartar in vitro under irradiation with white light were obtained by the method of reflection spectroscopy. Based on the performed analysis of the spectral differences, a primary diagnostic algorithm was created, allowing the determination of the tissue condition, based on the difference in the reflection coefficients of the lesions. The possibility of using the method of reflective spectroscopy for early diagnosis of caries and its previous conditions has been shown [№ 1].

Lipid nanotubes (LNTs) can mimic the lipid bilayer of biological membranes and are widely used as protein substrates in biotechnology. Since the binding of a protein to LNT depends strongly on the physicochemical properties of LNT, the magnitude and type of their electrical polarizability and their length were studied. The experimental results obtained by the electro-optical method of light scattering in an electric field are compared with the theoretical ones. Comparable results were obtained for the average values of the electric polarizability in three independent ways: from the change of the electro-optical effect with the time, the strength and the frequency of the applied electric field. The electro-optical method used may also be applicable to the characterization of other organic nanotubes [№16].