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Polyelektrolite Solutions and Molecular Descriptions of Biopolymer Macroions

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Abstract: Molecular mass characteristics of samples of ionic biopolymers, including chitosan and fibroin, the manifestation of physical conditions depending on the concentration of macroions, and hydrodynamic, rheological methods were used in the implementation of these studies. These processes depend on the fact that ionic polymers exhibit viscosity in relation to their molecular mass and are sensitive to the effects of the electric field at the expense of ionogenic groups. In order to determine this, the results of studies on the molecular characteristics of basic polymer objects were discussed. When polyelectrolytes are affected by external forces, including mechanical or electrical stresses, gradient fields are created, and macroions move along the lines of force of these fields. Such fields are observed, for example, when a liquid flows from a capillary under mechanical pressure, when the liquid is turned into a stable laminar flow using a rotor, or when ions and macroions move towards the poles (electrodes) during electrophoresis and electrolysis. In general, in the gradient field created under the influence of mechanical influence, the macroions move along the lines of force in rotation and advance, while in the gradient field created under the influence of electric voltage, the functional groups of macroions move towards the anode or cathode as anions or cations. The reason for the choice of poles is the sensitivity of anions or cations to the effect of an electric field.

Keywords: Macroion, Fibroin, Chitosan, Viscosity, Solution, Macromolecules

1. Introduction

Today, it is important to obtain ionic biopolymers for specific purposes, including surfactants, the solution of which can be achieved by in-depth study of the movement of macroions and ions in the electric field. The implementation of electrochemical reduction of biopolymers requires the preparation of their polyelectrolyte solutions and the study of the ability of ionic macromolecules to move as giant macroions under the influence of an electric field. These processes depend on the fact that ionic polymers exhibit viscosity in relation to their molecular mass and are sensitive to the effects of the electric field at the expense of ionogenic groups. Ionogenic biopolymers, including chitosan and fibroin as macroions, have the ability to move and electrochemically recover in solution under the influence of an electric field, as well as the formation of micro- and nanoparticles on its basis.

Viscosity of a polymer solution depends on concentration and size (i.e., molecular weight) of the dissolved polymer. By measuring the solution viscosity, an idea about molecular weight could be obtained [1]. Rheological techniques and methods have been used for many decades to describe polymers. Rheology, originally developed and used in synthetic polymers, later aroused great interest in the field of natural (bio) polymers [2]. The electrostatic, entropic and surface interactions between a macroion (nanoparticle or biomolecule), surrounding ions and water molecules play a fundamental role in the behavior and function of colloidal systems [3]. Chitosan based polyelectrolyte complexes exhibit favourable physicochemical properties with preservation of chitosan's biocompatible characteristics [4]. They are reported to promote rapid dermal regeneration and accelerate wound healing. A number of dressing materials based on chitin and chitosan have been developed for the treatment of wounds [5].

2. Experimental Part

Because the chitosan (ChZ) sample selected as the object of study was obtained by rheometry, i.e., deacetylation of chitin in the cutting area, it has a narrow polydispersity index (P = 1.25) and a high deacetylation rate (SDA = 0.75). A relatively convenient viscose method was selected to determine its molecular mass (M). For this purpose, a dilute solution of ChZ (C = 0.2 g / dl) in a 2% solution of acetic acid in water used as the main solvent, ie 2% CH_3COOH [6]. The studies were carried out on the Ubbelode viscometer on the principle of discretely diluting the solution at a temperature of 25°C $(C \to 0)$ and measuring the viscosity (η_c / C) given. The results are shown in Figure 1, a - in the form of a graph of the connection of (η_c / C) to C. In this case, a decrease in concentration (C) results in an increase in viscosity (η_c / C) , i.e., the Haggins formula $\eta_c / C = [\eta] + k[\eta]^2 C$ [7] observed the effect of a polyelectrolytic concentration anomaly without maintaining a linear relationship. This is due to the increase in the viscosity of macromolecules due to the increased interaction of active functional NH_2 groups with the dilution of the solution, ie partial adjustment of the conformation - a relatively large volume as a result of polyelectrolytic swelling, increased viscosity. Such a polyelectrolytic effect indicates that the chitosan molecule exhibits physical states depending on its concentration as a macroion. Such an effect indicates that chitosan is sensitive to the effects of the electric field, and its consideration plays an important role in the implementation of the electrolysis process.

For the study, a powder sample of fibroin (FB) pre-washed from natural silk fiber, washed from oil and minerals, dissolved in $CaCl_2$ (50%), dialyzed and precipitated in an amorphous state was used [6]. It is convenient to use an amorphous fibron solution containing formic acid (HCOOH) for electrochemical reduction experiments, but in this solvent the process of acid hydrolysis is observed [12]. Therefore, the use of its dilute solution, including HCOOH-H_2O (1: 1), had no additional effect, and moreover, the conformation of fibroin is highly dependent on the pH of the medium. Its isoelectric point (IEN) [8], in which experiments were performed using the Ionomer-75 device and it was found that the IEN was around 3.8–4.5.

3. Results and Discussion

Chitosanni Haggins [7] allows to determine its molecular mass by maintaining viscometric measurements, while maintaining a straight line connection, ie eliminating the polyelectrolyte effect. To do this, it is necessary to eliminate the polyelectrolyte effect of the solution, for which it is necessary to add 2% sodium chloride salt to the solvent in accordance with [9], ie 2% CH_3COOH - 2% NaCl system as a solvent. The result of this study is shown in Figure 1. The connection graph is a straight line corresponding to Haggins's formula, in which extrapolation to $C \to 0$ was found to be a characteristic viscosity index of $\eta_c / C = [\eta]$ from the condition $[\eta] = 2,00 \ dl / g$.

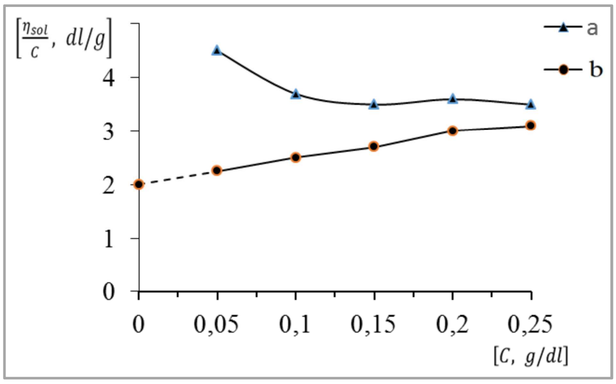

Figure 1. Binding graph of the given viscosity to concentration (η_c / C) (C): a-ChZ-2% CH_3COOH; b- ChZ -2% CH_3COOH-2% NaCl.

Using the quantity of $[\eta]$, the Mark-Kunn-Howing equation [10] and found that the average molecular mass of chitosan was $M_\eta \approx ([\eta] / 4,97 \cdot 10^{-5})^{1/0,77} = 130000$.

A dilute solution of fibroin $(C = 0,3 \text{ g/dl})$ was prepared and the polyelectrolyte properties were investigated by viscometry at 25°C. However, a 2.5 M LiCl-DMFA solvent for which the coefficients of the Mark-Kun-Howing equation [13] were found was used to determine the molecular mass. The results of the study are shown in Figure 2 below.

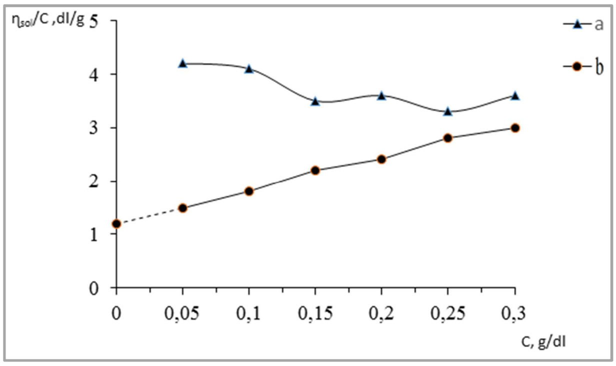

Figure 2. Graph of binding of the given viscosity to concentration (η_c / C) (C): a - FB-HCOOH: H_2O (1: 1); b - FB -2.5 MLiCl-DMFA.

In this figure, the graph of the FB-HCOOH: H_2O (1: 1) solution is curvilinear and is characterized by a polyelectrolyte concentration anomaly. Hence, the observation that the interaction of the main functional groups of FB (NH_2COOH) with the dilution of the solution changes unevenly leads to the conclusion that macromolecules as macroions actively interact with the acidic environment surrounding them [11].

The next FB -2.5 MLiCl-DMFA solution bond graph is linear and conforms to Haggins 'law. Extrapolated [14] from it to $C \to 0$ and found that the descriptive viscosity of the $\eta_c / C = [\eta]$ condition was $[\eta] = 1,2 \text{ dl/g}$. Mark – Kunn-Howing [15] equation using FB to calculate the mean molecular mass $M_\eta \approx ([\eta] / 1,23 \cdot 10^{-5})^{1/0,91} = 295000$.

The determined molecular masses of the samples were divided by the masses of elementary units (M_o), and the number of elementary units (n), that is, the degree of polymerization (PD), was found (Table 1). Considering that chitosan has one NH_2-amine group and fibroin has one NH_2 and one COOH-carboxyl group, it follows that there are 680 amine and 885 carboxyl groups in XZ and 885 in FB.

***Table 1.** Examples of ionogenic groups and electrochemical equivalent.*

Sample	η	M_η	M_o	N	Ionogen group		Electrochemical equivalent, k, mg/C
ChZ	2,0	130000	161	807	NH_2	680	0,16
FB	1,2	295000	345	782	NH_2	885	0,16
					COOH	885	0,46

The presence of so many ionogenic groups in a polymer macromolecule is a full reason to consider it as a macroion in a polyelectrolyte solution. One of the important parameters of ionogenic polymers is their electrochemical equivalent, which is calculated according to Faraday's law (*F = 96485 C/mol*) depending on the molar mass and valency *(z)* of the ionogenic group.

The results obtained for the ionogenic group of samples are included in Table 1. This case, in general, the parameters defined in this paragraph indicate that macromolecules can move, that is, shift and electrochemically recover under the influence of an electric field, depending on their ionogenic groups.

4. Conclusion

Based on the molecular mass characteristics of objects, ionogenic groups, properties of biopolymers as macroions in gradient areas, effective viscosity, macroions and their behavior in acidic environments, experimental studies have shown that, rheological studies revealed that the molecular masses (M_{FB} = 295000, M_{ChZ} = 130000). On the basis of the conducted studies, the molecular mass characteristics of the research objects, ionogenic groups and their electrochemical equivalent, the displacement properties of biopolymers as macroions in gradient fields, their effective viscosity were determined and entered as a scientific conclusion, and the practical significance and the behavior of macroions in the polymer solution in the electric field were described.

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