

Electrical impedance spectroscopy for monitoring the gum Arabic–chitosan complexation process in bulk solution



C. Roldan-Cruz^a, J. Carmona-Ascencio^b, E.J. Vernon-Carter^b, J. Alvarez-Ramirez^{b,*}

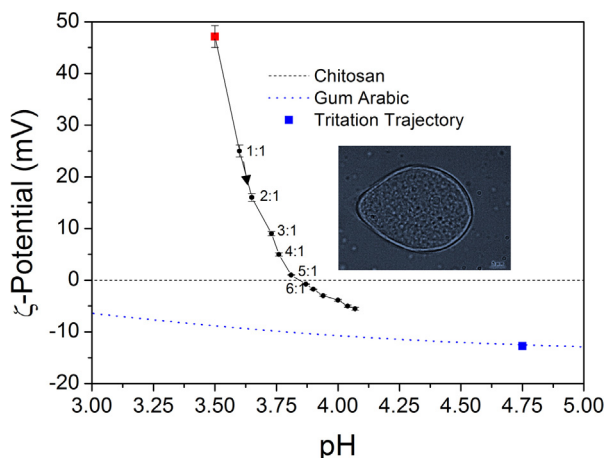
^a Departamento de Biotecnología, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, Iztapalapa D.F. 09340, Mexico

^b Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, Apartado Postal 55-534, Iztapalapa D.F. 09340, Mexico

HIGHLIGHTS

- Electrical impedance spectroscopy (EIS) tests were carried out to study the complexation process.
- Gum Arabic and chitosan in bulk solution were considered.
- Parameters from a fractional-order Randles circuit were used as indicators of coacervation changes.
- The EIS was compared with that obtained via traditional ζ -potential measurements

GRAPHICAL ABSTRACT



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ABSTRACT

Electrical impedance spectroscopy (EIS) tests were carried out to study the complexation process between gum Arabic (GA; aqueous dispersion, pH 4.75, 1% w/w) and chitosan (Ch; acetic acid dispersion, pH 3.5, 1% w/w) in bulk solution. EIS data were obtained for different GA/Ch mass ratios ($R_{GA/Ch} = 1:1-10:1$) at frequencies ranging from 1 Hz to 1000 Hz. A fractional-order Randles circuit was used to estimate resistance and capacitance parameters as function of $R_{GA/Ch}$. Complex coacervates were obtained by subjecting the bulk solutions to centrifugation, and quantifying the sedimentation velocity and height. The equivalent circuit parameters showed sharp changes at the isoelectric point of the complex coacervates. The capability and accuracy of the EIS was compared with that obtained via traditional ζ -potential measurements. The results indicated that the EIS technique can be used at specific frequency ranges as a practical method for monitoring the complexation process between biopolymers.

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1. Introduction

Biopolymers with opposite charge in solution can engage in complex interactions involving electrostatic attraction and charge transfer phenomena. Characterizing the physicochemical prop-

* Corresponding author. Fax: +52 55 58044649.
 E-mail address: jjar@xanum.uam.mx (J. Alvarez-Ramirez).

erties of biopolymer complexes is a topic of vital importance to engineers and scientists because they can determine to a great extent the texture, morphology and mechanical stability of colloidal matter [1]. The interactions between polyelectrolyte biopolymers can be manifested in several forms. Weak interactions lead to the formation of small soluble complex reflected as murky solutions, as well to the formation of homogeneous weak gels. On the other hand, strong interactions can lead to the precipitation of the complex colloids formed by both biopolymers [2]. The nature and extent of biopolymers complex formation are affected by molecular characteristics (e.g., charge density and distribution of reactive groups), relative biopolymer concentration and solution conditions (e.g., pH, ionic strength and temperature).

Complex coacervation, leading to the formation of a precipitate of both biopolymers, has found a large diversity of technological applications in the biotechnology, food and pharmaceutical industries. Protein/polysaccharide and polysaccharide/polysaccharide coacervates have been used for stabilizing emulsions [3], for immobilizing probiotics [4], as milk-fat replacers [5], for the microencapsulation and controlled the release of bioactives and drugs [6–9], and in many other domains [10].

In general, the coacervation process is affected by pH, ionic strength, charge density, chain length and the charge ratio [11]. The monitoring of the coacervation formation is an important issue for determining optimal conditions in terms of morphology, yield and functional properties. In fact, it has been pointed out that scale-up of complex coacervation for large-scale production is not trivial since the morphology and size are highly dependent of the processing conditions [12]. In this regard, the monitoring methods play an important role for tracking significant variations in the coacervation process. Because coacervation involves self-assembly driven by protolytic equilibrium, electrostatic attraction and complexation between oppositely charged polyelectrolytes, zeta potential is widely used to assess the formation of complex morphologies with desired properties [13]. Also, coacervation takes place when the thermodynamic conditions are not adequate to sustain the solubility of the charged polyelectrolytes. Hence, turbidity measurements have been also used to monitor the coacervate precipitation process [14]. Besides, microscopy is routinely used for visual evaluation of coacervate morphology. Small angle scattering has been also proposed to delimitate the size and spacing of coacervate domains [15].

A central feature of complex coacervation is the electrostatic attraction between oppositely charged polyelectrolytes. In this way, it has been considered that measurements of the mobility of charges within the coacervate domains provide valuable insights, as a complement to other methods, regarding the complexation process [6]. The electrical DC conductivity methods give simple, rapid and relatively inexpensive measurements of charge mobility. However, a drawback of DC conductivity is its low sensitivity and accuracy in many instances, especially with media displaying relatively high conductivity [16]. Electrical impedance spectroscopy (EIS) has been proposed as a direct and non-destructive alternative to DC conductivity measurements in colloidal systems [17–19]. The idea behind EIS is to estimate the electrical impedance of a medium as function of variable frequency. The potential of EIS for testing the evolution of colloidal systems is still under exploration. Galia et al. [20] studied the self-assembly behavior of amphiphiles soluble in supercritical carbon dioxide using EIS. The link between electrical impedance and the formation of aggregates in aqueous solutions of dyes and surfactants was explored by de Oliveira et al. [21]. Scandurra et al. [22] reported that EIS was a practical and rapid method for assessing the floral origin of honey. Ghasemi et al. [16] investigated changes in electrical impedance for determining the critical micelle concentration of ionic emulsifiers. Recently, Abdollahi et al. [23] used EIS to study the colloidal behavior of non-ionic emulsi-

fiers in non-polar solvents. Interestingly, EIS can be also used for estimating the size of microstructures [24].

In this work, EIS was used for evaluating the complexation process between low molecular weight chitosan (cationic) and gum Arabic (anionic) in the bulk of the aqueous phase. The EIS results were contrasted with those obtained using the traditional zeta potential method where the equivalence point between the biopolymers is determined.

2. Materials and methods

2.1. Materials

Low molecular weight chitosan (Ch; 92.2% degree of deacetylation, DDA) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Chitosan is a cationic heterogeneous binary polysaccharide consisting primarily of 2-acetamido-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glucopyranose residues [25]. Gum Arabic (GA; *Acacia senegal*) was purchased from Sigma–Aldrich (St. Louis, MO, USA). GA is a branched, neutral or slightly acidic, complex polysaccharide obtained as mixed calcium, magnesium and potassium salts [26]. Studies on the structure of GA indicate that the molecules consist of a β (1 \rightarrow 3) linked galactopyranose backbone chain with numerous branches linked through β (1 \rightarrow 6) galactopyranose residues and containing arabinofuranose, arabinopyranose, rhamnopyranose, glucuronic acid and 4-O-methyl-D-glucuronic acid, with small amount of proteinaceous material forming an integral part of the structure. Acetic acid, hydrochloric acid and sodium hydroxide were purchased from J.T. Baker (Xalostoc, State of Mexico, Mexico). Deionized water was used in all the experiments.

2.2. Preparation of biopolymer solutions

Chitosan (1% w/w) was dispersed in deionized water with acetic acid (1%, v/v) and gum Arabic (1% w/w) was dispersed in deionized water at 20 °C. The dispersions were gently stirred for 12 h and stored overnight at 4 °C to guarantee complete hydration of the biopolymers.

2.3. Protolytic titrations

Protolytic titrations were carried out to estimate the stoichiometric relation between chitosan and gum Arabic dispersions. A sample of chitosan dispersion (20 mL) was titrated with NaOH (0.1 M) and the pH was recorded (Vernier pH-BTA, Beaverton, OR, USA). Likewise, a sample of gum Arabic dispersion (20 mL) was titrated with HCl (0.1 M), with continuous monitoring of the pH. The titration results were contrasted with those obtained for the acetic acid solution (1% v/v) used for the preparation of the chitosan dispersion and for the deionized water used for the preparation of the gum Arabic dispersion. All titrations were made in triplicate.

2.4. Titration of chitosan dispersion with gum Arabic dispersion

The GA dispersion was slowly added into the Ch dispersion using gentle stirring conditions at 20 °C. The pH values for gum Arabic–chitosan mass ratios ($R_{GA/Ch}$) ranging from 1:1–10:1 were monitored with a Vernier pH-BTA (Beaverton, OR, USA) at 20 °C.

2.5. ζ -Potential

The ζ -potential measurements were performed with a Zeta-sizer Nano ZS90 (Malvern Instruments, Worcestershire, UK). The pH of the GA and Ch dispersions (10 mL) was adjusted using either 0.1 N HCl or 0.1 N NaOH with the help of the MPT-2 equipment

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