Gum Arabic−Chitosan Complex Coacervation

Hugo Espinosa-Andrews, Juan G. Báez-González, Francisco Cruz-Sosa, and E. Jaime Vernon-Carter*

DIPH and DBT Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco # 186, Mexico City 09340, Mexico

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The formation of electrostatic complexes of gum Arabic (GA) with chitosan (Ch), two oppositely charged polysaccharides, as a function of the biopolymers ratio ($R_{GA/Ch}$), total biopolymers concentration (TB_{conc}), pH, and ionic strength, was investigated. The conditions under which inter-biopolymer complexes form were determined by using turbidimetric and electrophoretic mobility measurements in the equilibrium phase and by quantifying mass in the precipitated phase. Results indicated that optimum coacervate yield was achieved at $R_{GA/Ch} = 5$, independently of TB_{conc} at the resulting pH of solutions under mixing conditions. High coacervate yields occurred in a pH range from 3.5 to 5.0 for $R_{GA/Ch} = 5$. Coacervate yield was drastically diminished at pH values below 3.5 due to a low degree of ionization of GA molecules, and at pH values above 5 due to a low solubility of chitosan. Increasing ionic strength decreased coacervate yield due to shielding of ionized groups.

Introduction

Macromolecules are the main components of formulated food products, and the control of structural properties of proteins and polysaccharides is a wide topic of investigation.[1,2] Interactions between food macromolecules can be either repulsive or attractive, underlining two opposite phenomena: biopolymer incompatibility and complex formation.[1−4] The complexes formation can be either soluble or insoluble.[5] The insoluble complexes concentrate in liquid coacervate drops, leading to a phase separation of the mixture into two liquid layers.[5] The word "coacervate" is derived from the Latin "co" (together) and "acerv" (a heap) to signify the preceding union of the colloidal particles.[6,7]

IUPAC defines coacervation as the separation into two liquid phases in colloidal systems (the phase more concentrated in colloid component is the coacervate, and the other phase is the equilibrium solution).[8] The phenomenon can be divided into "simple" and "complex" coacervation. Briefly, simple coacervation usually deals with systems containing only one colloidal solute, while complex coacervation usually deals with systems containing more than one colloid. Simple coacervation is a process involving the addition of a strongly hydrophilic substance to a solution of a colloid, which causes two phases to be formed: one phase rich in colloidal droplets and the other poor in such droplets. This process is dependent primarily on the degree of hydration produced, a variable difficult to control. On the other hand, complex coacervation has been found to be primarily dependent on pH and has been reported to occur in systems containing two dispersed colloids of opposite electrical charge. The optimum conditions for complex coacervation are achieved when pH is adjusted to a point where equivalents of oppositely charged molecules of the two colloids are present, because the greatest number of salt bonds form at this point.[9,10]

These complexes have many applications, including carbonless copy paper,[11] fat substitution,[12] protein separation,[13] microencapsulation,[14−17] cosmetics,[18,19] food,[20,21] and enzyme immobilization.[22]

* To whom correspondence should be addressed. Phone: (+52)-5558044648. Fax: (+52)5558044900. E-mail: jvc@xanum.uam.mx.

A number of studies have shown that complex coacervation could be obtained in protein−polysaccharide mixtures, provided that external parameters triggering electrostatic interactions (i.e., pH, ionic strength, biopolymers ratio, total biopolymers concentration, temperature, charge density, and polyelectrolyte stiffness) are accurately controlled.[6,23−29]

Complex formation is driven by the increase of entropy due to expulsion of small ions from the double layers around the individual polyelectrolyte chains, while in the case of weak polyelectrolytes, the polyelectrolyte is able to increase the charge of the polyelectrolyte groups, which implies a further decrease of the free energy.[30] The nature of protein−polysaccharide complexes also is influenced by entropic factors, such as flexibility and/or transitions between globular and extended conformations, and by enthalpy contributions, which in turn are regulated by the protein−polysaccharide ratio, the nature, and density of charges on the biopolymers. There is scarce information about factors influencing ionic polysaccharide−polysaccharide interactions. Recently, it was reported that mesquite gum, a polysaccharide very similar in chemical composition to gum Arabic, formed soluble complexes with chitosan at mineral oil−water flat interfaces[31] and around mineral oil-in-water emulsions.[32] In both cases, the systems exhibited viscoelastic properties that were highly dependent on the mesquite gum−chitosan ratio.

Chitosan (Ch) is the second polysaccharide most abundant in the world and is obtained by alkaline *N*-deacetylation of chitin. The use of chitosan in the food industry is particularly promising because of its biocompatibility and nontoxicity.[33] Chitosan is a heterogeneous binary polysaccharide that consists primarily of 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose residues, the latter residue being responsible for its cationic charge at acidic pH values. The properties of chitosan in solution depend on molecular weight, the deacetylation degree, pH, and ionic strength.[34,35] The pK_a value of the glucosamine segments is 6.3−7.[35] At low pH and low ionic strength, the intrinsic viscosity of chitosan increases rapidly, due to strong electrostatic segment−segment repulsion, adopts an extended conformation, and the rotational

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flexibility of its chains are relatively large for a polysaccharide polyelectrolyte. However, due to the bulky sugar rings, flexibility is limited if compared to that of polyelectrolytes with a hydrocarbon backbone.[35]

Gum Arabic (GA) is a negatively charged polyelectrolyte that is widely used in industry due to its high solubility and low viscosity at high concentrations, and good emulsifying and microencapsulating properties.[36,37] It is an arabinogalactan composed of three distinct fractions with different protein contents and different molecular weights.[3,38] The composition analysis of GA reveals the presence of a main galactan chain carrying heavily branched galactose/arabinose side chains. The carbohydrate moiety is composed of D-galactose (~40% of the residues), L-arabinose (~24%), L-rhamnose (~13%), and two types of uronic acids, responsible for the polyanionic character of the gum, D-glucuronic acid (~21%) and 4-*O*-methyl-D-glucuronic acid (~2%). It has been suggested that this polysaccharide has a "wattle blossom"-type structure with a number of polysaccharide units linked to a common polypeptide chain.[5,39] This feature is responsible for its good surface activity and viscoelastic film-forming ability.[40] The GA molecule is somewhat globular, but the openness of its structure and its possible existence in a coiled form are possible and, to a degree, dependent on the amount of ionic dissociation of the uronic acid units or their salts. In the normal salt form at near neutral pH, these carboxyl groups will be largely dissociated, and the resulting Coulombic repulsion of the negatively charged carboxylate groups will cause the molecule to assume an open, highly charged, expanded structure.[41]

Nevertheless, it has been reported that gum Arabic does not provide long-term stability against oxidation to monoterpenes[42] and orange oil.[43] So, an interesting research topic would be to investigate its interactions with other biopolymers to improve its barrier properties against oxidation. On the other hand, chitosan is extensively used in the food industry because it forms strong, flexible, clear films that exhibit good barrier properties against oxygen.[44] Thus, the combined use of gum Arabic with chitosan could provide an inter-biopolymer electrostatic complex that could form strong viscoelastic films around oil droplets and provide them with good barrier properties against oxidation. This work aims to investigate the complex coacervation formation between gum Arabic and chitosan as a function of biopolymers ratio (gum Arabic/chitosan), total biopolymers concentration, pH, and ionic strength, so as to gain information useful for its use in practical applications.

Materials and Methods

Materials. Chitosan (medium molecular weight, degree of deacetylation: 79%) was purchased from Sigma-Aldrich (St. Louis, MO). Gum Arabic (*Acacia senegal*) teardrops were purchased from Industrias Ragar, S.A. de C.V. (Mexico City, Mexico).

Preparation of Biopolymers Mixtures. Chitosan (2% w/w) and gum Arabic (20% w/w) stock solutions were prepared by dispersing the former in MilliQ-grade water with 0.1 N HCl and the latter in MilliQ-grade water, respectively. The solutions were gently stirred for 12 h and stored overnight at 4 °C, to ensure complete hydration of the biopolymers. Fifteen biopolymers solutions ($TB_{conc}R_{GA/Ch}$) were prepared, which contained different total biopolymers weight concentrations (TB_{conc}) and different weight ratios of gum Arabic to chitosan ($R_{GA/Ch}$), by mixing the amount of both stock solutions, and by adding MilliQ-grade water when required, and whose compositions were: $TB_{1.00}R_3$, $TB_{1.25}R_4$, $TB_{1.50}R_5$, $TB_{1.75}R_6$, $TB_{2.00}R_7$, $TB_{2.00}R_3$, $TB_{2.50}R_4$, $TB_{3.00}R_5$, $TB_{3.50}R_6$, $TB_{4.00}R_7$, $TB_{4.00}R_3$, $TB_{5.00}R_4$, $TB_{6.00}R_5$, $TB_{7.00}R_6$, and $TB_{8.00}R_7$. No preservatives were added to the solutions, because chitosan is reported to act as bactericide and fungicide.[44] The solutions were left to rest 72 h at room temperature prior to analysis. All of the measurements were done in triplicate, and their means are reported with their standard deviations.

Coacervate Yield. The equilibrium phase was separated from the coacervate phase by decantation, and the latter phase was dried at 36 °C until constant weight was achieved. The coacervate yield was determined by mass balance using the following equation:

$$\%\text{yield} = \frac{m_o - m_i}{m_o} \times 100$$

where m_o is the total biopolymers powders weight used to make the biopolymers solutions, and m_i is the weight of the dried coacervate phase.

Composition of the Coacervate Phase and of the Equilibrium Phase. The coacervate phase biopolymers ratio ($CPBR_{GA/Ch}$) was determined using an elemental analysis equipment PE2400 series II CHNS/O Analyzer (Perkin-Elmer, USA). In the CHN operating mode, the equipment uses a combustion method at 980 °C to convert the coacervate elements to simple gases (CO_2, H_2O, and N_2). GA and Ch, as blanks, and then the different coacervates were first oxidized in a pure oxygen environment. Products produced in the combustion zone include CO_2, H_2O, and N_2. The resulting gases were homogenized and controlled to exact conditions of pressure, temperature, and volume. The homogenized gases were allowed to depressurize through a column where they were separated in a stepwise steady-state manner and detected as a function of their thermal conductivities. Total C, H, and N were calculated with a precision of 0.1 μg by the equipment software. Experimental GA % ($\%GA_E$) in the coacervates was calculated with the following equation:

$$\%GA_E = \frac{\%\text{coacervate} - \%\text{Ch}}{\%\text{GA} - \%\text{Ch}} \times 100$$

where %GA, %Ch, and %coacervate corresponded to the %N found for GA, Ch, and the corresponding coacervate samples, respectively. N was selected for determining the mixture composition because it provided a reasonable element differential between GA and Ch. Equilibrium phase biopolymers ratio ($EPBR_{GA/Ch}$) was determined by mass balance.

Electrophoretic Mobility. The electrophoretic mobility of the equilibrium phase was determined using a particle electrophoresis instrument (Zetasizer Nano-ZS, Malvern Instruments, Worcestershire, U.K.). The essence of a classical microelectrophoresis system is a capillary cell with electrodes at either end to which a potential is applied. Particles move toward the electrode, and their velocity is measured and expressed in unit field strength as their mobility. Each undiluted equilibrium phase solution was put in a universal dip cell equipped with platinum electrodes. The apparatus was previously calibrated with latex standard (-50 ± 5 mV). The measurements were made at the resulting pH (3.8 ± 0.1) ("natural" pH) of the different $TB_{conc}R_{GA/Ch}$ solutions at 25 °C.

Turbidimetric Measurements. Turbidimetric measurements provide information regarding the soluble complexes. A Spectronic Genesys 2 UV/vis (Spectronic Unicam, Rochester, NY) spectrophotometer was used to follow the turbidity on the equilibrium phase at a wavelength of 600 nm at 25 ± 1 °C without stirring. Samples were placed in 1 cm path length cuvettes. Turbidity was recorded and then calculated as follows:

$$\tau = -\left(\frac{1}{L}\right) In\left(\frac{I_0}{I_t}\right)$$

where L is the optical path length (cm), I_t is the transmitted light intensity, and I_0 is the incident light intensity.

Effect of Salt and pH on Coacervate Yield. The biopolymer solution $TB_{conc}R_{GA/Ch}$ that produced the highest coacervate yield under

natural pH solution conditions either was added different concentrations of NaCl (0, 25, 50, 75, 100, 125, and 150 mM) or had its pH adjusted to 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, and 7.0 by adding either HCl (0.1 N) or NaOH (0.1 M) as required, to determine the effect of both factors on the coacervate yield.

Results and Discussion

Coacervate Yield and Composition. The coacervate yield was used to understand the effect of biopolymer weight ratio, pH, salt concentration, and total biopolymers concentration on the efficiency of complex coacervation between gum Arabic and chitosan. All of these factors influence the three-dimensional configuration and relative charge density between both biopolymers, which in turn affect the degree of electrostatic interaction between them. After phase separation, the coacervates phase remained viscous liquid-like, very similar to that reported by Weinbreck et al.[3] Figure 1a shows the coacervate yield as a function of biopolymer weight ratio and total biopolymer concentration (obtained from the chitosan wt % and $R_{GA/Ch}$). A maximum in coacervate yield was obtained at a biopolymers ratio of 5, independently of total biopolymer concentration used. Complex coacervation between the two biopolymers is the result of the interactions taking place between carboxylic groups ($-COO^-$) of gum Arabic and the amino groups ($-NH_3^+$) of chitosan.

Apparently, a stoichiometric charge ratio between both biopolymers occurs at a GA/Ch ratio of 5, inducing maximum electrostatic interaction between both biopolymers. This phenomenon implies that charge neutralization between both types of macromolecules occurs. As the $R_{GA/Ch}$ moves further away from R_5, the charge balance between the macromolecules also drifts further away from its stoichiometric ratio, and coacervate yield decreases more pronouncedly. The decrease in coacervate yield from R_5 to R_7 was noticeable, but was not affected in general terms by total biopolymer concentration. On the other hand, coacervate yield decreased markedly and was highly dependent on total biopolymer concentration at R_4 and R_3 (Figure 1a). These results are relevant as they indicate that at low biopolymers ratios (R_3 and R_4) relatively high biopolymers concentrations are required for obtaining coacervate yields of around 80% or more, but that at higher biopolymer ratios (R_5, R_6, and R_7) there is practically no difference in coacervate yield whether a 2, 4, or 8 wt % total biopolymers concentration was used. When designing specific food-products, these results should be taken into consideration. The effect of total biopolymer concentration on coacervate yield can probably be best explained in terms of the polyelectrolyte behavior of macromolecules.[45] Ionization of the attached function aids in the solubilization of the polyelectrolyte, which dissolves to yield a polyion and counterions. The polyion holds a large number of charges in close proximity because they are attached to the macromolecular backbone, and although the polyion has mobility, the individual charges attached to the chain do not. Not all of the counterions are free to move about. The free ions form a counterion cloud about the polyion, whereas the immobilized ions are bound to a specific site or point of the macromolecular backbone. As the polyelectrolyte solution is diluted, more and more of the site-bound counterions are released, building the charge of the macro ion, which expands. Expansion on dilution cannot occur indefinitely, due to flexibility constraints in the macromolecular backbone. The more expanded is the polyion, the higher is the "stiffness" of the macromolecular backbone, so that the exposed charged sites possess less freedom for interaction. This phenomenon in addition to the fact that the number of polyions available in diluted systems are lower explain the sharp decrease in coacervate yield at low biopolymers concentrations. At relatively high biopolymers concentrations, the degree of ionization of the macromolecule is lower, and the flexibility of the macromolecular backbone is much higher as it is less expanded, so that the charged sites are more readily available for interaction, thus resulting in higher coacervate yields. These results are important in that they pinpoint that neither too low nor high total biopolymers concentrations allow for an efficient coacervate formation.

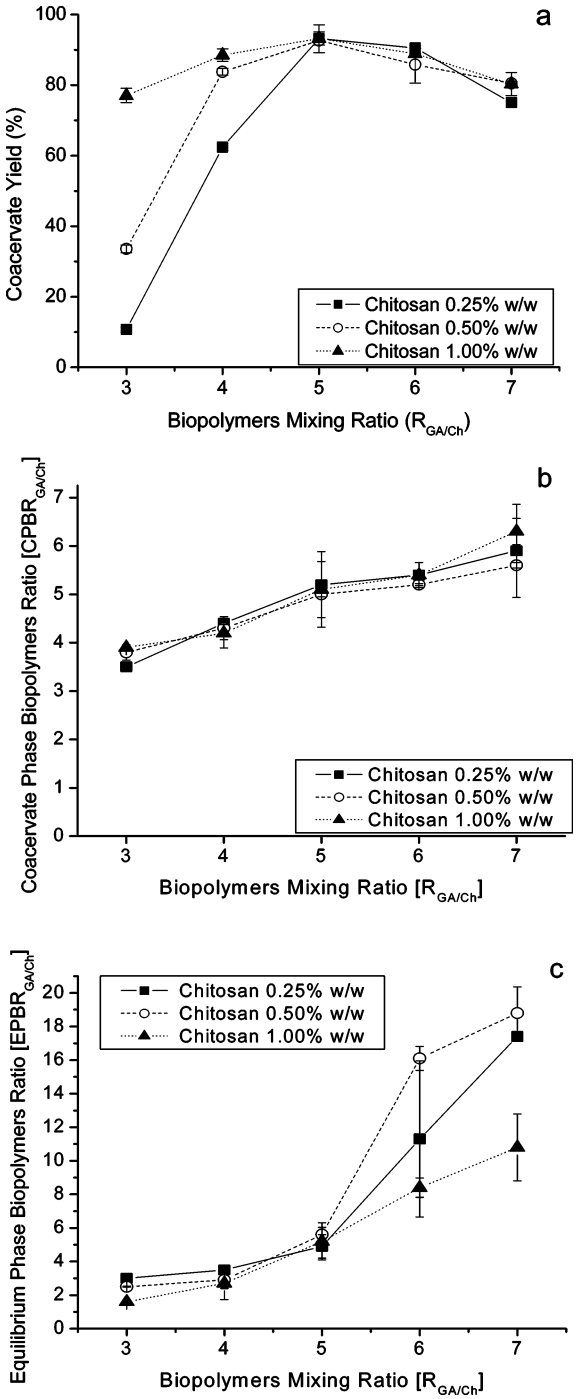

Figure 1. (a) Coacervate yield; (b) coacervate phase biopolymers ratio; and (c) equilibrium phase biopolymers ratio, as a function of biopolymers mixing ratio and total biopolymers concentration after 72 h.

The elemental analysis for GA was 42.64 %C, 6.20 %H, and 0.64 %N, whereas for Ch it was 34.14 %C, 6.58 %H, and 6.27 %N. Elemental analysis for the different coacervates varied in

Table 1. Experimental Gum Arabic % Found by Elemental Analysis in the Different Coacervates

$TB_{1.00}R_3$	8.00%	$TB_{2.00}R_3$	26.9%	$TB_{4.00}R_3$	60.2%
$TB_{1.25}R_4$	51.3%	$TB_{2.50}R_4$	67.5%	$TB_{5.00}R_4$	72.5%
$TB_{1.50}R_5$	80.6%	$TB_{3.00}R_5$	77.3%	$TB_{6.00}R_5$	79.0%
$TB_{1.75}R_6$	77.2%	$TB_{3.50}R_6$	68.9%	$TB_{7.00}R_6$	62.2%
$TB_{2.00}R_7$	67.4%	$TB_{4.00}R_7$	68.6%	$TB_{8.00}R_7$	67.4%

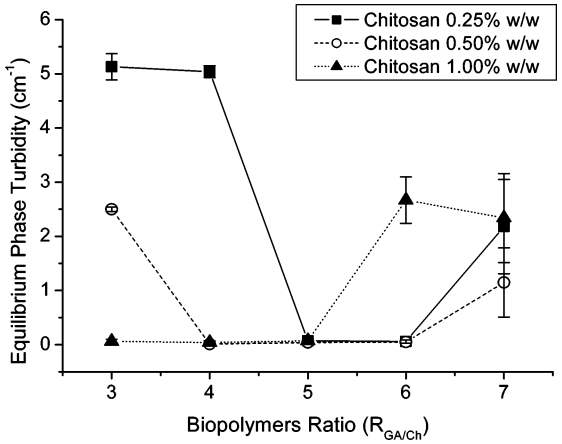

Figure 2. Equilibrium phase turbidity as a function of biopolymers ratio and total biopolymers concentration after 72 h.

between 42.38−45.51 %C, 6.05−6.81 %H, and 1.38−1.89 %N. The $\%GA_E$ found in the different coacervates is given in Table 1.

Figure 1b shows the coacervate phase biopolymer ratio as a function of the $TB_CR_{GA/Ch}$ solutions. In general terms, $CPBR_{GA/Ch}$ increased as the R increased in the staring biopolymers solutions, but was more or less independent of total biopolymers concentration. Figure 1c shows the equilibrium phase biopolymers ratio as a function of the $TB_CR_{GA/Ch}$ solutions. As in the case of Figure 1b, $EPBR_{GA/Ch}$ increased as the R increased but total biopolymer concentration also had an effect, particularly at R's above 5. Nevertheless, it is interesting to notice that by comparing Figure 1b and c, it can be observed that at R_5 both the $CPBR_{GA/Ch}$ and the $EPBR_{GA/Ch}$ values were very near 5, indicating that the coacervate phase and the equilibrium phase were very close to reaching equilibrium.

Turbidimetric Measurements. Turbidimetric measurements can also be employed to follow complex coacervation. Turbidity in the equilibrium phase is related to formation of a non-soluble phase, which may precipitate or remain stable for a short or long time. This implies that solutions with higher turbidity have a greater amount of macromolecules than translucent solutions, the latter indicative of a large coacervate yield. Turbidity data of the equilibrium phase of the GA−Ch system for different biopolymers ratios and total biopolymers concentrations are shown in Figure 2.

Turbidimetric measurement results agree with those of coacervate yield data. As can be seen, the biopolymer weight ratio at which minimum turbidity of the equilibrium phase occurred for whichever total biopolymers concentrations was at R_5. This behavior of the equilibrium phase indicates that neutral complexes between both biopolymers occurred that precipitated to form the coacervate phase. On the other hand, at $R_{GA/Ch}$ ratios lower and higher than 5, turbidity increased, probably due to the formation of soluble complexes. A biopolymer can adsorb on the surface of colloidal particles (e.g., another biopolymer) as a result of (a) a Coulombic (charge−charge) interaction, (b) dipole interactions, (c) hydrogen bonding, or

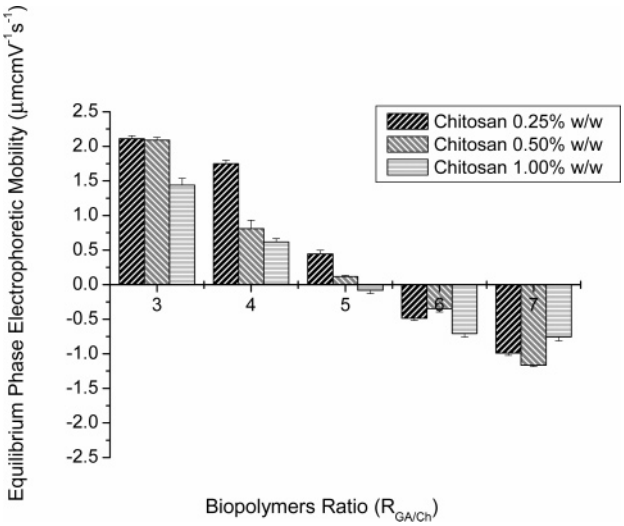

Figure 3. Equilibrium phase electrophoretic mobility as a function of biopolymers ratio and total biopolymers concentration after 72 h, at pH ≈ 3.8.

(d) van der Waals interaction. A balance must be struck between the affinity of biopolymer and the particle surface for one another and for the solvent. The usual result is that the biopolymer is tied to the surface at a number of points but for some of its length it is able to extend into the solution. When two particles are brought together, it becomes possible for a biopolymer to form a bridge between one particle and another, especially if the adsorption density on the particle surfaces is not too high and the biopolymer is of very high molecular mass.[46,47] At high R values, it is likely that Ch molecules act as a bridge between GA molecules (bridging flocculation), but at low R values the opposite may actually happen, with GA molecules bridging Ch molecules.

Electrophoretic Mobility. Electrophoresis measurements corroborate these findings (Figure 3). Positive electrophoresis data of the equilibrium phase indicated that predominance of free amine groups in the solution (occurring when $R_{GA/Ch}$ values were below 5), whereas when the electrophoresis data were negative, a larger amount of ionized carboxyl moieties predominated in the solution (occurring when $R_{GA/Ch}$ values were higher than 5). When the electrophoresis data approached zero, it was indicative that charge neutralization between both biopolymers was the predominant phenomena. This latter phenomenon occurred around a biopolymers ratio of 5 g of gum Arabic/g of chitosan, confirming that at this biopolymers ratio the greatest interaction between the biopolymers was achieved, independently of the total biopolymers concentration used. Again, it was corroborated that at low biopolymers ratios (R_3 and R_4) when total biopolymer concentration was relatively low (1−2 wt % for R_3 and 1.25−2.5 wt % for R_4), the interactions between GA and Ch were restricted probably due the stiffness of their macromolecular backbones, which were more extended at these dilutions. At biopolymers ratios above 5 and whichever total biopolymers concentrations, the macromolecular backbones of both polyions possessed greater flexibility, and thus enhanced ability for interacting.

pH and Salt Concentration on Coacervate Yield. The effect of pH and salt concentration on coacervate yield, based on the turbidimetric measurements of the equilibrium phase, was studied for a biopolymers ratio of 5 and total biopolymers concentration of 6.0 wt % (1.0 wt % Ch). The pH of the biopolymers solution affected the coacervate yield as shown in Figure 4.

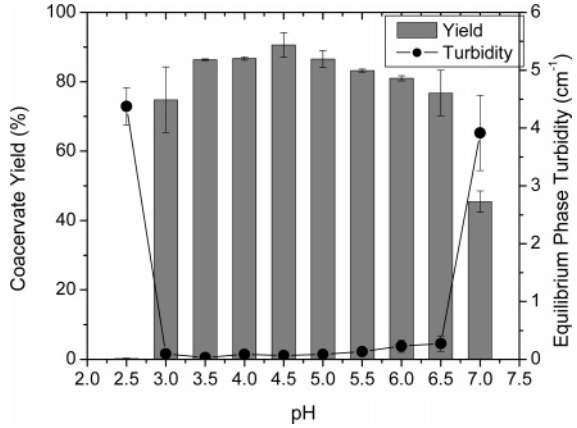

Figure 4. Gum Arabic−chitosan coacervate yield and equilibrium phase turbidity as a function of solutions pH, for biopolymers ratio of 5, total biopolymers concentration of 6 wt %, and after 72 h.

Coacervate yields obtained at pH values between 3.5 and 5 were relatively higher than those at other pH values, as at this pH range the biopolymers charge densities of opposite sign seem to be stoichiometrically balanced. These results are corroborated by the turbidity values, which at these pH values were relatively lower. At pH values below 3.5 and above 5, coacervate yield diminished, and as pH moved further away to pH values lower than 3.5 or pH values higher than 5, the coacervate yield decreased further. Coacervate yield decreased when pH values were below 3.5 due to the occurrence of two phenomena taking place: (i) protonation of the carboxylic groups of gum Arabic, and (ii) contraction of the molecular backbone, both of which seem to reach a maximum at pH 2.5, so that at this pH coacervation is completely suppressed. On the other hand, at pH values above 5, coacervate yield decreased mainly because of phenomena associated with the chitosan molecule. As the chitosan molecules approach their pK_a value[35] (∼6.3−7), their degree of ionization and solubility decrease, to such an extent that a fair amount of chitosan molecules precipitate at pH 7 (Figure 4). Additionally, a sharp increase in turbidity occurs from pH 6.5 to pH 7 due to the high solubility of GA molecules, which at pH 7 have achieved nearly maximum degree of ionization.[48] At this point, it is important to mention that all of the biopolymers solutions, irrespective of the total biopolymers concentrations and biopolymers ratio, exhibited a "natural" pH that fell within a value of 3.8 ± 0.1. This means that all of the biopolymers blends studied were near their optimum pH value for inducing biopolymers interaction. The dependence of coacervation with pH has been reported by various authors,[1,5,24,28] with the pH intervals where interactions occurred depending strongly on the macromolecules properties such as their charge density and macroion flexibility.

Coacervate yield was inversely proportional to [NaCl]. A large ionic strength is known to hinder the setting of small ions free, thus suppressing the driving force for complexation,[30,49] and effectively reducing the available sites for interactions between both macromolecules (Figure 5). As [NaCl] increased, interactions between the macromolecules changed. This phenomenon has been observed in gum Arabic−whey protein isolate[5] systems where the addition of NaCl concentrations >54 mM prevented complexation of the biopolymers. The amount of added salt necessary to diminish drastically coacervation, sometimes called the point of salt resistance, was found to be around a concentration of 150 mM NaCl where a noticeable decrease in coacervate yield was observed (Figure 5).

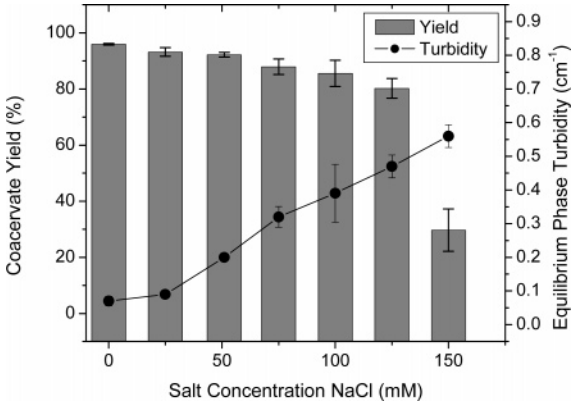

Figure 5. Gum Arabic−chitosan coacervate yield and equilibrium phase turbidity as a function of concentration of NaCl, for biopolymers ratio of 5, total biopolymers concentration of 6.0 wt %, and after 72 h.

Conclusions

It is possible to form insoluble polymeric complexes between two oppositely charged polysaccharides such as gum Arabic and chitosan, and an optimum ratio between the biopolymers exists. The equilibrium phase turbidity and electrophoretic mobility of results, plus those of coacervate yield, indicate that the best results were obtained at a gum Arabic−chitosan weight ratio of 5, independently of total biopolymer concentration used. The electrostatic complexes formed are dependent on pH and ionic strength, but maximum interaction between both biopolymers occurred in a pH range between 3.5 and 5, which is very close to the "natural" biopolymers solution pH. The addition of NaCl concentrations of around 150 mM caused a drastic decrease in coacervate yield. The use of complex coacervation between polysaccharides can provide an important alternative for formulating highly stable and functional oil-in-water emulsions against aggregation phenomena and diffusion of deteriorative agents such as oxygen, as presumably these complexes may form thick and viscoelastic adsorbed layers around the oil droplets.

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