PHASE DIAGRAM OF GELATINE-POLYURONATE COLLOIDS: ITS APPLICATION FOR MICROENCAPSULATION AND NOT ONLY

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Abstract. Phase state and the charge of colloidal particles in the gelatine-polyuronate system were studied. A method for comparative evaluation of molecular weight of colloids by means of viscosimetric measurements and electrophoresis was developed. It is shown that the Diagram {Phase state = f (composition, pH)} contains six well-defined regions. The diagram explains and predicts the behaviour of protein-polysaccharide colloids, which are included in beverages or forms the shells of oil-containing microcapsules.

Keywords: protein-polysaccharides, colloids, electrokinetic potential, phase diagram, microcapsules.

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Introduction

Poorly soluble or electro-statically agglomerated macromolecular compounds derive from interaction of protein zwitterions with polyanions, in particular, with polyuronic acids and their salts [1]. These interactions are of great practical interest, insofar as much of foods contain biopolymers in different combinations [2]. Recently, there were published many papers devoted to the joint use of the proteins and polysaccharides, originate from different natural raw materials, in various pharmaceutical and food systems [3-6]. These compounds have a greater ability to precipitate the colloidal suspensions, compared to pure linear polymers [7]. It is believed that these mixtures are in fact the covalent chemical compounds or supra-molecular three-dimensional structures with high molecular weight, charged as zwitterions due to the presence of proteins [8-10]. Due to this fact, the mixtures are capable to precipitate not only the neutral particles, but also charged particles, both positive and negative. Such three-dimensional structures (3D) appear also during the complex coacervation of oppositely charged macromolecules on the oil droplets surface in the microencapsulation processes [11]. The optimum conditions of precipitation of alginate-gelatine coacervates were obtained *in vitro,* using measurements of turbidity and viscosity [1].

The study led to the elaboration of different phase diagrams, which reflects complex interactions between the negatively charged polysaccharides and zwitterions of proteins [8,12,13]. The interaction of proteins with polysaccharides was described in numerous research papers, but not in the exhaustive form. Among the problematic issues it can be identified the determination of the molecular weight of the resulting supramolecular structures. In our view, the estimation of the molecular weights will be useful for calculating of the microcapsule shells parameters, as well as to determine the conditions of deposition of neutral colloidal particles. Detailed analysis of the phase state of the gelatine-polyuronate system is important to determine the optimal sedimentation conditions, or opposite, to prevent the coagulation of proteins by small amounts of extraneous poly-anions. In constructing of the phase diagram of the gelatine-polyuronate, it is important to consider the sign and magnitude of charge of generated complexes. Unambiguous information about the charge of colloidal particles is given by method of electrophoresis, allowing to measure the zeta potential and to fractionate the charged particles [14,15]. Values of charges are important for explanation and prognosis of the colloids behaviour in food systems containing proteins and polysaccharides. This equally applies to colloids used for the microencapsulation of biologically active substances [4,8,11].

Experimental part

Preparation of gelatine solutions

Macromolecular complexes were prepared using air-dried instant soluble food gelatine of premium grade (Lisichansk Gelatin Factory, ALC). All gelatine samples were incubated in a bath with boiling water for at least 5 minutes with continuous stirring until their complete dissolution. The native pH of gelatine solutions was in the range of 6.3…6.9. To adjust the desirable pH values, which were situated at the range of 2.5…8.0 units, the pH value was decreased by adding of small crystals of citric acid, or was increased by adding of solid potassium hydroxide. Pure gelatine solutions (0.5%) were prepared to determine the isoelectric point (IEP) of gelatine, in order to determine and to consider its type. The gels with the highest turbidity, indicating zero charge of macromolecules, were obtained after 24h in the vials with pH value ranged from 4.7 to 4.9. These values correspond to IEP of the gelatine type “B”, equal to 4.6…5.4, usually obtained by alkaline hydrolysis of skins [12].

Preparation of polyuronates

Pure preparations of alginic acid and hyaluronic acid were isolated from thallus of *Laminaria Japonica* [16]

and from cockscombs of *Gallus Domesticus* [17], respectively. Potassium salts were prepared by dropwise addition of KOH into suspensions of corresponding acids, up to their complete dissolution at pH = 5.5…7.5. Potassium alginate has been used as the main polyuronate, because of the possibility to separate it in pure form *in situ* [16]. Preparations of hyaluronic acid cannot be considered as "pure", because of inevitable presence of protein traces [9, 17]. Due to this fact, the salts of hyaluronic acid have been used to prepare coacervate microcapsules, in order to verify the applicability of results to similar systems, not only to gelatine-alginate system.

Specific viscosity and viscosimetric molecular weights

Viscosimetric measurements of high molecular compounds (HMC) were determined by viscosimeter "VPJ-1-0.34" (Apparatushhik Co., Russia).

Preparation of colloids

The gelatine-polyuronate colloidal systems only by leisurely addition of polyuronate solutions in the gelatine, never vice versa, were prepared. Combination of biopolymers was accompanied by vigorous stirring, and after that, the colloids were subjected to analysis immediately.

Oil-containing microcapsules

The microcapsules, containing walnut oil or sunflower oil, with gelatine-alginate or gelatine-hyaluronate shells, were obtained by complex coacervation method [18]. The ratio of gelatine/polyuranate in the shells of microcapsules was of 3.0...6.0. Mass fraction of encapsulated oil was no less than 75%. Their sizes were ranged from 5.0 to 50.0 microns. Estimated thickness of shells was approx. 0.38 microns.

Electrokinetic potential

Zeta potential (ζ) of colloids was measured by simply device (Figure 1).

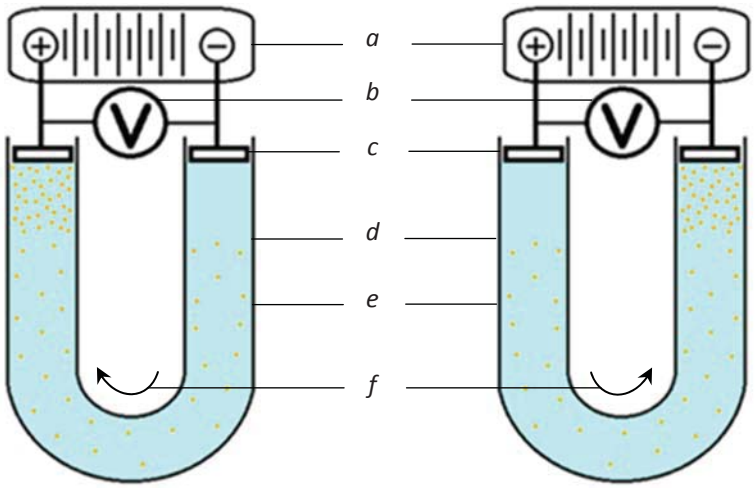


Figure 1. Electrophoretic device: a) source of voltage; b) digital multi-tester; c) stainless steel electrodes; d) sol border; e) U-shaped tube; f) movement of "–"charged particles (on left), "+"charged (right).

Electrophoresis was performed in U-shaped tubes of 1.0 cm width. Process has been occurred on the surface of hand-made integral electrodes, confectioned from stainless steel AISI 304 ("inox" for cookware). The distance between surfaces of the electrodes was from 15.0 to 25.0 cm. The field strength values (E) were adjusted in the range of 100…400 V/m by Stand for Testing of Automatically Equipment (STAE) "SPA-97" (Contragent Co., Ukraine). Operating voltage has been monitored by means of Digital Multi-tester "UT33C" (Shenzhen Sunkoo-Reid Electronic Co., China). The ζ-potential was calculated by the Helmholtz-Smoluchowski equation, Eq.(1) [7,14,15]:

$$\zeta = \frac{\eta \cdot V}{\varepsilon \cdot \varepsilon_0 \cdot H} = \frac{\eta \cdot l \cdot L}{\varepsilon \cdot \varepsilon_0 \cdot U \cdot \tau} \quad (1)$$

where, **constants:** $\eta = 1 \cdot 10^{-3}$ (Pa*)·s* –the viscosity of water; $\varepsilon = 89$, non-dimensional – dielectric constant of water; $\varepsilon_0 = 8.85 \cdot 10^{-12}$ (F/m*)* – electric permittivity of vacuum; **variables:** V (m/s*)* – velocity of colloid particles; H (V/m) – intensity of electric field; l (m*)* – run of colloidal particles in the electric field; τ (s) – time of electrophoresis; L (m) – distance between surfaces of electrodes (effective tube length); U (V) – voltage.

Results and discussion

Molecular weights of high molecular polymeric compounds (HMCs) pure samples

In contrast to the low molecular substances, HMCs do not have constant molecular weight. First, it is characteristic for *in situ* preparations of HMC, obtained from natural sources, having molecular weights that differ in function of characteristics of raw material. Thus, the molecular weights of linear biopolymers ranges from 10^3D to 10^6D (1…1000kD) [2,19]. Secondly, the HMCs molecular weight is almost always seeming, owing to intra- and intermolecular interactions, taking place in the HMCs solutions under the influence of various physical and chemical factors [20]. This is especially characteristic for the macromolecules of proteins and polysaccharides, such as gelatine, alginate, and hyaluronate, because their properties are pH-dependent, due to their polyionic structure, containing acidic or basic functional groups. So-called viscosimetric molecular weight of most types of polymers is usually calculated by Mark-Houwink-Sakurada equation, Eq.(2) [20,21]:

$$M_{HMC} = \left(\frac{[\eta]}{K}\right)^{1/\alpha} \tag{2}$$

where, K and α - constants, properly for the pair polymer-solvent; $[\eta]$ - intrinsic viscosity, which is calculated by extrapolation of function $\eta_{red.} = f\{C(HMC)\}$ to zero concentration of HMC (Figures 2 and 3). For calculations of M_{HMC}, we have considered maximum values of $[\eta]$, because of straightening of HMCs at high pH value [6-7].

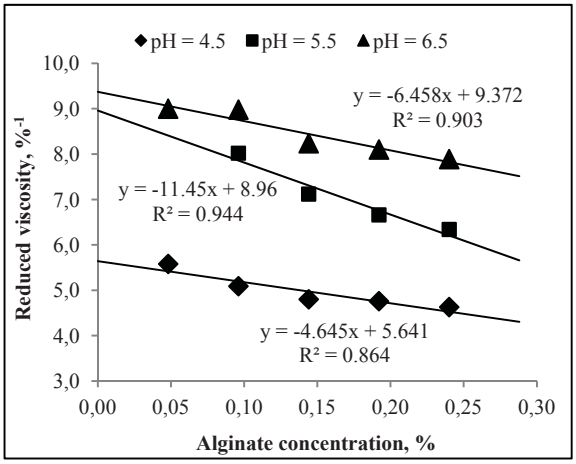


Figure 2. Viscosity of alginate.

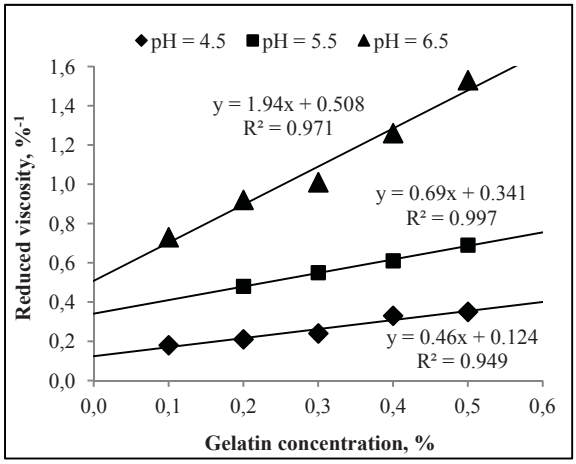


Figure 3. Viscosity of gelatine.

Samples of alginate, separated from thallus of *Laminaria Japonica*, possess intrinsic viscosity $[\eta] = 9.37$ %$^{-1}$, or 937 mL/g in other units. This value is close to intrinsic viscosity of commercial alginate (Sigma-Aldrich Corporation, USA), equal to 1040 mL/g [21]. For this reason, respective values of K (0.0073) and α (0.92) for commercial alginate were used to calculate molecular weight of "our" native alginate. Resulted value, 357 kD, is in good correlation with many reported results [20-22]. In case of linear proteins, as gelatine, the Mark-Houwink-Sakurada equation usually in form of Eq.(3) is written [19]:

$$\frac{M_{\text{protein}}}{M_0} = \left(\frac{[\eta]}{K}\right)^{1/\alpha} \tag{3}$$

For gelatine type "B", M_0 is equal to 110D, representing average molecular weight of structural unit of protein molecule ("average" amino acid). Experimental intrinsic viscosity of gelatine was 50.8 mL/g. Referenced values [19] of constants K (0.166) and α (0.885) have been used to calculate the molecular weight of gelatine, being equal to 70.8 kD.

Estimation of the molecular weights of colloids

It can be assumed that the formation of gelatine-polyuronate systems is possible in a wide range of pH (2.0...8.0). Extreme values of pH correspond to cationic form of gelatine (Gel^+) and its anionic form (Gel^-), respectively. However, in the pH range from 8.0 to 5.0, any types of condensed (solid) colloidal systems do not form, but their interaction is not excluded. Both polymers at pH > 5.0 contribute to total (specific) viscosity of solution. For transparent mixtures of

gelatine and polyuronic salts this dependence is different. Recall that the charge of polyuronate is an order of magnitude greater than gelatine (zwitter-ion) total charge. Due to this fact, one molecule of alginate or hyaluronate can neutralize several gelatine molecules. The analysis demonstrates that specific viscosity of mixtures depends logarithmically on ratio m_{Gel}/m_{Hur} (Figure 4). This function possesses a good value of approximation accuracy, $R^2 = 0.973$. It allowed us to represent this dependence in the linear form (Figure 5). In our view, this linear relationship is well explained by a large number of charges in polyuronate molecules, being ten times higher than that of gelatine at equal pH values.

The weight ratio of gelatine/polyuronate allowed us to calculate the number of gelatine molecules, accompanied with one molecule of alginate, *i.e.* molar ratio of the biopolymers, n_{Gel} / n_{Alg}, Eq.(4):

$$\frac{n_{\mathrm{Gel}}}{n_{\mathrm{Alg}}} = \frac{m_{\mathrm{Gel}}}{m_{\mathrm{Alg}}} \cdot \frac{M_{\mathrm{Alg}}}{M_{\mathrm{Gel}}} \tag{4}$$

There were also estimated the minimal possible molecular weight of *GelAlg* complexes, M_{GelAlg}, reported to the one molecule of alginate, deducing following equation, Eq.(5):

$$M_{\mathrm{GelAlg}} = M_{\mathrm{Alg}} + \frac{n_{\mathrm{Gel}}}{n_{\mathrm{Alg}}} \cdot M_{\mathrm{Gel}} = M_{\mathrm{Alg}} \left(\frac{m_{\mathrm{Gel}}}{m_{\mathrm{Alg}}} + 1 \right) \tag{5}$$

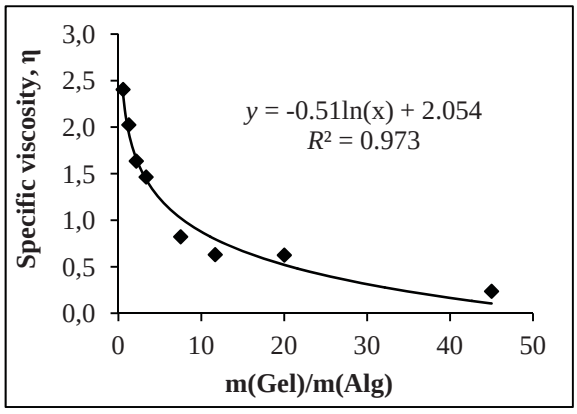


Figure 4. Specific viscosity: logarithmic function.

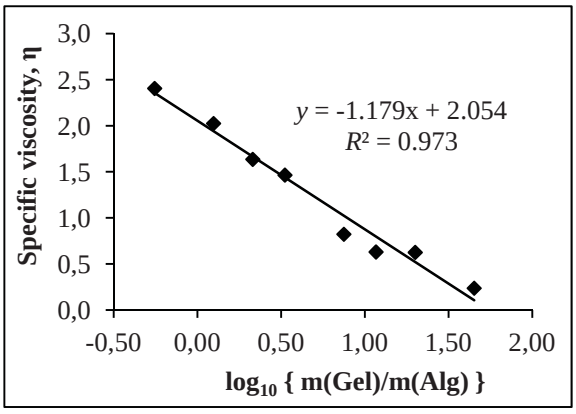


Figure 5. Specific viscosity: linear function.

At pH < IEP the interaction of gelatine with alginate leads to the formation of various colloids, including viscous solutions, large floccules, sols and gels. Naturally, the measuring of zeta-potential for solid colloids was possible only for the stable sols consisting from small particles, which does not precipitate immediately (Table 1).

Table 1

Type of colloidal systems and ζ-potential of stable sols.

m_{Gel}/m_{Alg}	*1.1*	*2.5*	*4.3*	*6.7*	*10*	*15*	*23*	*40*	*90*
$\log_{10}(m_{Gel}/m_{Alg})$	0.041	0.398	0.633	0.826	1.00	1.18	1.37	1.60	1.95
n_{Gel} / n_{Alg}	8	18	30	47	70	105	162	281	632
$M_{GelAlg.} \cdot 10^{-6}$, *D*	0.75	1.25	1.89	2.75	3.93	5.71	8.57	14.6	32.5
pH	*Colloids; sols, if ζ-potential values are showed; Δζ = ± 3.0 mV*								
4.5	high-viscous solutions						-40.7	-32.0	+14.5
4.0	-34.1	-39.8	-22.7	large dense floccules				+17.0	gels
3.5	-37.8	-34.9	-26.2	-20.3	+8.7	+11.6	+17.4	+29.1	gels

As follows from the ζ-potential (Table 1), the *GelAlg* complexes have negative charges, when m_{Gel}/m_{Alg} ratio is low, and they have positive charges, when this ratio is high. By lowering the pH value of biopolymer solutions, the recharging point of resulted particles is gradually shifting in the direction of increasing the alginate concentration. Intersection points of curves $\zeta = f\{\log_{10}(m_{Gel}/m_{Alg})\}$ with values of $\zeta = 0.0$, correspond to the composition of completely neutral colloids (Figure 6). In these conditions, the formation of neutral complexes $GelAlg^0$, able to precipitate quickly,

takes place. The sign inversion occurs at the $\log_{10}(m_{Gel}/m_{Alg}) \approx 1.7$ at the pH = 4.5 (Figure 6, *a*), decreases to ≈ 1.1 at the pH = 4.0 (Figure 6, *b*) and is reduced to ≈ 0.9 at the pH = 3.5 (Figure 6, *c*).

Charge of large floccules, not measurable by electrophoresis

It is problematically to study gelatine-alginate interaction at low pH value, because of precipitation of alginic acid (HAlg) and strong increasing positive charge of gelatine macromolecules. Moreover, the pH values lower than 3.0 are impossible to obtain by means of citric acid, and a small amount of HCl is necessary. In this condition, electrophoresis will be aggravated by electrolyze of HCl solution, resulting $H_{2(Gas)}$ at cathode and $Cl_{2(Gas)}$ at anode. This fact makes impossible to determine correct the zeta potential of colloid particles. The large floccules are formed quickly and are separated spontaneously from the supernatant solutions in many cases. Even in instances when floccules do not precipitate immediately and have been subjected to electrophoresis, they did not form a clearly defined borders so as it was shown in Figure 1. We cannot quantify the charge values in these conditions, but we can estimate the changes of charge sign due to the characteristic behaviour of colloidal suspensions [7]. Thus, after the stirring of obtained colloids about 20…30 minutes in each system was established an equilibrium. The system stability remains unchanged for the next several days (Figure 7).

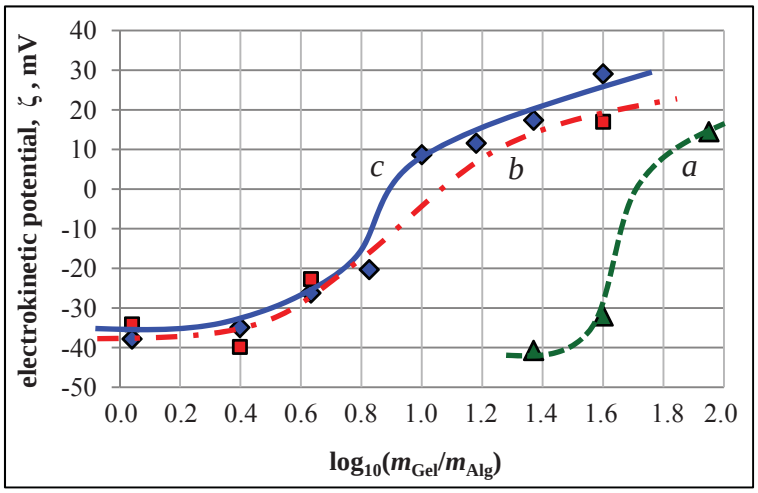


Figure 6. Dependence of electrokinetic potential ζ of the polyelectrolytes concentration ratio: a) at pH = 4.5; b) at pH = 4.0; c) at pH = 3.5.

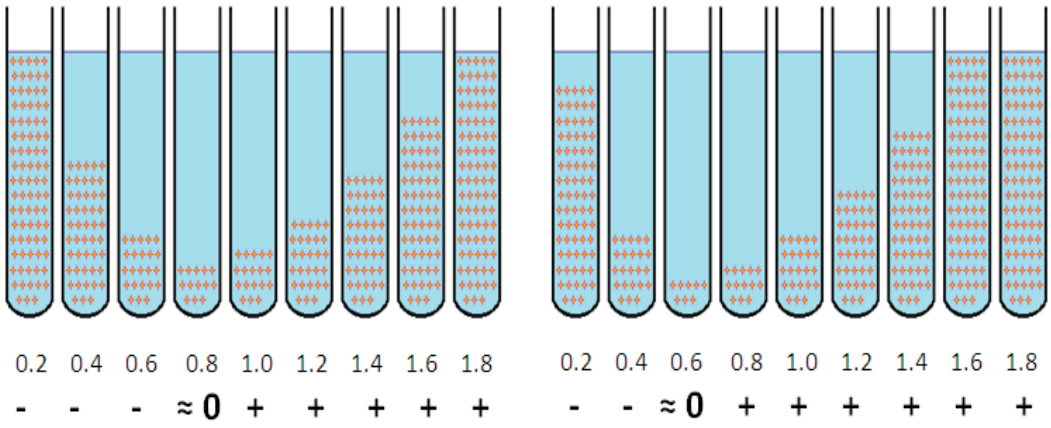


Figure 7. The sedimentation equilibrium aspect; $\log_{10}(m_{Gel}/m_{Alg})$; sign of the floccules charge. Left for pH = 3.0; right for pH = 2.5.

The maximum density of floccules formed at pH = 3.0 corresponds to the range of concentration m_{Gel}/m_{Alg} ratio from 4.0 to 10.0. In a more acidic medium (pH = 2.5) the range of rapid deposition of dense flocks shifted towards lower values of m_{Gel}/m_{Alg} ratio (from 2.0 to 7.0). At the same time, in each case the contents of both external vials remained

in suspension. It is obvious that the formation and rapid deposition of large floccules testifies zero charge of *GelAlg* colloids [7]. Conversely, decreasing the deposition rate in excess of one polyelectrolyte indicates the presence of large quantities of stabilizing charges. Naturally, this charge is negative in the left edge of series, because of excess of alginate anions, and is positive in the right edge of series. At low pH values (3.0 and 2.5), the changes of floccules charge correspond to the ζ-potential changes for particles of sols with high dispersion grade, obtained at pH > 3.0. During the increasing of m_{Gel}/m_{Alg} ratio, the charges of *GelAlg* colloids became positive, similarly with changes shown in Table 1. Neutralization points, obtained using Figures 4 and 5, allow to estimate n_{Gel}/n_{Alg} ratio by Eq.(4) and $M_{GelAlg}{}^{0}$ for neutral 3D-colloids by Eq.(5) (Table 2).

Table 2

Parameters of neutral 3D-colloids GelAlg⁰.

pH	*4.5*	*4.0*	*3.5*	*3.0*	*2.5*
$\log_{10}(m_{Gel}/m_{Alg})$	1.7	1.1	0.9	0.80	0.60
m_{Gel}/m_{Alg}	50.1	12.6	7.9	6.3	4.0
n_{Gel}/n_{Alg}	352	89	56	44	28
$M_{GelAlg}{}^{0} \cdot 10^{-6}$, *D*	18.2	4.86	3.18	2.61	1.79

Results of calculations showed in the Table 2 demonstrate clearly that inversion of charge (neutral) point shifts towards smaller values of the m_{Gel}/m_{Alg} ratio when pH became lower. In other words, at pH values approaching the IEP, even a small amount of polyuronic salts causes the coagulation of the proteins.

Phase diagram construction and its applications for microcapsules

The data obtained and discussed above can be extrapolated in visual interpretation of function pH–composition, resulting phase state diagram of the gelatine-alginate system (Figure 8).

The phase state diagram of gelatine-alginate at various pH values shows the phase phenomena occurring in the pH range of 2.0...6.0 at concentrations from 0.0 % to 3.0 % of gelatine and from 0.0 % to 0.3 % of alginate. These values correspond to the concentrations, used in the producing of beverages by means of protein-carbohydrate interaction [5], and to the conditions of microencapsulation by the method of complex coacervation [4,18]. Recall that at pH values more than IEP, gelatine is in form of negative-zwitterion, and is becoming "pure" anion at pH > 10. At the same time, gelatine is in form of positive charged zwitterion at pH lower than IEP, and is converted in "pure" cation, Gel^{+}, at pH < 2.0 [3,10].

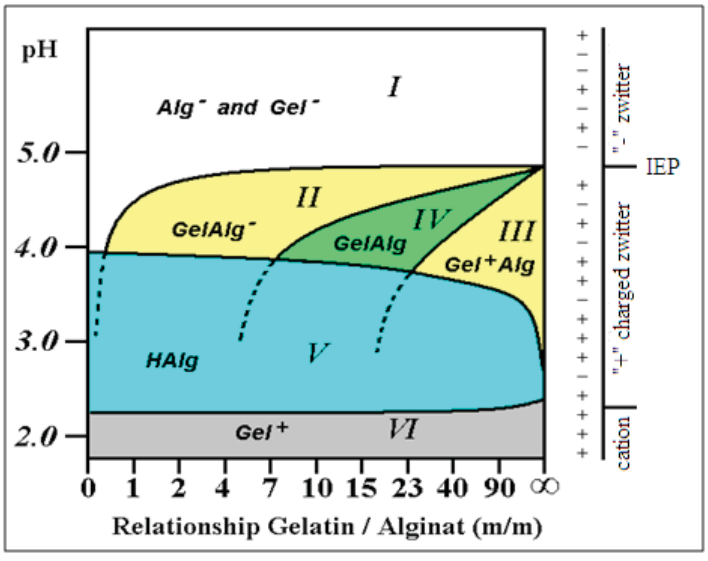


Figure 8. Phase diagram of the gelatine-alginate system.

The **Region I** corresponds to the mutual repulsion of negatively charged zwitterions $Gel^{\pm}$ and "pure" anions of Alg^{-}. Although the main part of the Region I is located at pH > 5 (above the isoelectric point of gelatine), it still comes down to a pH of ≈ 4.5 in the left side, wherein the ratio m_{Gel}/m_{Alg} is low. We explain this fact that at high concentrations

of alginate occur full repayments of positive charges of gelatine by the excess of negative charges, as evidenced by the formation of transparent viscous solutions instead of sols and floccules in these conditions.

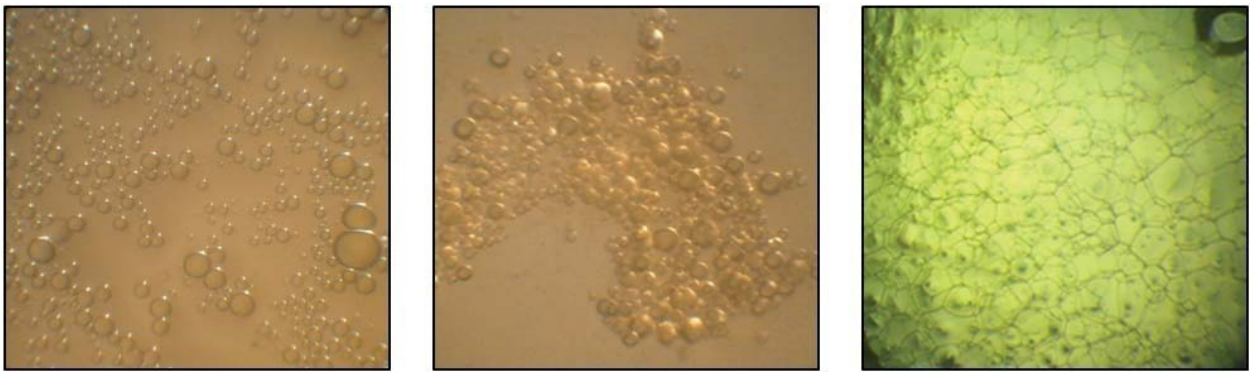
In the **Region II**, the formation of a high-negatively charged sols or suspensions formed from the large floccules takes place. In such colloidal systems the sedimentation does not occurs for several days. Deposition delay takes place because of powerful repulsion between surfaces of floccules. It is known that alginic or hyaluronic acid occurs in the anionic form at pH greater than 3.5 [9,23]. Due to this fact, there is a sufficient number of negative charges of alginate in this Region, which can neutralize many molecules of gelatine-zwitterion. Excess of negative charges, derived from alginate, is decisive for electrokinetic potential of the colloidal system in this Region, and total charge of resulting colloids ($GelAlg^-$) are negative. Colloids, formed in this Region, can minimize the using of gelatine in production of wines for the consumers, which abstain from the proteins of animal origin [24]. Electrokinetic properties of so charged colloids can be similar to agent properties for the binding of metal ions [25], and in our opinion, can substitute these agents in the production of wines and beverages.

In the **Region III**, there is an interaction similar to that observed in the Region II: colloids are kinetic stable and do not precipitate quickly, i.e., large excess of the gelatine in the form of zwitterions causes the global charge of colloids to be positive. Therefore, we have named as Gel^+Alg the floccules and sols obtained in these conditions.

The **Region IV** characterizes the formation of dense large flocks that undergo rapid sedimentation, which occurs in few minutes. The impossibility to determine their charge by electrophoresis proves that charges of sols and floccules, resulting in the Region IV, are close to zero. Numerically, the change of charge point is shifted to the higher gelatine concentrations, when pH increases (Table 1). Control experiments showed the greatest turbidity of pure gelatine solutions at pH 4.75-5.00. Therefore, the top point of this area corresponds to the isoelectric point of gelatine type "B" [12]. This fact explains nearly neutral charge of complexes *GelAlg* in the conditions, when m_{Gel}/m_{Alg} ratio tends to infinite and pH is near IEP value. Moreover, the neutral flocks form the agglomerates, which quickly lose their ability to peptize. According to the basic knowledge of colloid chemistry, the conditions, corresponding to the Region IV, are of practically importance for the deposition of undesirable colloids in beverages by means of co-sedimentation mechanism [7]. Therefore, it can be argued that the formation of neutral 3D-structures $GelAlg^0$ is not desirable in other cases, when the repulsion between the colloidal particles, but not their mutual coagulation, is necessary. Thus, it should be demonstrated that neutral charge of protein-polyuronate complexes *GelAlg* or *GelHur* is undesirable for stability of oil-containing microcapsules, possessing the shells, which are formed from these biopolymers.

In the **Region V** that is characterized by low pH values, the pattern is a somewhat peculiar. At pH < 4 gelatine solutions acquire high transparency, inherent for the true solutions of HMC and for non-colloids. This transparency appears because of straightening of the molecules due to the intra-molecular repulsion (excess of positive charges in the zwitterions $Gel^{+>}$) [6,7]. At the same time, the solutions of alginate in this pH range, behave quite differently. At pH values below 3.8, the alginate solutions lose their transparency and the alginate precipitates in form of alginic acid at pH ≈ 3.5, taking place a reaction: $Alg^- + H^+ \rightarrow HAlg$. Solutions of the hyaluronates behaved similarly: hyaluronic acid precipitates in the form of gelled sticks by lowering the pH below 3.5. Thus, in the **Region V** the formation of *GelAlg* or *GelHur* floccules is accompanied and is aggravated by the protonation of polyanions.

The above-described phase diagram "gelatine-alginate" explains well the behaviour and stability of lipid-containing microcapsules with gelatine-polyuronate shells under various conditions. In the model solutions with pH corresponding to the Regions II...VI, microcapsules behave differently. In the conditions of Region II the microcapsules are high stable and do not stick (Figure 9, *a*). For neutral $GelAlg^0$ or $GelHur^0$ complexes, microcapsules suffer agglomeration (Figure 9, *b*) and total destruction (Figure 9, *c*).



a ***b*** ***c***

Figure 9. Microcapsules with gelatine-hyaluronic shells: a) stable, in the conditions of Region II; b) coagulated in the conditions of Regions V or VI; c) destroyed after 3 days in the conditions of Region VI.

It can be noted that gelatine-alginate or gelatine-hyaluronate shells of microcapsules, being under the conditions of **Region VI**, undergo following reactions:

$$GelAlg^{-} + H^{+} \rightarrow GelAlg^{0} \text{ (or: } GelHur^{-} + H^{+} \rightarrow GelHur^{0}) \quad (6)$$

$$GelAlg^{0} + H^{+} \rightarrow HAlg + Gel^{+} \text{ (or: } GelHur^{0} + H^{+} \rightarrow HHur^{0} + Gel^{+}) \quad (7)$$

In our opinion, the complete destruction of high-molecular structures does not occur immediately. Only structural recombination of shells, described by Eq.(6) and Eq.(7), accompanied by a change of their charge and, obviously, with latent changes in the conformation of macromolecules, take place. Due to this fact, the destruction of microcapsules with removal of lipid phase completed after 3…4 days. Conglutination of microcapsules and recombination of their shells, occurring in Regions V and VI, are accompanied by the release of encapsulated content and with the formation of foam-like dodecahedron structures, consisting of protein-poliuronate colloids (Figure 9, *c*).

The regularities of formation of charged colloids, probably, also refer to protein-based colloids, which are formed with different polyuronic acids, pectins and other polysaccharides possessing acidic functional groups.

Conclusions

There were found the conditions for the formation of negatively charged, the positively charged and the neutral colloids. It was observed that the properties of protein/polyuronate system depend on their mass ratio logarithmically. The molecular weight of neutral charged colloids decreases with diminishing the pH value. A phase state diagram, which reflects the influence of pH and ratio of the components (gelatine and alginate) on electric charge and stability of the resulting polymer complexes, was developed. The Diagram is of great practical interest for predicting the properties of different food systems. In particular, the Diagram shows the most suitable conditions for obtaining of microcapsules with stable gelatine-alginate or gelatine-hyaluronate shells with a negative electric charge {Region II, pH = 3.0...4.5, m_{Gel}/m_{Alg} ratio 2...8, $GelAlg^{-}$, $M_{GelAlg} = (1...3) \cdot 10^{6} D$}. Due to their negative charge, the colloids, obtained in the Region II, can be used for sedimentation of different positively charged particles in different food systems, inclusive wines and beverages. The Region III, with strong positive charge of colloids {pH = 3.0...4.0, m_{Gel}/m_{Alg} = 40...90, $Gel^{+}Alg$, $M_{GelAlg} = (15...35) \cdot 10^{6} D$}, is suitable for microencapsulation, but is characterized by great consumption of gelatine for shell's constructing. Phase diagram shows that gelatine-alginate colloids with $\zeta \approx 0$ {Region IV, pH = 3.0…4.5, m_{Gel}/m_{Alg} ratio 10...30, $GelAlg^{0}$, $M_{GelAlg} = (4...10) \cdot 10^{6} D$} are not suitable for microencapsulation. At the same time, the complexes with zero charge, obtained under the conditions of Region IV, are of greatest interest for quickly clarification of beverages.

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