



# Adsorption and viscoelastic properties of chitosan lactate at the liquid-gas interface



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## ABSTRACT

The surface tension and dilational rheological properties (viscoelasticity modulus and phase angle) of chitosan lactate solutions at the liquid-gas interface are investigated by the oscillating drop shape method. The results were analyzed using the adsorption model proposed earlier for proteins in the framework of non-ideal two-dimensional solution theory. It was found that the experimental values of equilibrium surface tension of chitosan lactate solutions are in good agreement with this model. The results of the dynamic surface tension and adsorption kinetics analysis showed that chitosan lactate is characterized by a non-diffusion (barrier) adsorption mechanism. This fact determines the qualitative predictive value of the applied theoretical model to describe the extreme behavior of the dependence of the viscoelasticity modulus on the surface pressure.

## 1. Introduction

Recently, processes occurring at the interfaces of solutions of poly-electrolytes and their mixtures with surfactants has attracted more and more attention of researchers [1–4]. Such systems are not only of theoretical interest, but also widely used in various technologies. Besides, the mixtures including high-molecular surfactants are more effective regulators of the properties of dispersed systems and the processes occurring in them [5–7].

Surface tension is traditionally the most widely studied characteristic of surfactant solutions. However, tensiometry methods can be insensitive to the existence of structural or conformational transitions in the adsorption layer of the regarded surfactants. Methods of surface rheology are more informative when applied to adsorption layers of polymers, for which conformational transitions can occur at a constant surface pressure [8].

An interesting object of research is the natural polysaccharide chitosan, built from the units of 2-amino-2-deoxy- $\beta$ -D-glucopyranose residues linked by  $\beta$ -(1  $\rightarrow$  4)-glycosidic bond. Despite the fact that chitosan is used for the stabilization of various dispersed systems - foams [9], emulsions [10–12], there are few works devoted to the study of its behavior at interfaces. It is known that chitosan has a low surface activity [9,10,13–15]. The effect of the nature and concentration of solvent on

the surface tension of chitosan was shown using as an example acetic and lactic acids [15]. Transition from acetic to lactic acid and an increase of the acid concentration leads to rise of the chitosan surface activity. The possibility of increasing the surface activity of chitosan due to complexation with anionic surfactants, as well as alkylation of chitosan, was shown in Refs. [9,10,13,16–18]. Increase in the linear density of alkyl radicals along the macromolecular chain leads to the fact that molecules can be almost irreversibly adsorbed [13,17]. This interfacial behavior of alkylated chitosans is similar to that for proteins, the desorption rate of which is very low, and the desorption mechanism is barrier [29].

Only a few works have been devoted to the study of the rheological properties of adsorbed layers of chitosan. Viscoelastic adsorption layers were found for chitosan solutions: the real and imaginary parts of the viscoelasticity modulus are comparable in this case [13,19–21], that is explained by weak intermolecular hydrophobic bonds, which do not lead to the formation of a gel-like structure, in contrast to the case of alkylated chitosan with strong hydrophobic interactions. The concentration dependence of the surface elasticity of chitosan solutions was not measured. An increase in the electrolyte concentration in solutions of chitosan and alkylated chitosan leads to an increase of the elastic modulus of the adsorption layers [20].

The aim of this work is to study the adsorption and dilational

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rheological properties of chitosan lactate at the liquid-gas interface, as well as to evaluate the possibility of using the previously proposed for proteins model of adsorption to describe these characteristics. These studies will expand theoretical knowledge about the mechanism of formation of chitosan adsorption layers and allow predicting the properties of systems stabilized by it.

## 2. Materials and methods

Chitosan with a molecular weight of 75 kDa and a degree of deacetylation of 70% is used in this work. The molecular weight of chitosan was determined by the viscometric method at a temperature of  $(25 \pm 0.2)$  °C on an Ubbelohde capillary viscometer, its capillary diameter is 0.54 mm. Calculation of molecular weight was done according to the Mark-Kuhn-Houwink equation [22]. The degree of deacetylation of chitosan was determined by potentiometric titration using a laboratory ionometer I-160 M.

A solution of chitosan lactate was prepared by dissolving a weighed portion of chitosan in an aqueous solution of 2% lactic acid. The pH of the resulting solution was 4.0.

The surface tension and dilational rheological characteristics of the chitosan lactate surface layers were studied at a temperature of  $(25 \pm 0.1)$  °C by the oscillating drop shape method (PAT-2P, SINTERFACE Technologies, Germany), the principle of operation of which is described in detail in Refs. [23,24]. Capillary radius is 1.4 mm. The essence of the method is as follows. A drop of the studied solution of preassigned volume is formed at the end of the capillary. After reaching the adsorption equilibrium, the area of the drop  $A$  undergoes periodic sinusoidal deformation (oscillations) of small amplitude ( $\Delta A/A = \pm 7-8\%$ ), with a frequency  $\nu$  in the range of (0.005–0.2) Hz. Equilibrium surface tension was achieved at a surface lifetime of 20000 s. The results of experiments with harmonic oscillations of the drop surface were analyzed using the Fourier transformation [25,26]:

$$E(i2\pi\nu) = A_0 \frac{F[\Delta\gamma]}{F[\Delta A]}, \quad (1)$$

where  $A_0$  is the initial drop surface area.

At a small amplitude  $\Delta A$  of harmonic oscillations of the surface with an angular frequency  $\Omega = 2\pi\nu$ ,  $\Delta A = \Delta A \exp(i\Omega t)$ , the expression for the dilational viscoelasticity modulus has the form [23,24]:

$$E = \frac{\Delta\gamma}{\Delta A/A_0} = \frac{d\gamma}{d \ln A}. \quad (2)$$

The dilational modulus  $E$  characterizes the viscoelastic properties of the surfactants surface layers. It takes into account all relaxation processes that affect the surface tension  $\gamma$ . Modulus  $E$  is a complex number that includes real and imaginary components:  $E(i\Omega) = E_r + iE_i$ . The real part  $E_r$  reflects the accumulation of energy, and the imaginary part  $E_i$  is the energy loss in the surface layer due to relaxation processes. The expressions for the viscoelasticity modulus  $|E|$  and phase angle  $\varphi$  are:

$$|E| = \sqrt{E_r^2 + E_i^2}, \quad \varphi = \arctg(E_i / E_r). \quad (3)$$

## 3. Results and their discussion

### 3.1. Equilibrium surface tension of chitosan lactate solutions at the liquid-gas interface

Fig. 1 shows the experimental dependence of the equilibrium surface pressure on the chitosan lactate concentration at pH 4.0 at the liquid-gas interface. The surface pressure increases with an increase of chitosan concentration to 1.0 g/l, after which it remains almost constant. The onset of plateau for low molecular weight surfactants corresponds to the critical micelle concentration. For proteins such constant level of surface

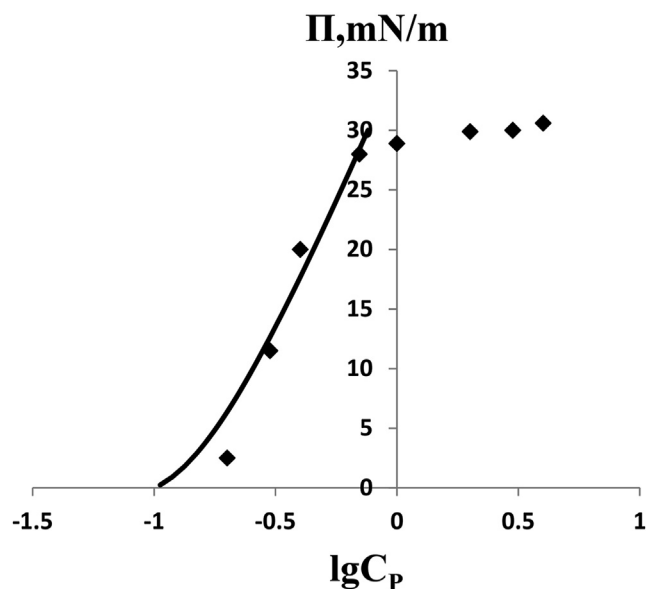


Fig. 1. Dependence of the equilibrium surface pressure on the chitosan lactate concentration: points – experimental data, curve – calculated data for the pre-critical concentration range according to Eqs. (4) and (5) with the parameters described in the text below.

pressure can be explained by changes in the surface layer structure (two-dimensional condensation of molecules) or multilayer formation [5,29,30]. Unlike surface tension adsorption of proteins tends to slight increase in this case. Similar processes may take place in surface layers of chitosan after achieving a certain critical pressure.

Chitosan is a weak cationic polyelectrolyte. It is known [27,28] that its macromolecules can take on different conformational states changing their shape from a linear line to a chaotic and compacted coil depending on the molecular weight, degree of acetylation, environmental conditions (pH, ionic strength, temperature). In diluted solutions, the polymer chains are isolated from each other by the solvent and the chitosan takes the form of a linear rod. With an increase of the concentration the conformation of chitosan macromolecules tends to be more spherical and compact, the chaotic interweaving of macromolecules increases, and their sizes become independent of the polymer concentration. Therefore, an attempt of description of the equilibrium surface pressure of chitosan lactate by nonideal two-dimensional solution model proposed for proteins in Refs. [29,30] was done. Previously, we applied this model to describe the adsorption and rheological properties of the natural anionic polyelectrolyte sodium humate and showed good agreement between experimental and calculated data [31].

The main idea of the model [29,30] is that polyelectrolyte molecules can exist in surface layer in  $n$  states with different molar surface varying from the maximum value,  $\omega_{\max}$ , at very low surface coverage by polyelectrolyte molecules to a minimum value,  $\omega_{\min}$ , at high surface coverage. The molar surface of the polyelectrolyte in the  $i$  state is equal to  $\omega_i = \omega_1 + (i - 1)\omega_0$ , ( $1 \leq i \leq n$ ), and the increment of the molar surface during the transition from one state to another is taken equal to  $\omega_0$ . Thus,  $\omega_1 = \omega_{\min} \ll \omega_0$  and  $\omega_{\max} = \omega_1 + (n - 1)\omega_0$ . This model is described in detail in Refs. [29,30], so here we will restrict ourselves only to the basic equations.

The equations of state of the surface layer and the adsorption isotherm for each  $j$  state of the polyelectrolyte molecule in the surface layer have the form:

$$-\frac{\Pi\omega_0}{RT} = \ln(1 - \theta_p) + \theta_p(1 - \omega_0 / \omega_p) + a_p\theta_p^2, \quad (4)$$

$$b_{pj}c_p = \frac{\omega_p \Gamma_{pj}}{(1 - \theta_p)^{\omega_j/\omega_p}} \exp \left[ -2a_p \frac{\omega_j}{\omega_p} \theta_p \right], \quad (5)$$

where  $\Pi = (\gamma_0 - \gamma)$  is surface pressure;  $\gamma$  and  $\gamma_0$  is the surface tension of the solution and pure solvent;  $R$  is the universal gas constant;  $T$  is the temperature;  $a_p$  is the parameter that accounts intermolecular interaction between adsorbed molecules,  $c_p$  is the concentration of the polyelectrolyte in the bulk solution,  $b_{pj}$  is the equilibrium adsorption constant in  $j$  state,  $\theta_p = \omega_p \Gamma_p = \sum_{i=1}^n \omega_i \Gamma_{pi}$  is the total surface coverage by polyelectrolyte molecules,  $\omega_p$  is the average molar surface,  $\Gamma_p$  is the total adsorption of the polyelectrolyte in all  $i = n$  states  $\Gamma_p = \sum \Gamma_{pi}$ ,  $\omega_i = \omega_1 + (i-1)\omega_0$  is the molar area in state  $i$ , with  $\omega_1 = \omega_{\min}$ , and  $\omega_{\max} = \omega_1 + (n-1)\omega_0$ .

Surface compressibility proceeds in small steps equal to  $\omega_0$ . It is assumed equal adsorption probability for all polyelectrolyte states, with equal values of the  $b_{pj}$  constants for all states  $j$  from  $i = 1$  to  $i = n$ . Thus the adsorption constant for the protein molecule as a whole is  $\sum b_{pj} = nb_{pj}$ .  $\Gamma_{pj}$  is the distribution function of adsorptions of polyelectrolyte in different states determined by the ratio:

$$\Gamma_{pj} = \Gamma_p \frac{(1 - \theta_p)^{(\omega_j - \omega_1)/\omega_p} \exp \left[ 2a_p \theta_p \frac{\omega_j - \omega_1}{\omega_p} \right]}{\sum_{i=1}^n (1 - \theta_p)^{(\omega_i - \omega_1)/\omega_p} \exp \left[ 2a_p \theta_p \frac{\omega_i - \omega_1}{\omega_p} \right]} \quad (6)$$

At high concentrations solutions of polyelectrolytes (in particular, proteins) are capable of forming bilayers (or polylayers) at liquid interfaces [30]. The degree of coverage of the second layer is proportional to the adsorption equilibrium constant  $b_{II}$  and the coverage degree of the first layer (it is assumed that the formation of the second and subsequent layers does not affect the surface pressure). The bilayer adsorption isotherm is given by Ref. [30]:

$$\Gamma_{\Sigma} = \Gamma_p \left[ 1 + \frac{b_{II} c_p}{1 + b_{II} c_p} \right] \quad (7)$$

where  $\Gamma_{\Sigma}$  is the total adsorption in the first and second layers.

For description of the polyelectrolytes adsorption behavior by the model described above the following parameters should be used:  $\omega_{\max}$ ,  $\omega_{\min}$ ,  $\omega_0$ ,  $a_p$ ,  $b_p$ . Maximum and minimum surface areas ( $\omega_{\max}$  and  $\omega_{\min}$ ) can be determined from the results of measurements of the thickness of the adsorption layer  $\delta \cong V/\omega_{\max(\min)}$  [30], where  $V$  is the molar volume of the polyelectrolyte. The thickness of the adsorption layer for various chitosan samples at different pH values can vary within 2–15 nm [9,32]. If we assume that the molar volume of chitosan is  $V \cong 75000 \text{ cm}^3/\text{mol}$ , then the molar area of chitosan can vary from approximately  $5.0 \times 10^6$  to  $3.75 \times 10^7 \text{ m}^2/\text{mol}$ . The parameters  $\omega_{\max}$  and  $\omega_{\min}$  were chosen close to these values. The parameters  $\omega_0$ ,  $a_p$ , and  $b_p$  were found by fitting the experimental dependence  $\Pi = f(c_p)$ .

The curve in Fig. 1 for chitosan lactate was calculated for the pre-critical concentration range according to Eqs. (4) and (5) with the following parameter values:  $\omega_{\max} = 1.1 \cdot 10^7 \text{ m}^2/\text{mol}$ ,  $\omega_{\min} = 6.9 \cdot 10^6 \text{ m}^2/\text{mol}$ ,  $\omega_0 = 1.1 \cdot 10^5 \text{ m}^2/\text{mol}$ ,  $a_p = 0.9$ ,  $b_p = 10 \text{ m}^3/\text{mol}$  (for the whole molecule  $\Sigma b_p = nb_p = 380 \text{ m}^3/\text{mol}$ ). This figure shows good agreement between the experimental and calculated dependences  $\Pi = f(c_p)$  in the concentration range before reaching a plateau.

Fig. 2 shows the dependences of the adsorption  $\Gamma_p$  (curve 1) and the surface coverage  $\theta_p$  (curve 2) on the concentration of chitosan lactate for monolayer adsorption, as well as the adsorption values for the bilayer adsorption model (curve 1\*,  $b_{II} = 8 \text{ m}^3/\text{mol}$ ). The values of  $\Gamma_{\Sigma}$  obtained for the case of bilayer adsorption in the concentration range of more than 0.2 g/l are higher than the corresponding values obtained for monolayer adsorption of  $\Gamma_p$ . While the maximum discrepancy between the corresponding values does not exceed 7%. However, it will be shown below that the use of the bilayer model is in better agreement with rheological experiments.

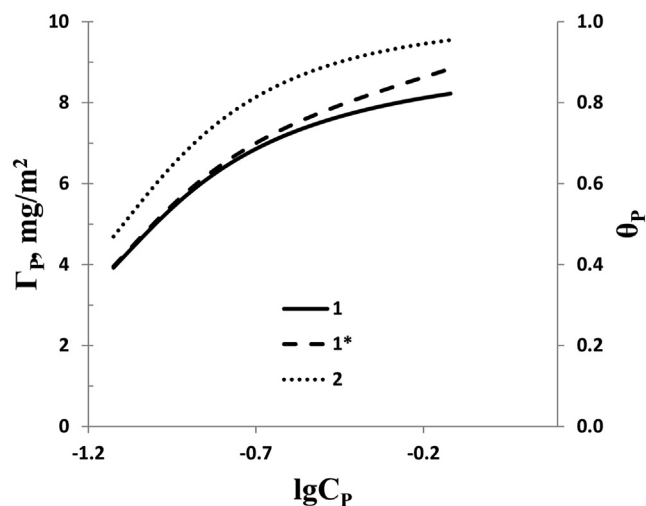


Fig. 2. Calculated dependences of the adsorption value  $\Gamma_p$  (1) and the surface coverage  $\theta_p$  (2) for monolayer adsorption on the concentration of chitosan lactate, and  $\Gamma_{\Sigma}$  (1\*) - for bilayer adsorption.

### 3.2. Dynamics of the surface layer formation and adsorption mechanism of chitosan lactate

Isotherms of dynamic surface tension  $\gamma(t)$  for different concentrations of chitosan lactate are listed in Fig. 3. At first glance, the type of these dependences at low bulk concentrations is similar to those for protein solutions [29] and consistent with the results obtained in Refs. [13,17,21] for alkylated chitosans. For the latter, the following adsorption stages were found: “induction”, “post-induction” and the final stage. In our case it is also possible to distinguish similar adsorption stages in the  $\gamma(t)$  curves. For low concentrations of chitosan lactate (Fig. 3, curves 1–3) a very slow decrease of surface tension is characteristic at the first stage. This stage is often observed in the case of hydrophilic polymers and proteins, the adsorption of which is determined by the diffusion of macromolecules from the bulk solution to the interface [13,29]. At the next adsorption stage the surface tension strongly decreases, and the rate of decrease in the surface tension reaches a maximum, after which the

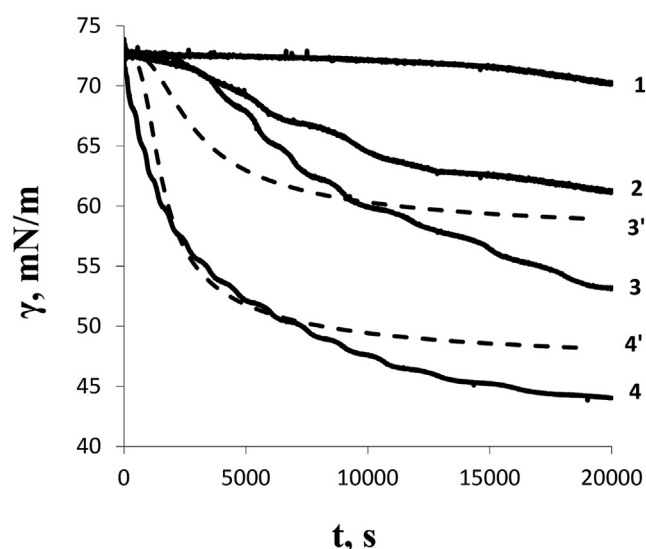


Fig. 3. Dependences of dynamic surface tension on time for chitosan lactate solutions: solid lines 1–4 are experimental data for concentrations 0.2; 0.3; 0.4; 0.7 g/l respectively; dashed lines 3', 4' are calculated data according to Eqs. (4)–(7) and (9) for concentrations 0.4 and 0.7 g/l with diffusion coefficients  $2 \cdot 10^{-13}$  and  $1 \cdot 10^{-13} \text{ m}^2/\text{s}$  respectively.

decrease rate goes down.

The first two adsorption stages of the chitosan from very dilute solutions (curves 1–3 in Fig. 3) are characterized by relatively loose packing of macromolecules in the surface layer and low intermolecular interactions. The decrease rate of surface tension for the considered very narrow concentration range 0.2–0.4 g/l changes by several orders of magnitude. Similar behavior is also revealed for such polyelectrolytes as sodium poly(styrenesulfonate) and poly(methylalkyldiallylammonium) chloride, when a concentration increase accelerates not only molecular diffusion in the bulk, but also reduces the electrostatic adsorption barrier due to an increase of the solution ionic strength [33,34].

At the end of the second and at the last stage the already formed adsorption layer begins to act as a repulsive barrier towards macroions reaching the surface. A decrease in surface tension over long time periods indicates that already adsorbed macromolecules control the diffusion of the active segments by their own redistribution in the adsorption layer [13,17]. An increase of chitosan lactate concentration (Fig. 3, curve 4) leads to disappearance of the first stage characterized by a slow decrease of  $\gamma(t)$ , and only two subsequent stages are observed with a strong decrease of surface tension, which is replaced by a decrease of the rate  $d\gamma/dt$ .

In order to analyze the adsorption mechanism of chitosan lactate an attempt is made to describe the experimental data using a theoretical model characterizing the diffusion mechanism of adsorption. The relation between the dynamic adsorption  $\Gamma(t)$  and the subsurface concentration  $c(0, t)$  of the surfactant proposed by Ward and Tordai for a freshly formed undeformable surface has the form [35]:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}} \left[ c_P \sqrt{t} - \int_0^{\sqrt{t}} c(0, t-t') d(\sqrt{t'}) \right], \quad (8)$$

where  $c_P$  is the concentration of the polyelectrolyte in the bulk solution,  $D$  is the diffusion coefficient,  $t$  is the time, and  $t'$  is the integration variable.

When a molecule is adsorbed from a solution on a spherical surface, the surface curvature can be approximately taken into account (for surface concentration  $c(0, t)$ , which is far from the equilibrium concentration) by introducing an additional term into Eq. (8)

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}} \left[ c_P \sqrt{t} - \int_0^{\sqrt{t}} c(0, t-t') d(\sqrt{t'}) \right] - \frac{c_P D}{r} t, \quad (9)$$

where  $r$  is the curvature radius.

If one solves jointly Eq. (9) with Eq. (5) or (6), which are boundary conditions for Eq. (9) for diffusion mechanism of adsorption, the dependence of the adsorption value on the surface lifetime,  $\Gamma = f(t)$ , can be found, and then consequently dynamic surface tension according to the equation of state (4) [36].

The diffusion coefficient of chitosan molecules is calculated using the Polson formula proposed for polymer solutions [37]:  $D = 2,74 \cdot 10^{-9} M^{-1/3}$ . The diffusion coefficient of chitosan molecules is calculated:  $D = 6.5 \cdot 10^{-11} \text{ m}^2/\text{s}$ .

Fig. 3 shows the results of measurements of the dynamic surface tension for chitosan lactate solutions. The experimental curves of dynamic surface tension are compared with the calculated dependences according to the model Eqs. (4)–(7) and (9). The values of the model parameters given above are used for this purpose. The experimental data turned out to be not satisfactorily described by this model even at very low values of the chitosan diffusion coefficient ( $D = 10^{-13} \text{ m}^2/\text{s}$  comparatively to the real value of  $10^{-11} \text{ m}^2/\text{s}$ ). This indicates a non-diffusion (barrier) mechanism of chitosan adsorption, since the rate of equilibrium establishment between the surface and subsurface layers is significantly lower than the rate of surfactant diffusion to the surface.

### 3.3. Rheological properties of chitosan lactate surface layers

Fig. 4 shows the dependences of the viscoelasticity modulus and phase angle of chitosan lactate solutions on the frequency of droplet oscillations. The viscoelasticity modulus for low concentrations of chitosan lactate is almost independent of frequency. As the concentration of chitosan lactate increases an increase in the viscoelasticity modulus is observed with an increase in the oscillation frequency. The value of the phase angle decreases with an increase of the oscillations frequency for solutions in the entire studied range of concentrations. At the same time for the dependences of the phase angle at different concentration of chitosan lactate one can observe the maximum values  $\varphi = f(\nu)$  corresponding to concentrations of 0.4–0.55 g/l. These regularities are stipulated by the influence of exchange processes both between the surface layer and the bulk solution and in the surface layer itself. An increase of the solution concentration intensifies the exchange processes, and vice versa an increase of the oscillation frequency suppresses them.

Fig. 5 shows the dependences of the viscoelasticity modulus and phase angle of chitosan lactate solutions on concentration at two

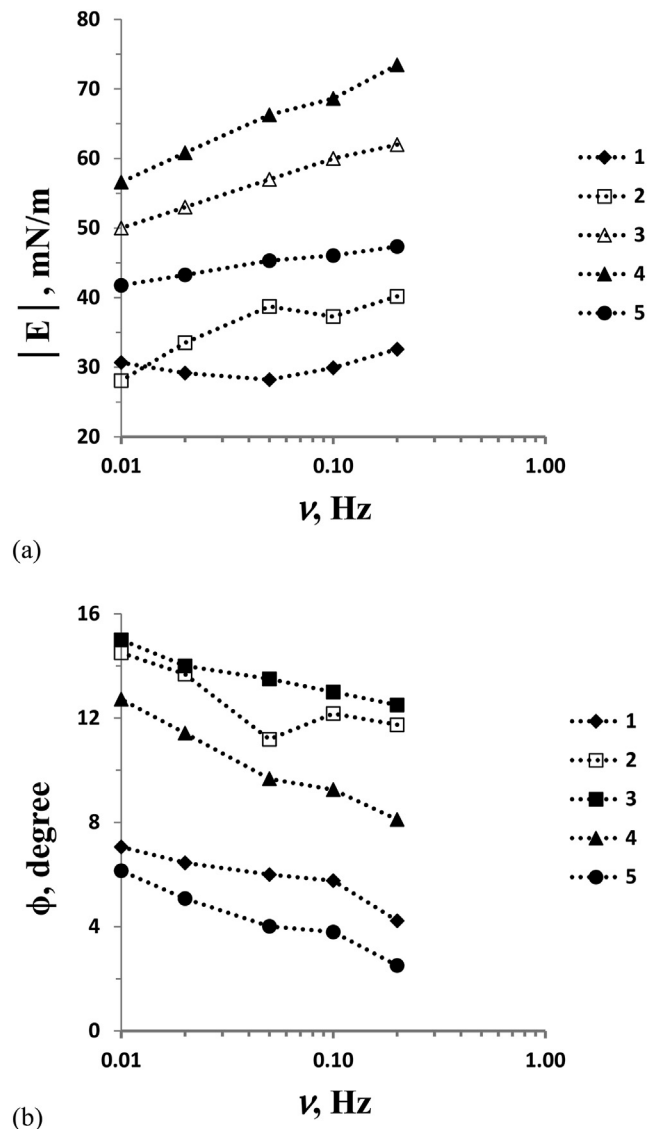


Fig. 4. Dependences of the surface viscoelasticity modulus (a) and phase angle (b) on the frequency of droplet oscillations at various concentrations of chitosan lactate solution, g/l: 1–0.2; 2–0.4; 3–0.55; 4–0.7; 5–1.0. Points represent experimental data, dotted lines are guides for the eye.

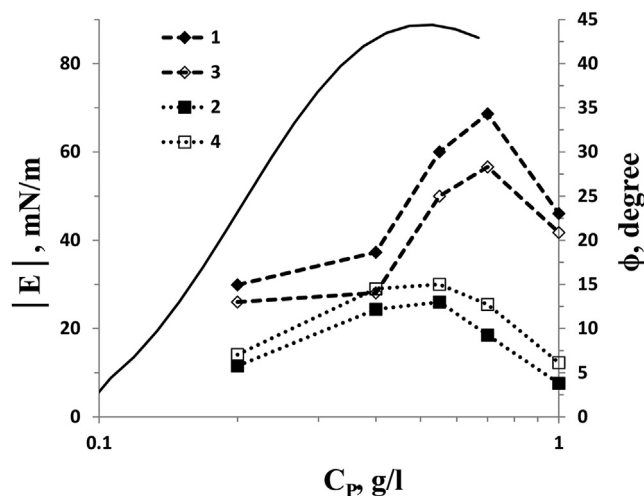


Fig. 5. Dependences of the surface viscoelasticity modulus (1, 3) and phase angle (2, 4) on the concentration of chitosan lactate solution at an oscillation frequency: 1, 2–0.1 Hz; 3, 4–0.01 Hz. Points represent experimental data, dotted and dashed lines are guides for the eye. Solid line is the limiting (high-frequency) elasticity calculated by Eqs. (4)–(7) for the case of bilayer adsorption.

frequencies: 0.01 and 0.1 Hz. As can be seen, the dependences of the viscoelasticity modulus have a pronounced maximum at a concentration  $C_p \approx 0.5\text{--}0.7$  g/l. This behavior of the viscoelasticity modulus is stipulated to a significant extent due to the fact that the molar surface of the polyelectrolyte at the surface layer decreases with adsorption increase as follows from Eqs. (4)–(7) [29]. For example, proteins with flexible chains are able to unfold at the surface layer at low values of adsorption and surface pressure. Thus, the molar surface of a protein can change significantly with a change of surface pressure [29,30].

Due to the barrier mechanism of chitosan lactate adsorption processing of our experimental data on dilational rheology according to the theoretical model [38] developed for the diffusion adsorption mechanism gives unrealistic values of the diffusion coefficient ( $10^{-14}$  m<sup>2</sup>/s and less). Probably, for theoretical analysis it is necessary to use a more general theory [39], which takes into account the barrier mechanism of adsorption. However, considering that the experimental values of the phase angle at a frequency of 0.1 Hz are less than  $10\text{--}15^\circ$  an attempt was made to compare the values of the viscoelasticity modulus at this frequency with the value of the limiting (high-frequency) elasticity modulus. A similar technique was used in Refs. [29,40] for some proteins and in Ref. [31] for anionic natural polyelectrolyte sodium humate.

The calculated dependence of the limiting elastic modulus  $E_0$  predicts an infinite increase of the viscoelasticity modulus for the case of monolayer adsorption. The bilayer adsorption model better describes the experimental data and (in contrast to the monolayer) reproduces the extreme behavior of the dependence of the viscoelasticity modulus on the surface pressure; however, it was not possible to achieve complete agreement between the experimental and calculated values which is most likely to confirm the need to use a theory that takes into consideration the barrier mechanism of adsorption.

The experimental dependence of the viscoelasticity modulus on the surface pressure for chitosan lactate is compared with the data for proteins and the previously studied anionic natural polyelectrolyte sodium humate (Fig. 6). Dependencies  $|E| = f(\Pi)$  for  $\beta$ -casein and  $\beta$ -lactoglobulin at a surface oscillation frequency of 0.1 Hz obtained in Ref. [41] by the oscillating drop shape method and also for sodium humate according to Ref. [27] are shown in Fig. 6. Nevertheless the data for protein solutions in Ref. [41] are obtained under dynamic conditions and data on chitosan lactate and sodium humate dilational modulus correspond to the approach to equilibrium it is possible to compare dependences of viscoelasticity modulus on the surface pressure. Phase angles determined

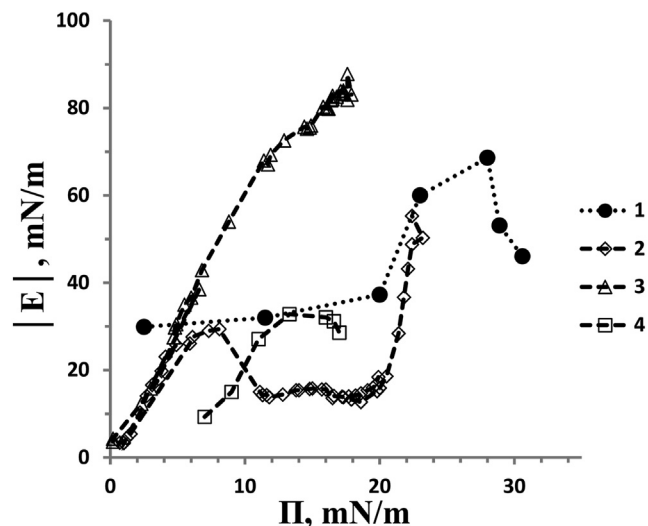


Fig. 6. Dependences of the viscoelasticity modulus on the surface pressure for solutions of chitosan lactate (1) according to the data of this work, as well as for  $\beta$ -casein (2) and  $\beta$ -lactoglobulin (3) according to the data of Ref. [41] and sodium humate (4) according to the data of Ref. [31] at an oscillation frequency 0.1 Hz. Lines are guides for the eye.

under dynamic conditions for  $\beta$ -casein and  $\beta$ -lactoglobulin in Ref. [41] were low (no higher than  $6^\circ$ ) up to quite high surface pressures (no higher than 20 mN/m). Viscoelasticity modulus for mentioned above proteins at different concentrations and different surface ages all almost coincide on a single  $|E|$  vs  $\Pi$  curve. Moreover, it was shown in Ref. [42] that presented  $|E|$  vs  $\Pi$  dependences obtained under dynamic conditions for  $\beta$ -casein and  $\beta$ -lactoglobulin are in good agreement with the applied two-dimensional solution model adopting change of molecular areas with increasing surface pressure for adsorbed proteins [29,30].

As seen from Fig. 6, the experimental values of the surface viscoelasticity modulus for chitosan lactate are comparable with the values  $|E|$  for proteins. Moreover, the dependence  $|E| = f(\Pi)$  for chitosan lactate stands at an intermediate position in comparison with globular  $\beta$ -lactoglobulin and flexible-chain  $\beta$ -casein. The maximum values of the modulus of viscoelasticity for chitosan lactate are achieved in the region of higher values of surface pressure, as well as for flexible-chain  $\beta$ -casein. While sodium humate, which has a more rigid structure, is characterized by lower values of the viscoelasticity modulus, the maximum of which is reached at lower values of surface pressure (comparable to the values for globular  $\beta$ -lactoglobulin). The mechanism of difference in the rheological behavior of globular and proteins with flexible chains was discussed in Refs. [29,40] and to large extent is stipulated by the fact that flexible polyelectrolyte molecules, as compared to globular ones, change their molar surface to a greater extent.

The chitosan lactate studied in this work has a relatively low degree of deacetylation of 70%, which probably contributes to a decrease in the charge density and allows it to change its molar surface forming more compact structures. However, this behavior is manifested to a lesser extent in comparison with flexible-chain proteins due to repulsive effects between positive charges of the same name.

#### 4. Conclusions

Using the method of the oscillating drop shape the values of the equilibrium surface pressure, dynamic surface tension, surface rheological properties of chitosan lactate solutions were obtained at the liquid-gas interface. The experimental data found for the equilibrium surface tension of chitosan lactate were analyzed from the standpoint of the adsorption model, which was developed earlier for proteins in the framework of theory of a nonideal two-dimensional solution in Refs. [29,

30]. Good agreement between the calculated and experimental values of surface pressure depending on the concentration of chitosan lactate confirms the possible application of this theory not only for protein polymers, but also for ones of different nature.

Analysis of the dynamic surface tension of chitosan lactate solutions shows that they are characterized by a barrier mechanism of adsorption, as in the case of sodium humates considered earlier [31]. The study of the rheological characteristics of the formed adsorption layers of chitosan lactate reveals that the dependences of the surface viscoelasticity modulus and phase angle are extreme in nature with a pronounced maximum at a concentration near 0.7 g/l. This is due to the possibility of changing the molar surface area of the polyelectrolyte at the interface depending on the amount of adsorption and its structural properties. Attempts to theoretically describe the modulus of surface viscoelasticity within the framework of a mono- or bilayer adsorption model did not lead to a satisfactory result because they better describe adsorption layers with a diffusion mechanism of formation, to which chitosan lactate does not belong. The values of the surface viscoelasticity modulus of chitosan lactate occupy an intermediate position in comparison with the data available in the literature for globular and flexible-chain proteins, which is consistent with its molecular structure.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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