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Surface tension measurement of chitosan aspartate nanoparticle dispersions by a modified Wilhelmy method

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Abstract. A modification of the Wilhelmy method is proposed for measuring the surface tension of polymer nanoparticle dispersions, whose key feature is the static nature of the Wilhelmy plate when measuring the surface tension force. Tests on the example of nanostructured chitosan aspartate showed satisfactory accuracy of the modified method in estimating the surface activity of nanodispersions in a wide range of polymer concentrations. The concentration dependence of the surface tension of the dispersion of chitosan aspartate nanoparticles was obtained, and concentration ranges with different surface effects were outlined. The contribution of individual components used in obtaining nanoparticles to the surface activity of the nanodispersion was estimated.

Keywords: chitosan, L- and D-aspartic acid, nanoparticles, surface tension

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Измерение поверхностного натяжения дисперсий наночастиц аспарагината хитозана модифицированным методом Вильгельми

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Аннотация. Предложена модификация метода Вильгельми для определения поверхностного натяжения дисперсий полимерных наночастиц, ключевой особенностью которой является статичность пластины Вильгельми при измерении силы поверхностного натяжения. Тестирование на примере наноструктурированного аспарагината хитозана показало удовлетворительную точность модифицированного метода при определении поверхностной активности нанодисперсий в широком диапазоне концентраций полимерного вещества. Получена концентрационная зависимость поверхностного натяжения дисперсии наночастиц аспарагината хитозана, определены концентрационные диапазоны с различающимися поверхностными эффектами. Оценен вклад индивидуальных компонентов, используемых при получении наночастиц, на поверхностную активность нанодисперсии.

Ключевые слова: хитозан, L- и D-аспарагиновая кислота, наночастицы, поверхностное натяжение

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Introduction

Chitosan (CS) nanoparticles with targeted functional action are very promising in nanophotonic biosensors, nanofluidics, nanoelectromechanics, as well as in medical and biological applications and the agro-industrial complex [1, 2]. This is due not only to the biological activity of CS and dimensional features of its nanomaterials (high specific surface area and reactivity of the interacting substance), but also to non-trivial surface properties of nanodispersions [3–5]. E.g., the surface tension of nanosized aggregates of the salt form of CS and aspartic acid (AspA) is determined by the force of electrostatic interaction between positively charged polymer chains and counterions of the acid residue and plays a key role in stabilizing nanoparticles [6]. In the process of forming chitosan-containing nanodispersions, the Coulomb repulsion of charged monomer units is compensated by the dipole–dipole attraction of ionogenic groups of macrochains with condensed counterions, so the nanosized structure is stabilized by hydrogen bonding and hydrophobic interactions [7, 8]. The ability to reduce the surface tension of water was noted for oleoyl chitosan [9]. Chitosan nanoparticles obtained by dispersing salt chitosan in an alkaline medium promote emulsification of edible oil or petroleum in water [3, 4].

The decrease in the surface tension of the main liquid upon introduction of nanoparticles is due to the high adsorption energy and is largely similar to the behavior of surfactant molecules [10]. However, measuring the surface energy of nanodispersions is associated with such methodological difficulties as system metastability, size effects and nanoparticle surface heterogeneity, double electric layer, deformation of the interfacial surface and lateral interactions of particles in the surface layer, the influence of steric effects of stabilizers and artifacts [10–12]. In the case of polymer nanodispersed systems, the problem is also experimental limitations in studying low concentrations of the substance and, accordingly, a limited number of nanoparticles. Minimization of the influence of the above features predetermines modifications of classical methods of experimental evaluation of the surface tension of nanoobjects. In this work, a modification of the Wilhelmy method is proposed to measure the surface energy of dispersions of nanostructured chitosan aspartate.

Materials and Methods

The starting reagents were CS with a viscosity-average molecular mass 200 kDa, a degree of deacetylation 82 mol% (Bioprogress Ltd., RF); L-AspA (JSC Bioamid, RF); D-AspA (Vekton Corp., RF); silicon tetraglycerolate in a 3-molar excess of glycerol ($Si(OGly)_4 \cdot 3\,GlyOH$, Ural Branch of Russian Academy of Sciences, Institute of Organic Synthesis named after I.Ya. Postovsky, RF); distilled water. In obtaining the dispersion of chitosan aspartate nanoparticles (CS·L-(D-)AspA), the concentrations of CS (C_{CS}), L- and D-AspA (C_{AspA}) were varied in a range of 0.05–1.2 g/dL, maintaining the molar ratio [Asp]/[CS] = 1.3 mol·(mol of NH_2)$^{-1}$. To form an aggregation and sedimentation resistant dispersion of nanoparticles, their surface was functionalized with a polysiloxane shell (CS·L-(D-)AspA·Si). A detailed procedure for obtaining shell nanoparticles is described in Ref. [6]. Nanodispersions were obtained by accurately weighing CS and L-(D-)AspA (method A), or by diluting the initial solution with C_{CS} = 1.2 g/dl with distilled water (method B).

Gravimetric measurements were carried out on an analytical balance "OhausDiscovery" (USA), weighing accuracy ±0.01 mg. Interfacial surface tension (σ, mN/m) was measured by the Wilhelmy plate method at the liquid–gas (air) interface at 24±2 °C on tensiometers KSV NIMA Langmuir & Langmuir–Blodgett Troug (Biolin Scientific, Sweden), the accuracy being 0.1 mN/m. Three replicate experiments with 10 measurements each were carried out. When calculating σ values, a correction was introduced for the temperature coefficient of the surface tension of water. Ultrasonic treatment was performed on a JY96-IIN ultrasonic homogenizer (Ningbo Scientz Bio-Technology Co., Ltd., China). Exposure time was 15 s, power was 40 W, frequency was 150 kHz, and temperature was 22±2 °C. The probe was immersed into the surface layer of the system under study.

Results and Discussion

The following modification of the Wilhelmy method was proposed to determine the surface tension of aqueous dispersions of polymer nanoparticles. Unlike the classical method, which consists in measuring the force of plate separation from the surface of the tested liquid (International Standard ISO 304), the key feature of the modified approach is the static nature of the Wilhelmy plate during the experiment (Fig. 1). To comply with these conditions, the polymer liquid was placed into a transparent laboratory vessel in the form of a low flat cylinder (e.g., in a Petri dish), which was raised vertically until contact of the studied liquid with the plate fixed on the strain gauge was achieved. The laboratory vessel with the system under study was moved by regulating the distilled water level. This approach allows minimizing the hydrodynamic effects during plate movement which occur in the standard Wilhelmy method and increasing the accuracy of σ measurements due to the directed movement of the test system toward the sensor. A paper deashed filter "Blue Ribbon" was used as the Wilhelmy plate, ensuring rapid complete wettability of the plate with the liquid medium.

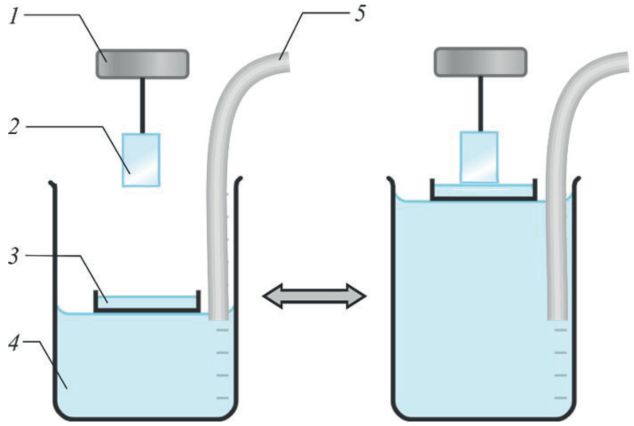

Fig. 1. Scheme of the modified setup for measuring surface tension: *1* – tensiometric sensor, *2* – Wilhelmy plate, *3* – laboratory vessel with the system under study, *4* – laboratory beaker with distilled water, and *5* – liquid level control system

Testing our modified version of the Wilhelmy method on standard liquids showed that the obtained surface tension values were identical to the reference data. The σ values of aqueous solutions of surface-inactive L-(D-) chitosan aspartate and L-(D-) AspA were also reproducible with known literature data. Verification testing also confirmed the manifestation of surface activity by CS·L-(D-)AspA·Si shell nanoparticles, which was more pronounced for CS·L-AspA·Si nanoparticles [6].

The positive approbation of the proposed modification of the Wilhelmy method justified our study of the surface tension of nanostructured CS L-(D-)aspartate in a wide range of polymer concentrations. It was found that the concentration dependence of σ of aqueous CS·L-(D-)AspA·Si nanodispersions had a non-monotonic character and did not depend on the method of obtaining the nanostructured system (Fig. 2, curves *1*, *2* and *4*). In the range of medium concentrations (C_{CS} = 0.3–1.2 g/dl) the surface tension decreased with decreasing C_{CS} (region I), which could be due to weakening of the interactions between the components of the aqueous medium and a decrease in the surface energy at the liquid–gas interface. In the range of low concentrations (C_{CS} = 0.1–0.3 g/dl) an increase in the surface tension of the nanodispersions was observed with a decrease in C_{CS} (region II). When C_{CS} < 0.05–0.1 g/dl the system was surface-inactive and the experimentally determined σ values became comparable with the surface tension of water (region III). This character of $\sigma = f(C_{CS})$ may be caused by a small number of nanoparticles in the dispersion, which is insufficient to exhibit surface activity and reduce the surface tension at the phase boundary. Since the structure of the nanoparticles contains the salt form of CS, the effect of increasing σ can be also associated with polyelectrolyte swelling of shell macrocoils and, accordingly, an increase in the size of the nanoparticles up to the rupture of their protective polysiloxane shell. In this case, the aqueous medium will be filled with isolated macromolecules of surface-inactive chitosan aspartate. The latter is consistent with the hydrodynamic behavior of the studied nanodispersions, which showed an increase in the viscosity number upon dilution of the system.

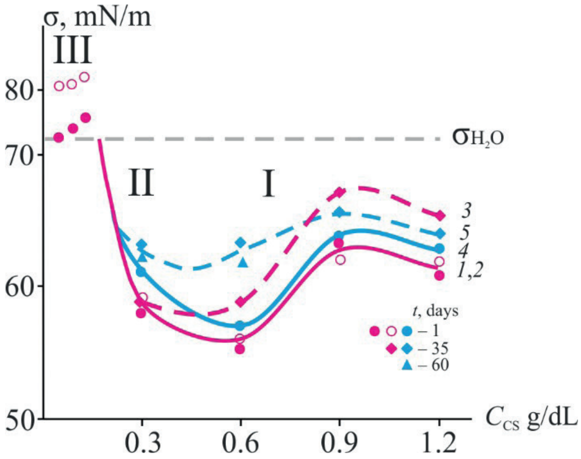

Fig. 2. Concentration dependence of the surface tension of aqueous dispersions of CS·L-AspA·Si (*1–3*) and CS·D-AspA·Si (*4*, *5*): freshly prepared (*1*, *2*, and *4*) and after aging under room atmosphere conditions for *t* = 35–60 days (*3*, *5*), obtained by method A (*1*, *3–5*) or method B (*2*); 24 ± 2 °C, The dotted line shows the σ value of distilled water at 25 °C. Roman numerals indicate concentration regions with different surface effects, explanation in the text

When freshly prepared nanodispersions were aged under room atmosphere conditions, an increase in their surface tension was observed (Fig. 2, curves *3* and *5*). This may be a consequence of partial aggregation of particles, but not very significant, since the realized σ values weare lower than the surface tension of the main liquid (water), and the greatest effect was observed in the region with a high concentration of the polymer substance, C_{CS} > 0.4 g/dl (Fig. 2, region I). The greatest tendency for such aggregation over time was shown by the CS·L-AspA·Si nanodispersion when C_{CS} > 0.8 g/dl. It is noteworthy that after a short-term dispersing ultrasonic effect (15 s), the σ values returned to the initial readings, characteristic of a freshly prepared nanostructured system.

The influence of the individual components (GlyOH and $Si(OGly)_4$) of the glycerol solution of silicon tetraglycerolate on the surface activity of aqueous solutions of CS in L-(D-)AspA and L-(D-)AspA (the main ingredients in obtaining the target substance of nanodispersion) was also assessed. The concentration of GlyOH and $Si(OGly)_4$ corresponded to that in forming the shell coating of CS·L-(D-)AspA·Si nanoparticles. It turned out that glycerol incorporation had little effect on the surface tension of aqueous solutions of chitosan and acid (Table). However, silicon tetraglycerolate introduction led to a significant decrease in σ compared to the control solutions. In this case, for chitosan L-(D-)aspartate solutions, the effect of decreasing surface activity upon introduction of $Si(OGly)_4$ was expressed to a greater extent than for L-(D-)aspartic acid solutions. Therefore, the surface energy of the nanodispersion was largely due to the contribution of the shell polysiloxane coating formed as a result of chemical functionalization of silicon tetraglycerolate on the surface of the nanoparticles.

Table

Effect of the individual components of $Si(OGly)_4 \cdot 3$ GlyOH used in the formation of the shell coating of CS·L-(D-)AspA·Si nanoparticles on the surface tension of aqueous CS solutions in L-(D-)AspA with C_{CS} = 0.3 g/dl, C_{AspA} = 0.3 g/dl and L-(D-)AspA with C_{AspA} = 0.3 g/dl

Aqueous solution	Surface tension **σ**, mN/m		
	Individual components $Si(OGly)_4 \cdot 3$ GlyOH		
	–	GlyOH	$Si(OGly)_4$
CS + *L*-AspA	67.4	69.2	58.5
CS + *D*-AspA	70.5	68.7	62.8
L-AspA	74.0	74.1	62.5
D-AspA	72.0	68.5	64.3

Conclusion

The use of filter paper as a contacting test element in the modified capillary-gravimetric Wilhelmy plate method and its static nature when measuring the gravitational tensile force allows measuring the surface tension of chitosan aspartate nanoparticle dispersions with satisfactory accuracy even at low concentrations of the polymer substance. Satisfactory accuracy of σ measurements in the modified Wilhelmy method is manifested up to chitosan aspartate concentrations of ~0.05 g/dl. It was found that the surface tension of nanodispersions depends on the concentration of chitosan aspartate and the isomeric form of aspartic acid and is largely determined by the contribution of silicon tetraglycerolate, which participates in nanoparticle functionalization with a polysiloxane shell coating.

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