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Sensors

Nonmonotonic (in concentration) conductivity of aqueous solutions of fungal melanin

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Abstract. The conductivity of aqueous (distilled and natural water) solutions of fungal melanin (purified and non-purified) has been studied. It has been shown that, in the presence of impurities, the conductivity of solution increases (for the concentration 0.1 wt% about an order of magnitude). On the concentration dependences of the melanin conductivity within the range of 0.0001 to 1 wt.% at least three particular sections have been detected. It was suggested that the presence of such sections is caused by three types of aggregation of melanin molecules: aggregation of several (mostly oppositely charged) molecules under the lowest melanin concentration, formation of nanoscale melanin clusters for the concentration of 0.002 to 0.06 wt.% and formation of micelles, when the melanin concentration is higher than 0.1 wt.%.

Keywords: melanin, conductivity, concentration, aqueous solutions.

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1. Introduction

Modern electronics increasingly focuses on the use of organic materials and, in particular, materials of biological origin. Melanin can be one of these materials [1-4].

Our previous studies [5, 6] showed that nanoclusters of the stack type can be formed in the melanin films of biological origin.

Cluster structures of melanin are formed most rapidly already in solution, from which solid layers were obtained. In this case, the structure of melanin clusters in a film should substantially depend on the type of structural ordering in the solution. Therefore, studying the features of the structural organization of melanin in its aqueous solutions makes it possible to explain the features of the structure of films themselves.

Since when forming different types of structures in solution, not only the local concentration of neutral molecules but also charged particles should change, it could be assumed that the conductivity of the solution can be sensitive to formation of structures of different types. In so doing, the conditions for formation of structures of various types in aqueous solutions of melanin must depend on the concentration of melanin, the presence of impurities of various types in it and on the ionic composition of water.

Our analysis of publications [1-6] has shown that the features of possible ordering in aqueous solutions of melanin clarified on the basis of electrical conductivity measurements were not previously studied in detail. Therefore, the purpose of this work was to deepen the study of conductivity inherent to aqueous solutions of melanin of biological origin with varying its purity and ionic composition of water.

2. Experimental and discussion of results

We investigated electrical properties of aqueous solutions of fungal melanin: non-purified and purified. In addition to different types of melanin, we used two types of water: distilled and mineralized from a natural source.

At the first stage of this research, a solution of fungal melanin with the highest possible concentration was prepared. For this, a mixture of melanin and water was heated to the temperature 50–60 °C and stirred. First, the stirring was carried out using a magnetic stirrer, and then sonication was performed. Thus, we obtained the maximum concentration of the aqueous solution of melanin 1 wt.%. Further, by successively diluting this

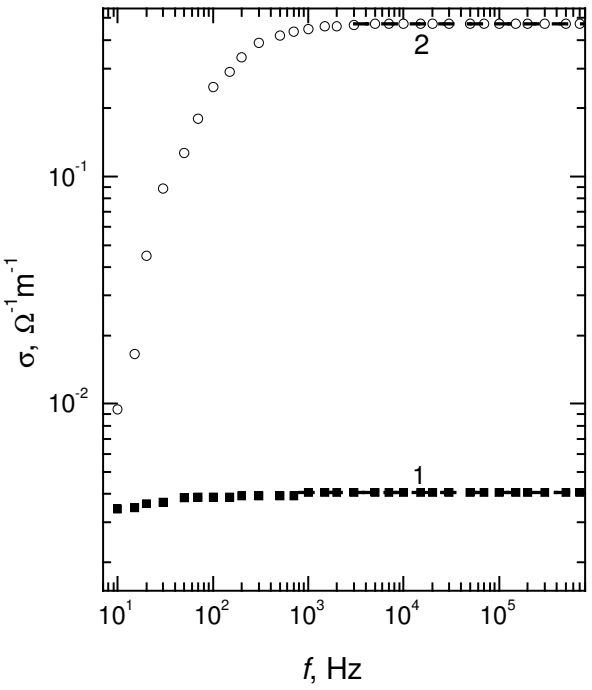

Fig. 1. Frequency dependences of the conductivity of distilled water (curve *1*) and 1 wt.% solution of purified melanin in distilled water (curve *2*).

solution with water, lower concentrations of melanin in water were obtained.

For electrical measurements, we used two platinum lamellar electrodes of the area 1 cm^2. The distance between these electrodes was 2 mm. For electrical measurements, the electrodes were immersed into a melanine solution to the depth 3 mm. Using the oscilloscopic method [7, 8], we measured the resistance *R* and capacitance *C* of the solution within the frequency range 10^{-1} up to 10^6 Hz.

Before each new measurement, the electrodes were rinsed with distilled water and dried. To reduce the effect of melanin molecules adsorption on the electrodes, measurements were performed with increasing the melanin concentration (at the beginning of the study, pure water was used, and at the end of the measurements – a solution with the maximum concentration of melanin).

All the measurements were carried out at the temperature 293 K.

Fig. 1 shows the frequency dependence of the conductivity of distilled water (curve *1*) and 1 wt.% solution of purified melanin in distilled water (curve *2*). As it follows from the obtained data, starting from the frequencies $f > 10^3$ Hz, the conductivity does not depend on the frequency. This value corresponds to the conductivity of solution σ. The value of σ was the main parameter, by which the electrical properties of the solutions were analyzed.

The dependence of the conductivity on the frequency for $f < 10^3$ Hz is caused by the influence of the near-electrode layer and was investigated in detail in the works [8, 9].

Studies of aqueous solutions of melanin showed that the dependences of the conductivity of solution on the melanin concentration are most informative. Fig. 2 shows the concentration dependences of the conductivity of solutions of non-purified (*1*) and purified (*2*) melanin in distilled water. Two important conclusions can be drawn from the data obtained. First, the conductivity of solution strongly depends on the presence of impurities in melanin. Second, the conductivity of melanin solution non-monotonically depends on the concentration of melanin.

From the data shown in Fig. 2, it follows that the conductivity of purified melanin is less than that of the non-purified one (for the concentration 0.1 wt.%, about an order of magnitude). Based on this result, it can be assumed that it is the impurities that form the charge carriers. Therefore, the conductivity of the aqueous solution can be one of the parameters by which the presence of impurities in melanin can be estimated. This result can have practical application.

From the scientific viewpoint, the concentration dependence of the conductivity of melanin is more informative. Moreover, it has peculiarities also in the case when this melanin solution was obtained in natural water (Fig. 3). As it follows from Fig. 3, the conductivity of melanin solution based on natural water changes significantly less than in the case of distilled water. However, in this case, too, there is a non-monotonic dependence of the conductivity on the concentration of melanin. Here, it is clearer pronounced than in the case of solutions based on distilled water.

In the curve *1* of Fig. 2, we see three sections, where the concentration dependence of the conductivity has peculiarities. We designated them by the letters **a**, **b** and **c**.

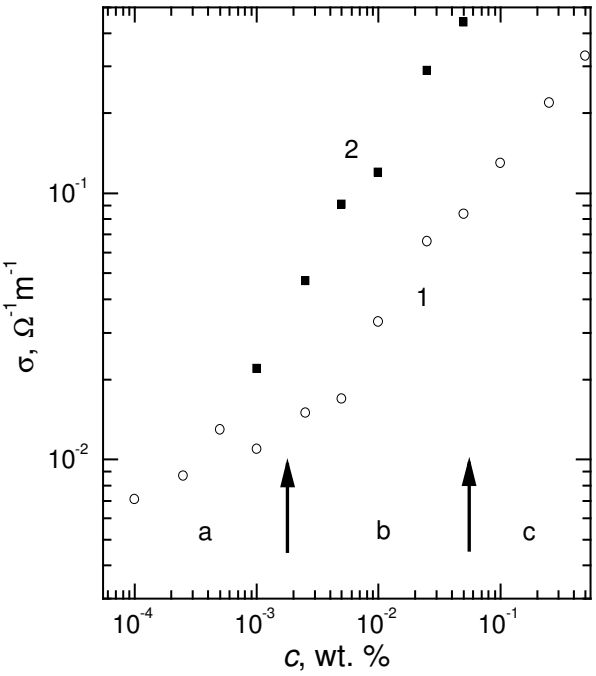

Fig. 2. Concentration (on the content of melanin) dependences of the conductivity for non-purified (*1*) and purified (*2*) melanin in distilled water.

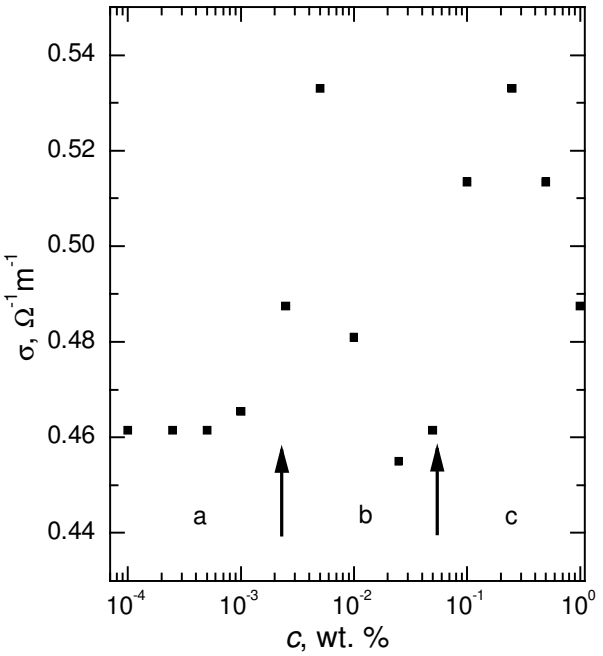

Fig. 3. Concentration dependence of the conductivity of purified melanin in natural water.

As it follows from Figs. 2 and 3, in the section **a** (the melanin concentration is 0.0001 to 0.002 wt.%) of the dependence of solution conductivity on the melanin content, the features are clearly manifested only in the case of solution of purified melanin in distilled water. It can be assumed that the cause of its manifestation is formation of certain structures at the molecular level. If these elements of structural organization have charges of the opposite sign, then formation of different structures with the melanin concentration increase should lead to a decrease in the conductivity, which is observed in the case of purified melanin. At this moment of melanin research, it is difficult to determine which precisely molecules form these structures.

Features in the section **b** (the melanin concentration is 0.002 to 0.06 wt.%) were observed for all the concentration dependences of conductivity inherent to aqueous solutions of melanin. If in the case of solution of purified fungal melanin in distilled water the "plateau" in the concentration dependence of conductivity was observed, and in the case of solution of purified melanin in natural water, we see a decrease in the conductivity with an increase in the melanin concentration (Fig. 3).

Our data on the investigation of luminescence of solutions give reason to assume that the cause of this effect can be formation of aggregates (most likely a nanometer size) from melanin molecules. Not only melanin molecules, but also predominantly melanin impurities, which are the main charge carriers in solution, can participate in formation of aggregates. The capture of such ions, when forming the nanoaggregates, is most likely the main mechanism for reducing the conductivity with increasing the melanin concentration in the section **b** of the concentration dependence of conductivity.

Features of the section **c** (the melanin concentration is higher than 0.06 wt.%) most clearly manifest themselves in the concentration dependence of conductivity of purified fungal melanin solution in natural water (Fig. 3). Only in this solution in the section **c**, like to the section **b**, the conductivity decrease with increasing the melanin concentration is observed. Analysis of the frequency dependences of capacitance and resistance shows that at the concentrations of melanin higher than 0.2 wt.% within the frequency range 0.1 to 100 Hz, a change in the sign of the dielectric loss tangent tgδ is observed.

Experimental data on the frequency dependence of tgδ for a solution of purified melanin in natural water with the concentration 1 wt.% are plotted in Fig. 4. From the data shown in this figure, it is especially important to note the presence of a section of positive value of the tgδ value within the frequency range 1 to 30 Hz.

From the theory of alternating current circuits, it is known that

$$tg\delta = \frac{\omega L - \frac{1}{\omega C}}{R},$$

where $\omega = 2\pi f$ is the cyclic frequency and L – inductance.

Based on this relation, the change in the sign of tgδ is caused by the transition from a capacitive load to an inductive one. For the solutions under study, it is difficult to assume what could be the cause of the inductive load appearance. Therefore, the more appropriate term for this case is the concept of "negative capacitance" introduced to explain the properties of solid-state heterostructures [10] and is also used to explain the properties of organic light-emitting diodes [11].

Since the "negative capacitance" is manifested at low frequencies, at which the electric field is applied to

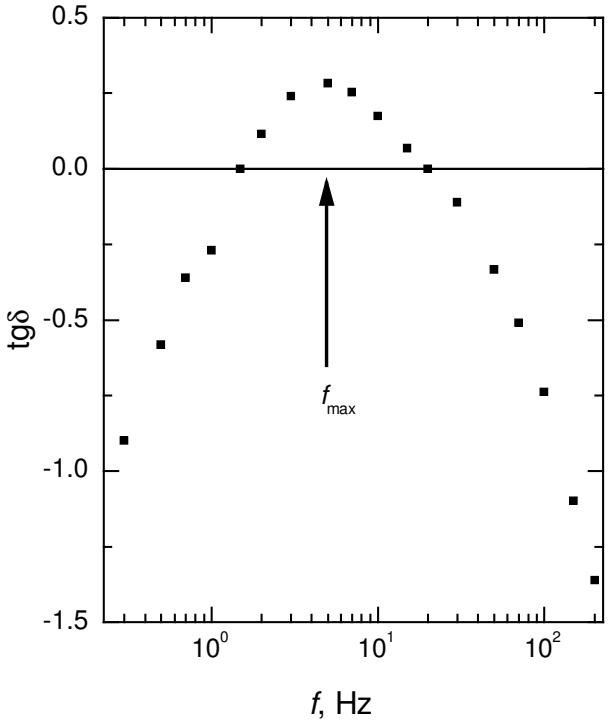

Fig. 4. Frequency dependence of tgδ inherent to the solution of purified melanin in natural water. The concentration of melanin is 1 wt.%.

the near-electrode layer [8, 9], its appearance is caused by the peculiarities of the dynamics of charge transfer in double electric layers. To clarify the mechanism of this effect, it is necessary to carry out more detailed experimental and theoretical studies. It will be the subject of a separate research work.

The presence of a "negative capacitance" region for the frequency dependence of tgδ gives grounds to assume what causes the specific features of the section **c** in the concentration dependence of conductivity of melanin aqueous solutions.

The "negative capacitance" region for the frequency dependence of tgδ was previously observed in the study of the dielectric properties of water-alcohol solutions with surface active agents. One of the most possible mechanisms of the "negative capacitance" effect for these solutions was formation of micelles. This was confirmed by a decrease in the density of water-alcohol solutions with the addition of surface active agents.

It can be assumed that also in the case of solution of fungal melanin in water, the peculiarities of the concentration dependence of the conductivity in the section **c** are caused by formation of micelles from melanin molecules. Surface active agents in this case may be impurities present in the melanin itself.

One more important experimental result should be added to the features of the concentration dependence of conductivity in the section **c**. As it follows from Fig. 4, the maximum value of tgδ corresponds to a certain frequency f_{max}. For the data shown in Fig. 4, f_{max} = 5 Hz. Analysis of the experimental data shows that the value of f_{max} increases with increasing the melanin concentration.

3. Conclusions

Thus, our studies have shown that the conductivity of aqueous solutions of fungal melanin depends on the purity of melanin, ionic composition of water and does not depend monotonically on the concentration of melanin.

The conductivity of melanin solution in distilled water is significantly (by an order of magnitude when the melanin concentration is 0.1 wt.%) increased at the presence of impurities in melanin. Therefore, the conductivity can be one of the parameters for evaluating the purity of melanin. To increase the sensitivity of this method, it is necessary to use water with as low as possible conductivity.

The dependence of the conductivity of the aqueous solution of fungal melanin on the amount of impurity is non-monotonic and includes at least three sections:

1. Reduction of conductivity with increasing the melanin concentration in the concentration range 0.0003 to 0.002 wt.% (the section **a** in the concentration dependence of conductivity) is most likely caused by combination of dissociated fragments of molecules.

2. Reduction of conductivity with increasing the melanin concentration in the concentration range 0.005 to 0.03 wt.% (the section **b** in the concentration dependence of conductivity) can be explained by formation of aggregates from the nanometer-sized melanin molecules.

3. Reduction of conductivity with increasing the concentration of melanin in the concentration range of more than 0.2 wt.% (the section **c** in the concentration dependence of conductivity) is due to formation of micelles.

This assumption is confirmed by the effect of "negative capacitance".

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