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POSSIBLE USE OF LOW-ENERGY ELECTRONS FOR STRUCTURE STUDYING OF DILUTE SOLUTIONS OF SURFACE-ACTIVE SUBSTANCES

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The article presents the study of using low-energy electrons to determine the positional order and features of the interaction between micelles and electrons passing through a colloidal solution. The transformation in the positional order in the arrangement of micelles with a change in the concentration of surfactants in a solution are associated not only with their geometric factor, but also with the intensity of intermicellar interaction.

Key words: *surfactants, low-energy electrons, channeling, order, micelles.*

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ИСПОЛЬЗОВАНИЕ ЭЛЕКТРОНОВ С НИЗКОЙ ЭНЕРГИЕЙ ДЛЯ ИЗУЧЕНИЯ СТРУКТУРЫ РАЗБАВЛЕННЫХ РАСТВОРОВ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ

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В статье представлено исследование возможности использования электронов с низкой энергией для определения позиционного порядка и особенностей взаимодействия мицелл и электронов, проходящих через коллоидный раствор поверхностно-активного вещества (ПАВ) – цетилтриметиламмония бромистого (CTAB). Изменения позиционного порядка в расположении мицелл при изменении концентрации ПАВ в растворе связано не только с их геометрическим фактором, но и с интенсивностью межмицеллярного взаимодействия.

Ключевые слова: *поверхностно-активные вещества, низкоэнергетические электроны, каналирование, порядок, мицеллы.*

Introduction

The movement of low-energy electrons through two-component colloidal solutions is accompanied by the emergence of effects that ensure the anisotropy of their angular distribution after leaving the liquid medium. The manifestation of these effects depends on the features of the interaction of electrons moving along the "facilitated" movement channels with a medium's molecular bindings, as well as with positional order of the colloidal solutions [1, 2]. Therefore, the state of molecular bindings or associates after passing the electrons through a colloidal solution can be judged by these electrons' angular distribution [3]. This indicator is noticeably affected by the concentration of molecules of a substance dissolved in the liquid phase, as well as by external factors. Among external factors, we especially note the effect of weak electric or magnetic fields. For weak pulsed magnetic fields, such an effect has been studied in some detail for solids – see, for example, [4–6] and, in part, for liquids [7, 8], that are the subject of this study.

Micellar solutions are known as promising objects for studying processes that ensure a change in the positional order in the arrangement of molecular associates. They are often used as models of biological structures [9]. The orientational and positional orders of biological structures elements play a major role in the transport of electrons and ions. In the short-range order, the arrangement of these elements in micellar solutions leads to the formation of channels facilitated for the electron or ion movement. As a result, the passage of electrons or ions through the medium features a noticeable anisotropy of their angular distribution [10]. In this case, the features of the electron channeling in the solution and, subsequently, the effect of concentration or external factors on the positional order of molecular bindings or their ensembles, as well as the interactions between them and moving electrons, can be judged by the angular distribution of electrons passing through the solution [11]. The paper contains the research of the parameters of low-energy electron channeling in dilute aqueous solutions of the cetyltrimethylammonium bromide surfactant (CTAB) depending on their concentration in the solution in order to implement this approach.

Materials and methods

The objects of the research were aqueous solutions of the cetyltrimethylammonium bromide surfactant, $[(C_{16}H_{33})N(CH_3)_3]Br$ (CTAB), in the concentration range of $(0.14 \div 54.88) \times 10^{-3}$ M/l. The studies were carried out in a pulsed electric field of a gas discharge visualization (GDV) camera (electric field strength 4.5×10^6 V/m, pulse frequency 1024 Hz, pulse duration $(3 \div 5) \times 10^{-6}$ s) [12]. A GDV-camera's block diagram is shown in Figure 1.

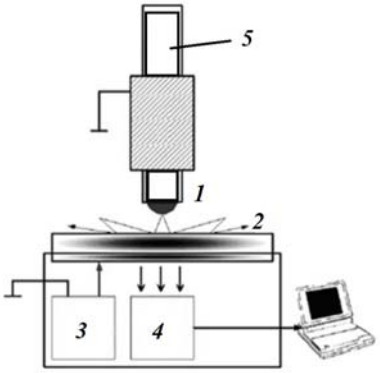

Fig. 1. The block diagram of a GDV-camera: liquid meniscus (1), quartz electrode with conductive coating (2), voltage pulse generator (3), optical system (4), metal electrode (5) [9]

The studied solution was taken into an inert polypropylene cylinder, made by injection modeling, in which there was a metal electrode emitting electrons. An optically transparent electrode with a conductive coating on the lens was placed 2×10^{-3} m away from a drop of meniscus formed at the end of the cylinder. An electrical voltage pulse from a generator was applied to the conductive coating with an amplitude of 9 kV and a duration of 2×10^{-6} s. The electric pulses stimulated the emission of electrons from the metal electrode, their acceleration, and diffusion through the biological fluid drop. Accelerated electrons, leaving the liquid, ionized the air. Gas ionization between the drop meniscus and the electron causes a sliding gas discharge. Its emission is recorded by a camera, converted into a digital code, and displayed on a screen as a set of streamers, defined by the projection of the facilitated channels of electron movement inside the drop, through its surface, and onto the matrix of the camera lens. A parametric analysis of ten consecutive luminescence patterns, performed using «GDV Scientific Laboratory» software, shows details about the distribution of low-energy electrons that display stereographic projections of the channels of facilitated electron movement in the studied liquid and through its surface.

Therefore, the features of the channels of facilitated electron transport through solutions, as well as the interaction of electrons with molecular bindings, and their ensembles participating in the channels' formation, can be defined by the angular location of the emission coefficient's maxima, their width, shape, and number of streamers [7, 8].

Results

Figure 2, *a*, *b*, *c*, *d* shows patterns of the angular distribution of electrons passing through CTAB solutions with different concentrations. The changes in the CTAB concentration in the solution affect the number of maxima in the angular distribution of electrons, differing in their angular position, width, shape, and intensity. The analysis of the obtained dependencies shows that the parameters of the maxima are determined by the number of channels of facilitated movement of electrons through solution drops, as well as by the features of the interaction of electrons with molecular bindings, forming the walls of the channels, and the parameters of water environment. This is confirmed in the abstract provided in the paper [13]. In case of a solution with a CTAB concentration of 1.4 mM, the picture of the angular distribution of electrons shows four maxima corresponding to four directions of their movement in a liquid medium. With an increase of CTAB concentration in the solution to 20 mM, the number of maxima increases to 5–6. At the same time, their width, area, intensity, and shape change. These changes are linked to the change of the energy of electrons passing through solution drops, the number and position of the facilitated movement channels. The table shows the average energy of electrons transmitted through a drop depending in the concentration of CTAB in the solution and the type of self-orientation of molecular bindings in the corresponding concentration regions [8, 9]. The concentration is a ratio of the areas and intensities of the maxima. These data were used for the interpretation of the results.

Table. **Average values of the electron energy (relative units) emitted by from solutions at various CTAB concentrations [8]**

CTAB concentration, mM	1.4	2.74	5.09	27.46	54.88
Average values of electron energy, rel. units	3.6	40.7	38.9	34.2	33.7
Type of CTAB self-orientation	Spherical micelles	Spherical micelles	Spherical micelles	Cylindrical micelles	Cylindrical micelles

It is evident that the average energy of electrons passing through the solution changes with an increase of CTAB concentration. The causes of such changes can be the changes in the molecular bindings' (associates) positional order, as well as the changes of their interaction with moving electrons. Based on the data on the studied CTAB concentration range [8], its molecular bindings create spherical or cylindrical micelles with various spatial orientation. The maxima in the angular dependence of electrons, channeled through a solution with a CTAB concentration of 2 ÷ 5 mM, have notably the same intensity and are located at the same distance from each other.

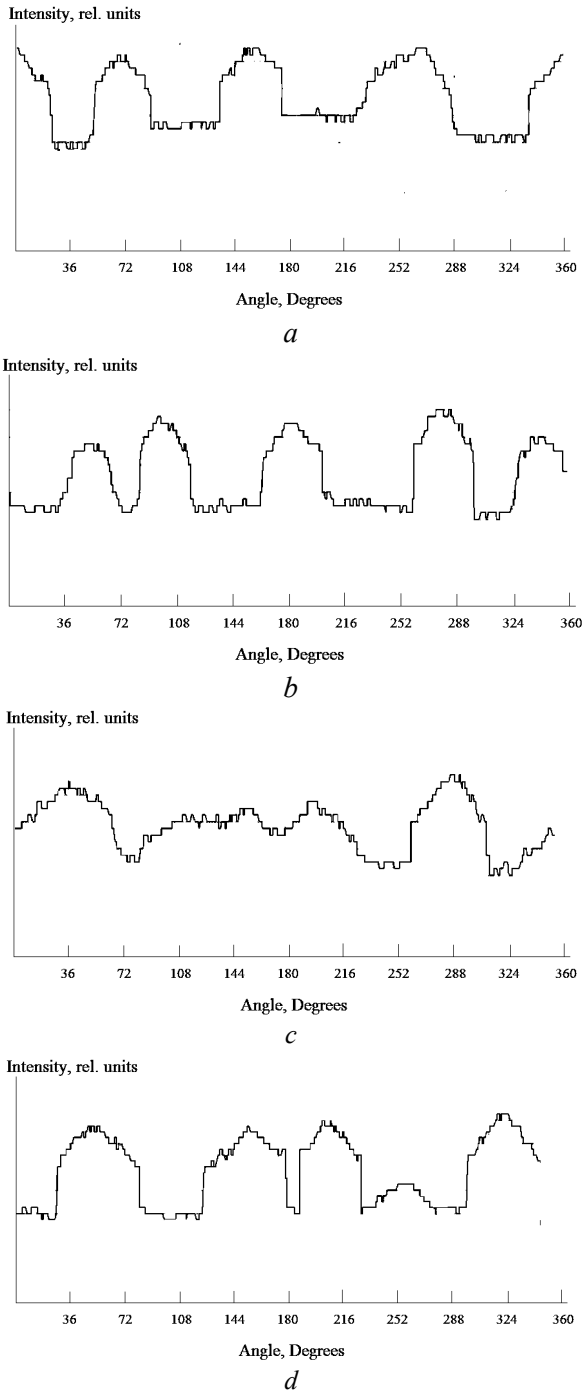

Fig. 2. Angular dependencies of the intensity of gas-discharge luminescence for CTAB solutions with different concentrations: 13.72 (*a*), 27.46 (*b*), 50.25 (*c*), and 54.88 mM (*d*). The calculations were done in angles with a range from 0 to 360° on the *x*-axis on a linear scale. The ordinate shows the intensity in relative units on a linear scale too

This is based on the data [8], showing that micelles are spherical and their short-range order matches one of the polymorphic modifications of the cubic or hexagonal package. The maxima of the angular distribution of electrons expand (Fig. 2, *b*) as the CTAB concentration increases to 27 mM. Thus, their equidistance is disrupted, which indicates a change in the structural orientation of the solution and a partial change in the geometry of the micelles. The observed pattern of the angular distribution of electrons can be explained by the fact that the solution contains cylindrical micelles. Their spatial orientation is different from the cubic package. There is a noticeable change in the shape and structural composition of the solution in the concentration dependence of the length of the contour lines (L). The lines describe the energy and the number of emitted electrons passing through the solutions (Fig. 3).

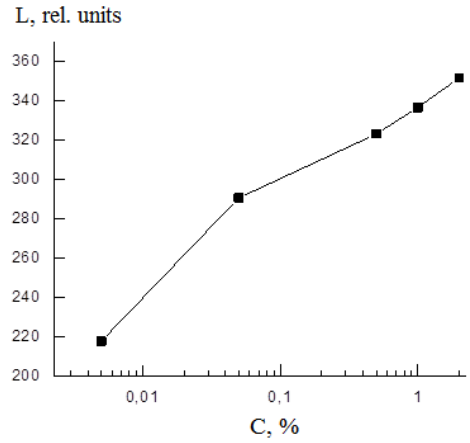

Fig. 3. The ratio of the contour's length, indicating the energy and number of channeled electrons, and the natural logarithm of CTAB concentration in the solution

Discussion

The process of the micelle formation is indicated by a bend in the concentration range of 0.05 wt. % (1.4 mM). The bend in the concentration range of 1 wt. % (27.47 mM) can be linked to the polymorphic transformation of spherical micelles into cylindrical. These transformations correlate with a decrease in the average electron energy, which can be linked either to a change in the charge state of micellar regions. Apart from that, they are linked to a change in the voltage of the electric field created by the micellar cell and slowing down the movement of electrons. Both factors can cause an increase in the Coulomb interaction between electrons and molecular associates that form channels. The vertical slopes in the emission maxima indicate that the energy of the Coulomb interaction between electrons moving near the walls of the channels is at maximum. Therefore, the electrons are repulsed from the walls. Meanwhile, the decrease in the maxima's width and the absence of axial electron channeling in the central part of the channel indicate a significant impact of the aqueous medium in its wide part. Hence, there is a significant impact on the electric field on the channeling process created by the micelle charges, justified by the presence of multiple energy minima for electrons in wide channels formed by cylindrical micelles. As a result, the increase in CTAB concentration contributes to the change on the electrostatic interaction between the micelles. Consequently, it contributes to the increase of the aggregation coefficient, i.e. increasing the number of large aggregates and changing their positional order. While studying the features of the distribution of electrons in energy, these processes can be clearly traced. With an increase of CTAB concentration in the solution, several minima can be observed in the electron distribution pattern, which can be associated with the impact of the positional order of the mycelial aggregates on the energy of moving electrons, as well as the intensity of micellar interactions on them. The aqueous medium plays an important role in influencing the interaction between electrons and micelles. However, comparing the areas of the maxima of the angular distribution of electrons indicates the causes of the change in the positional order of the micelle arrangement with an increase in CTAB concentration in the solution. After increasing CTAB concentration in the solution to a certain level, the positional order was determined by the shape of the micelles. This leads to the fact that the prevailing factor is their volume. Further research will be made to clarify the role of other factors on changes in the energy of electrons passing through colloidal solutions.

Conclusion

The performed studies show the possibility to use the results of the evaluation of the low-energy electron (up to 10 keV) channeling's features to determine the positional order in micellar solutions. The differences in the angular distribution of electrons after the change of CTAB concentration in the solution prove that there are changes in the shape, positional order, and charge state of the micelles. At the same

time, the aquatic environment also plays an important role as it influences the interaction between channeled electrons and micelles.

The reasons causing changes in the positional order in the arrangement of micelles with an increase of CTAB concentration in the solution are shown by comparing the emission areas' maxima. With increasing CTAB concentration in the solution, the way the positional order changes is determined by the change in the size of micelles. Therefore, the prevailing factor is their volume.

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