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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Production and Stabilization of Fullerene Dispersions in Liquid Media in the Presence of Nonionic Surfactants

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Abstract—Dispersion of C_{60} fullerenes in water and ethanol in the presence of nonionic surfactants, ethylene oxide derivatives, was studied. It was found that the quality of the dispersion process and the stability of dispersions depend on the structure, degree of oxyethylation, and concentration of surfactants. The optimal conditions are found in which stable fullerene dispersions are obtained as ingredients of cosmetic preparations with antioxidant properties.

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Application of fullerenes in biochemistry, medicine, and technology of cosmetics is due to their antioxidant and bactericide properties [1–4]. The ability of fullerenes and their derivatives to inactivate free oxygen radicals was described as far back as 1991 in [5]. C_{60} fullerene, compared to a “sponge imbibing free radicals” owing to the donor-acceptor properties of the pseudo-aromatic structure, could, in fact, be used as an effective antioxidant. However, the possible toxicity of these compounds is still a matter of discussion [6], and problems associated with the synthesis and purity of the product and introduction of fullerenes into matrices of varied nature remain unsolved [7].

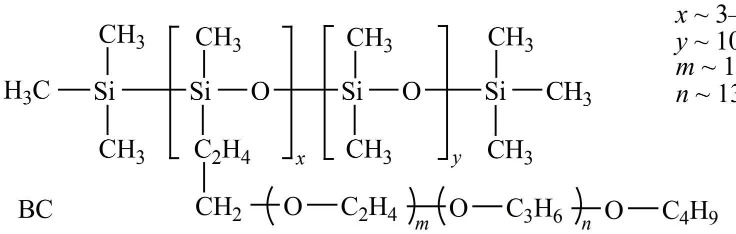
It is known that C_{60} fullerene is only soluble in organic nonpolar or weakly polar solvents [4]. C_{60} is insoluble in water; however, there exist methods for obtaining its colloidal dispersions in aqueous-organic media, with the subsequent removal of the organic solvent [8]. The introduction of fullerenes into composites intended for various purposes is complicated by the fact that the starting nanoparticles are, as a rule, aggregated and, therefore, are hardly dissolved in formulation components: the aggregates are as large as hundreds of nanometers. In this case, there should be no way of telling that a “nanoproduct” or “nanocomposite” is obtained, because this state of the system cannot fully provide manifestation of the unique properties of fullerenes. Deaggregation is also necessary when fullerenes are used to dope polymeric materials in order to obtain nanocomposites with improved physicomechanical properties [10, 11].

The aforesaid stimulates a scientific search in the field of development of methods for obtaining stable dispersions of carbon nanoparticles in liquid media. One of promising research areas is application of surfactants to intensify the processes of dispersion and stabilization of nanoparticle aggregates [12–16]. Previously, the effect of nonionic surfactant additives on the ultrasonic dispersion of carbon nanotubes has been studied and positive results have been obtained [17, 18].

The goal of our study was to examine the conditions in which stable fullerene dispersions can be obtained to be used as cosmetic ingredients and the effect of the nature and concentration of nonionic surfactants on the dispersion process and stability of the systems obtained.

EXPERIMENTAL

As objects of study served nonionic surfactants, a block-copolymer of oligo-organosiloxane and oxides of alkylenes (BC), manufactured by Silan OAO (Dankov town) and oxyethylated higher fatty alcohols (OE HFA) with varied medium degree of oxyethylation $n = 7–10$:



BC

$x \sim 3–4$
$y \sim 10–15$
$m \sim 17$
$n \sim 13$

$C_mH_{(2m+1)}O \left(C_2H_4 — O \right)_n H$

OE HFA $m = 12–14$ $n = 7–10$

The surface tension of surfactant solutions was determined with a K6 KRUSS tensiometer by the du Nouy's anchor-ring method at a temperature of 25°C. The critical micelle concentration (CMC) of the surfactants obtained was in agreement with published data [19].

C_{60} fullerenes of 99.98 wt % purity, manufactured by Piligrim OOO (St. Petersburg), were used in the study.

Dispersions of C_{60} fullerenes in water and ethanol were produced by dispersion in a YX-3560 ultrasonic bath. The process was performed during 20 min at a frequency of 40 kHz and power of 60 W. The initial concentration of the dispersed phase was 0.02–0.1 wt %. The centrifugation of the C_{60} dispersions was carried out with an OPN-8 laboratory centrifuge at 5000 rpm during 20 min. The dispersion intensity and the stability of the system were evaluated by the spectrophotometric method in the visible spectral range on a PD-303 single-beam spectrophotometer.

The C_{60} fullerene dispersions were studied by confocal microscopy on an LSM 510 META inverted microscope (Carl Zeiss), the particle sizes were determined by the method of dynamic light scattering on a PhotoCor Complex photon-correlation spectrometer.

The antioxidant activity (AOA) of the fullerene dispersions was evaluated by the amperometric method on a TsvetYauza 01-AA instrument by the known procedure [20] in which the role of reference substances can be played by the commonly known anioxidants: quercetin, dihydroquercetin, mexidol, trolox, gallic acid, etc. [21]. In the present study, the calibration was made against Chaga mushroom melanin produced by boiling [22]. The measurements were made at a voltage of 1.3 V.

The structure of the cosmetic cream with fullerenes was examined with an Olympus BX-51 microscope.

RESULTS AND DISCUSSIONS

Production of stable aqueous fullerene dispersions is of particular interest for biochemical, medical-biological, and ecological studies and in development of composite materials in which water is a formulation component.

We evaluated the fullerene dispersion intensity in relation to the surfactant concentration in the system by using the optical density data. The stability of the systems was determined by comparison of the results obtained in 1 and 24 h after the ultrasonic (U) processing. Additional information about the effect of surfactant additives on the stability of dispersions can be obtained by examining centrifugation processes as a means for forced sedimentation of particles under the action of centrifugal forces. By analyzing the optical properties of the supernatant fluid, we can make a conclusion about the stability of the systems we obtained, which is primarily associated with the quality of the deaggregation and solubilization of particles by nonionic surfactants.

Figures 1a and 1b present the results of a study of how the concentration of a surfactant, OE HFA with various contents of oxyethylated groups, affects the optical density of the fullerene dispersions in water before and after the centrifugation. The centrifugation removes large aggregates of nanoparticles, these data can provide evidence about the intensity of the stabilizing effect of surfactants as a result of the adsorption interaction with fullerene clusters. It can be seen that the addition of the surfactant leads to a substantial increase in the optical density of the dispersions. This indicates that water-insoluble fullerenes pass into the state of a colloidal system. The optimal surfactant concentration at which the optical density of dispersions is at a maximum after the ultrasonic processing and centrifugation corresponds to the CMC. These data show that the intensity of dispersion and stabilization is affected by the number of polar oxyethylene groups in the surfactant molecule. The strongest dispersing and stabilizing effect is observed at the degree of oxyethylation $n = 10$. This agrees with a number of published data on the dependence of the dispersion efficiency of carbon nanostructures on the

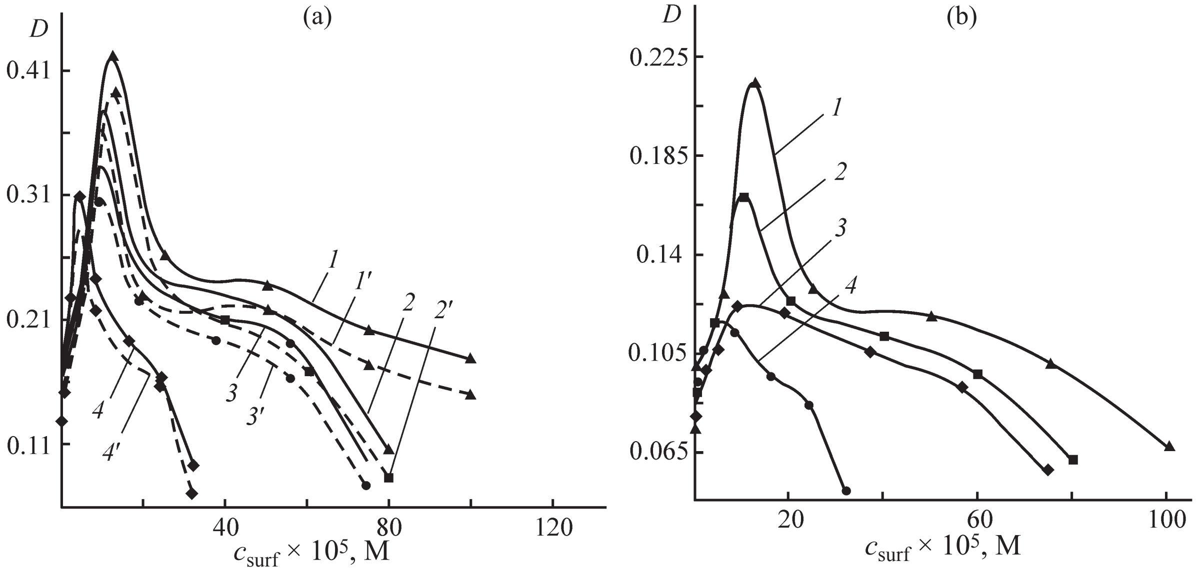


Fig. 1. Optical density *D* of fullerene dispersions vs. the concentration csurf of OE HFA surfactants with various degrees of oxyethylation. Initial content of the dispersed phase 0.02%. (a) Before U treatment and (b) after U treatment and centrifugation. *N*: (*1, 1*') 10, (*2, 2*') 8, (*3, 3*') 7 and (*4, 4*') 3; (*1*'–*4*') 24 h after the *U* treatment.

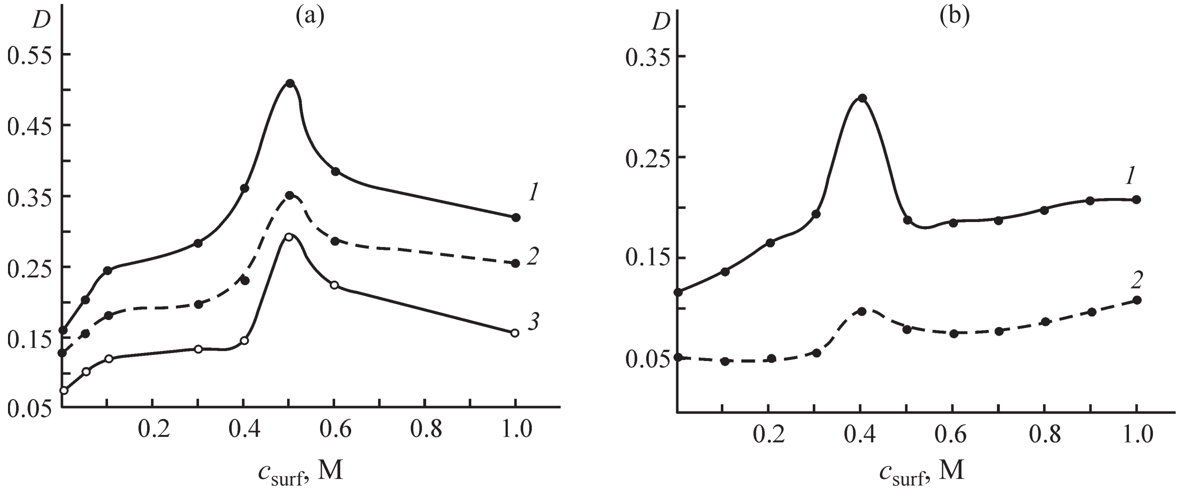


Fig. 2. Optical density *D* of fullerene dispersions vs. the concentration csurf of the oxyalkylene-organosiloxane block-copolymer surfactant in (a) water and (b) ethanol. (a) (*1, 2*) 1 and 24 h after *U* treatment, (*3*) after centrifugation; (b) (*1*) after *U* treatment and (*2*) after centrifugation.

molecular mass and degree of oxyethylation of nonionic surfactants [17, 23].

Figures 2a and 2b show the results obtained with an organosilicon surfactant, oxyalkylene-organosiloxane block-copolymer BC, as a dispersing and stabilizing additive. We also studied the effect of the centrifugation on the stability and size of dispersion particles. Comparison of the results obtained with BC and OE HFA before and after the centrifugation suggests that BC in a concentration of 0.5 wt % is the most efficient dispersing and stabilizing agent.

Figures 3a and 3b show curves describing the dependence of the optical density of the dispersions on the initial concentration of fullerenes in the presence of OE HFA (n = 10) in water and ethanol. Apparently, the fullerene dispersions in ethanol containing no surfactants are more dispersed than those in water, and their stability is also higher. Introduction of the OE HFA additive intensifies the dispersion process at higher concentrations of the dispersed phase, but by no more

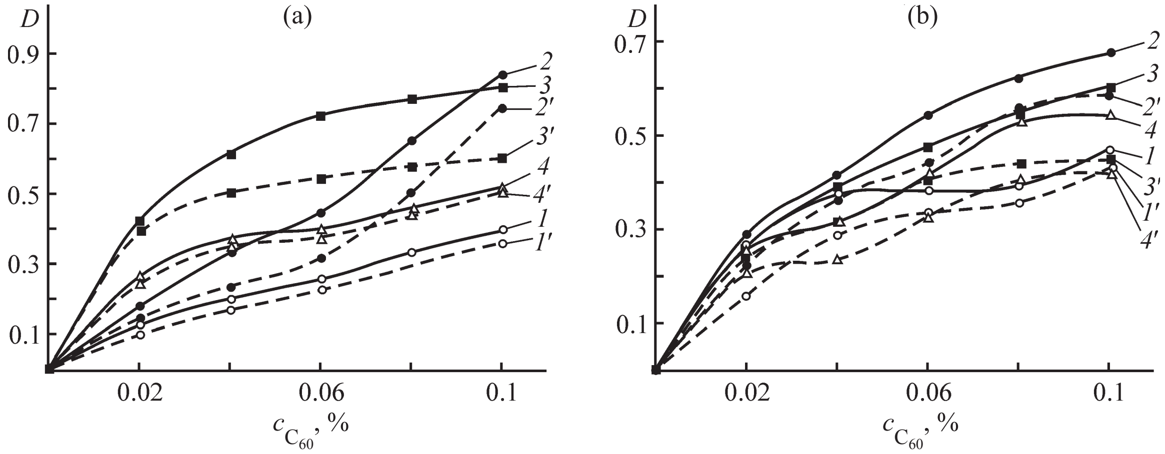


Fig. 3. Optical density *D* of C_{60} suspensions in (a) water and (b) ethanol vs. the concentration cC_{60} in the presence of an OE HFA surfactant ($n = 10$). (*1, 1'*) without a surfactant; c_{surf} (M): (*2, 2'*) 1×10^{-3}, (*3, 3'*) 1×10^{-4}, and (*4, 4'*) 1×10^{-5}. Time elapsed after the *U* treatment (h): (*1–4*) 3 and (*1'–4'*) 24.

than a factor of 1.5. It can be seen that the dispersions we obtained on the whole retain stability during 24 h after the ultrasonic treatment.

The confocal microscopy is a promising method for studying fullerene dispersions produced by ultrasonic dispersion. It was employed to estimate qualitatively and quantitatively the extent to which fullerenes undergo deaggregation in liquid media and to analyze the effect of surfactants on the properties of the resulting systems. Aqueous and ethanolic solutions of surfactants served as dispersion media. It was found that the dispersion efficiency becomes higher in the presence of surfactants, which is indicated by the decreased size of dispersion particles and smaller degree of polydispersity of the system. There are no coarse fullerene aggregates in the dispersion (Figs. 4a and 4b).

The method of dynamic light scattering was used to determine the average hydrodynamic radii of C_{60} fullerene particles and the diffusion coefficients in the dispersion in the presence of the most efficient dispersing agents, organosilicon block-copolymer BC and OE HFA ($n = 10$). The data in Table 1 demonstrate that addition of OE HFA does not lead to any significant change in the hydrodynamic radius of particles. In the presence of

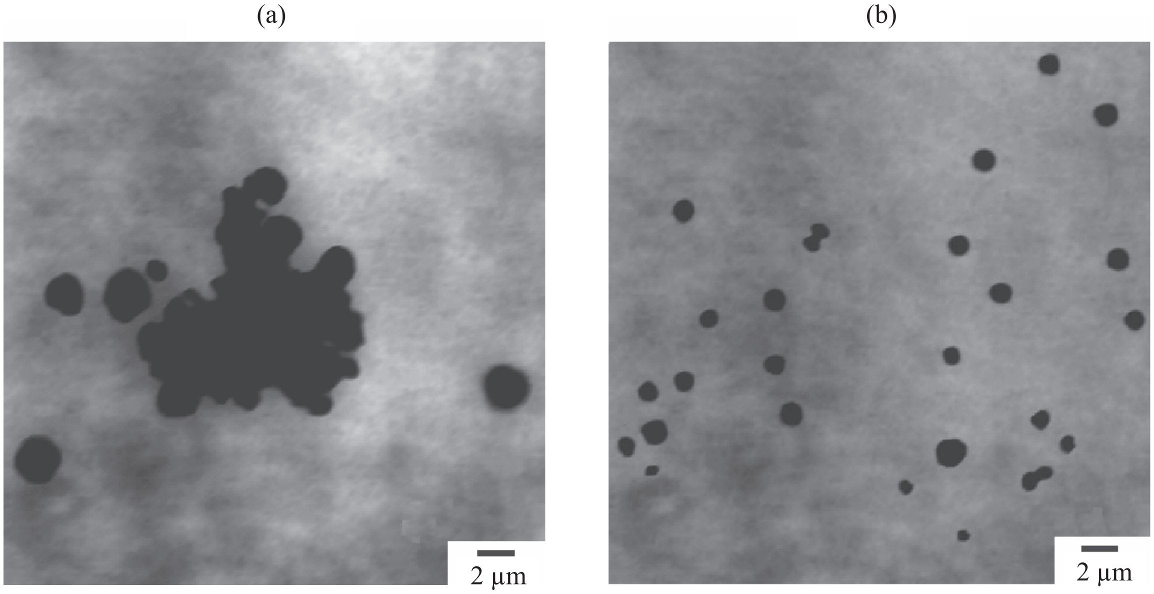


Fig. 4. Micrographs of fullerene dispersions in water (a) without a surfactant and (b) in the presence of an OE HFA surfactant ($n = 10$).

Table 1. Average hydrodynamic radii of C60 fullerene dispersion articles

System	R_h, nm	D, 10^{-8} cm^2 s^{-1}
C_{60}/H_2O	220.7	1.06
C_{60}/H_2O/ OE HFA (n=10), M:		
1×10^{-5}	219.8	1.12
1×10^{-4}	214.0	1.21
1×10^{-3}	217.5	1.18
C_{60}/H_2O/BC, 0.5 wt %:		
before centrifugation	175.0	1.27
after centrifugation	114.4	1.37

BC, the particle size decreases, which indicates that this surfactant has a dispersing effect. Possibly, the extremely high hydrophobicity of C_{60} fullerene molecules and their ability to form rather stable aggregates make the ultrasonic treatment in the presence of surfactants insufficient for full disintegration of particles.

At the same time, the stability of the dispersions obtained in the presence of surfactants is indicative of the stabilizing effect, which may be due to the adsorption of surfactants on the fullerene surface. The given colloid system can be described by the scheme of solubilization of nC_{60} fullerene aggregates by surfactant molecules, suggested in [12]. Figure 5 shows the solubilization scheme for OE HFA. The formation of adsorbed surfactant layers possibly diminishes the toxic effect of fullerenes. The BC molecule has a more complex structure that contains, in addition to hydrophilic oxyethylene groups, also hydrophobic oxypropylene groups, which evidences that the mechanism of interaction between organosilicon surfactant molecules and the surface of fullerene clusters is ambiguous and the clusters are solubilized.

Table 2. Antioxidant activity of the dispersions obtained

Fullerene dispersion in aqueous solutions of surfactants	X, mg L^{-1}
C_{60} fullerene, 0.02%/ OE HFA (n = 10), 0.0125%	7.12
C_{60} fullerene, 0.2%/ OE HFA (n = 10), 0.0125%	8.87
C_{60} fullerene, 0.02%/BC, 0.5%	23.72
C_{60} fullerene, 0.2%/BC, 0.5%	24.40

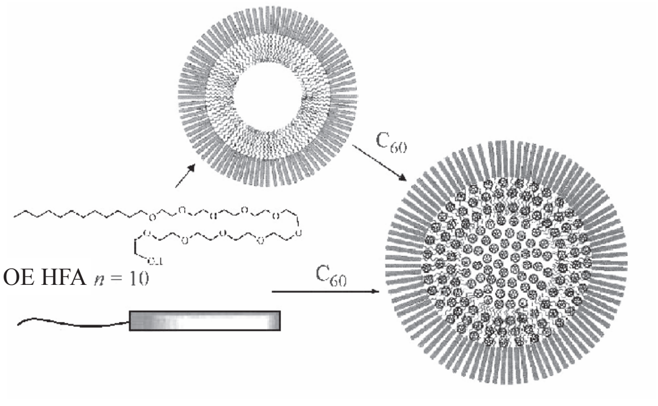


Fig. 5. Scheme of stabilization of fullerene aggregates nC_{60} by surfactant molecules. OE HFA n = 10.

It is noteworthy, in addition, that C_{60} fullerene exhibits acceptor properties and can form noncovalent compounds of the donor-acceptor type with various low-molecular and macromolecular compounds. Moreover, fullerenes affect the process of micelle formation from amphiphilic block-copolymers: they change the CMC, aggregation number, and shape of micelles formed in solubilization [10, 12]. Possibly the effective action of the organosilicon BC can be attributed to the formation of more stable complexes.

The interest in antioxidants in cosmetics is due to their ability to block the harmful influence exerted on a human organism by free radicals, which are, according to modern theories of aging, the reason why the human skin is changed and hair keratin is damaged. As noted above, fullerenes can be used as innovative antioxidant agents. We determined the antioxidant activity of the fullerene dispersions obtained in water and aqueous solutions of surfactants. The results obtained are summarized in Table 2, where X is the correlation coefficient of the antioxidant activities of the dispersions with respect to Chaga mushroom melanin. It can be seen that systems in which BC is the dispersing and stabilizing agent exhibit a higher antioxidant activity that systems with OE HFA.

Based on these results, we introduced fullerenes into formulations of a cosmetic hand cream and anti-age shampoo. Nonionic surfactants, derivatives of ethylene oxide and various organic compounds, are conventional emulsifiers in production of cosmetic emulsion systems. An emulsion system, hand cream, was prepared by

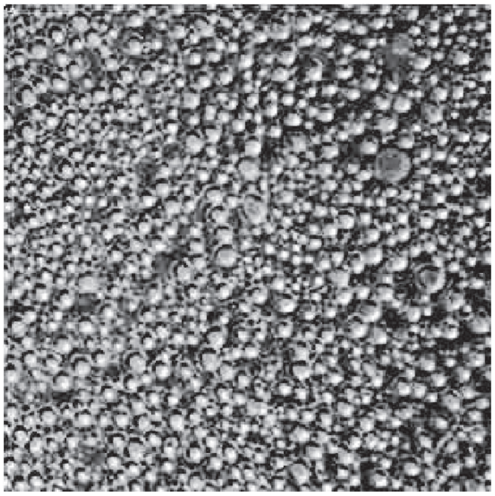


Fig. 6. Micrograph of the structure of a cosmetic cream containing C_{60} fullerene. Magnification 500×.

the hot/hot method in a PE-8100 mixer at 2000 rpm. Figure 6 shows a micrograph of this cream, indicative of its homogeneous, nearly monodisperse, structure. This cosmetic preparation is a light cream with a silky texture. The pH of the cream (6.0) fully satisfies the requirements of GOST (State Standard) R 52343–2005 (pH 5–9.0).

Organosilicon (silicone) surfactants have a good foaming capacity and conditioning effect [24]. The fullerene dispersions obtained in the presence of BC were introduced into a foam-detergent formulation, a shampoo, fully conforming to the regulations (GOST R 52345–2005). The possibility of obtaining an alcohol-containing lotion with fullerenes was analyzed.

The results obtained in the study can also be used to produced fullerene-doped nanocomposites with improved physicomechanical properties.

CONCLUSIONS

(1) It was found using spectrophotometric and confocal-microscopic data that the dispersion of fullerenes in the liquid media under study is intensified in the presence of nonionic surfactant additives. A comparative analysis of the effect of oxyethylated fatty alcohols and a block-copolymer of oligo-organosiloxane and alkylene oxides demonstrated that use of an organosilicon macromolecular surfactant results in that the most stable dispersions are formed.

(2) It was shown that the number of oxyethylated groups in molecules of oxyethylated higher fatty alcohols affects the quality of dispersion and the stability of dispersions.

(3) The optimal concentrations of dispersing and stabilizing additives were found. A decrease in the hydrodynamic radius of fullerene aggregates in the presence of the organosilicon surfactant was revealed.

(4) It was shown that fullerene dispersions obtained in the presence of the optimal concentration of nonionic surfactants exhibit the highest antioxidant activity. This circumstance enabled their use as ingredients of cosmetic preparations.

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