



The Influence of The nature of AOT, Sodium bis (2-ethylhexyl) Sulfosuccinate on the Spectral Characteristics of the Optical Absorption of Silver Nanoparticles in Reverse Micelles solution

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ABSTRACT

In this paper we studied the influence of the nature of the surfactant sodium bis(2-ethylhexyl) sulfosuccinate on the spectral characteristics of silver nanoparticles in reverse micelles solution.

Key words: Silver nanoparticles, molecular assembly, reverse micelles, AOT, quercetin

INTRODUCTION

The decision of actual problems of modern nanochemistry is closely associated with the development and improvement of methods of synthesis, stabilization of nano-sized structures and the creation of composite materials with desired properties and multifunctional activity. However, the production of stable nanoparticles (NPs) associated with the problem of aggregation, clumping and spontaneous formation of larger structures¹. One way of solving this problem is the synthesis of nanoparticles in reverse micellar solutions. In such solutions, the aggregation of nanoparticles decreases due to surfactants and nanosized particles remains

stable for a long time in the liquid phase and in the composition of the nanocomposite materials^{2,3}. There are a large amount of data on the synthesis and properties of nanoparticles in domestic and foreign literature⁴⁻⁹. In recent years important results was provided confirming high catalytic, bactericidal activity of AgNPs in many reactions in which the silver in the film state is not working [10-13]. In order to manage the process of synthesis of metal nanoparticles we paid a special attention to the nature, concentration, composition, components and the conditions of preparation of solutions. In this paper we raised the question about the influence of the nature of the surface active compound AOT.

Spectrophotometric investigations were directed on the elucidation of the influence of the nature AOT of the solubility of quercetin solution AOT / isooctane and the formation of Ag nanoparticles, stability and evolution during storage. We found significant differences in the mechanism of micelles formation and the formation of nanoparticles by using four kinds of AOT produced by different companies, namely: Sigma Ultra, with the mass concentration 99% of the basic substance, Fluka 96% ($H_2O < 2\%$), Sigma USP 99%, AcrosOrganic 96% ($H_2O < 2\%$).

EXPERIMENTAL

We used the following reagents: silver nitrate, isooctane, quercetin - ALDRICH- 95% AOT: AOT Sigma Ultra. 99% - I, AOT Fluka 96% - II, AOT Sigma USP 99% - III, AOT AcrosOrganics 96% - IV.

Synthesis of silver nanoparticles

To prepare the initial reverse micellar solutions 0.15 M solution of AOT in isooctane was added the required amount of aqueous 0.3-0.6 M salts $AgNO_3$ in accordance with the selected values ω from 1.0 to 8.0. For the measurement of optical absorption spectra using UV-vis spectrophotometer Hitachi U-3010 in the wavelength range from 195 nm to 900 nm (quartz cuvette, $l = 1.0$ mm), the reference solution 0.15M AOT / isooctane.

RESULTS AND DISCUSSION

We studied the optical properties of silver nanoparticles synthesized by the method of "molecular assembly" using chemical reactions (Chem) recovery of Ag^+ ions and the subsequent formation of AgNPs in reverse micelles in the presence of a natural pigment flavonoid quercetin, Qr. Scheme reverse micelles is

shown in Fig. 1.

The choice the concentration of AOT in isooctane was based on the results of the study nanoparticle formation and stability in the return micellar solutions.

Table 1 shows the volumes of aqueous solutions of $AgNO_3$ at 25 ml Qr / AOT / isooctane for working solutions with starting set values of the degree of hydration, w_i from 1.0 to 8.0. The degree of hydration ω was defined by molar ratio of water molecules and AOT, $\omega = [H_2O] / [AOT]$. Accordingly, the concentration of Ag^+ in the aqueous solution at 0.3 M. It was chosen to be 0.3 M, and solution $[Ag^+]$ was dependent w_i and varied from 0.8 mM to 6.4 mM. The absorption spectrum of quercetin in inverse micellar solution (0) is shown in Fig. 2.

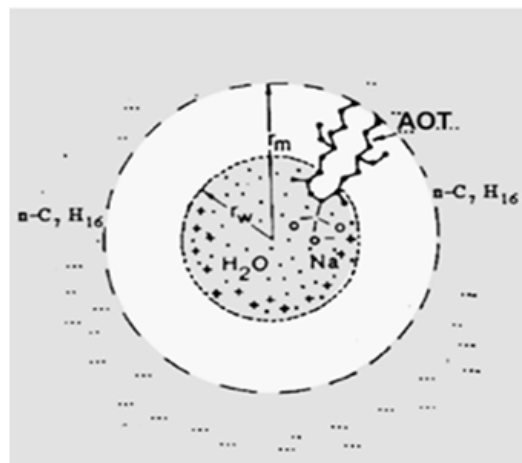


Fig. 1: Scheme of reverse micelles where AOT (bis (2-ethylhexyl) sulfosuccinate Na, r_w - water pool size, r_m - micelle size, degree of hydration, $w = [H_2O] / [AOT]$, $n-C_7H_{16}$ - isooctane

Table 1: The concentration of silver ions $[Ag^+]$ for different values of the degree of hydration, ω

Degree of hydration, ω	Volume of aqueous solution $AgNO_3$, mkl	$[Ag^+]$ in Qr / AOT / isooctane, mM
1,0	67,5	0,8
2,0	135,0	1,6
3,0	202,5	2,4
4,0	270,0	3,2
8,0	540,0	6,4

Fig. 2 shows the optical absorption spectra of silver NPs immediately after the introduction of the solution of AgNO_3 103,6mMqr / 0.15M AOT / isooctane (a) and 24 hours (b).

We have prepared a solution of 200 mMqr in solutions 0.15 M AOTi / isooctane, optical absorption spectra are shown in Fig. 3, where AOT Sigma Ultra 99% - I, AOT Fluka 96% - II, AOT Sigma USP 99% - III, AOT AcrosOrganics 96% - IV.

We carried out synthesis of Ag NPs (Chem) in micellar solutions (200 mMqr / 0.15 AOT (i) / iso-octane). Optical absorption spectra (electron plasmon resonance) Ag in the solution 200 M Qr / 0.15 AOT (i) / iso-octane at a value $\epsilon = 5.0$ are shown in Fig. 4.

Optical absorption spectra Qr 0.15 M solution of AOT (i) with iso-octane are shown in Figure 3. It should be noted that the solubility of Qr (the intensity of the band at $\lambda = 371$ nm) is the highest in the AOT-I (Sigma). However, the band intensity of the

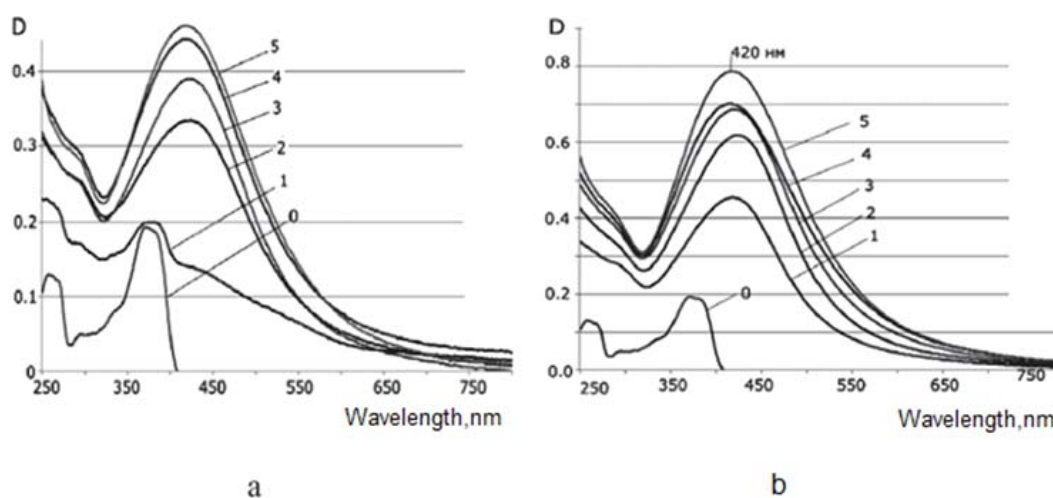


Fig. 2: The optical absorption spectra of solutions of nanoparticles Ag ($\lambda_{\text{max}} \sim 420$ nm) with value of the degree of hydration, ω : 1- 1.0, 2- 2.0, 3- 3.0, 4- 4.0, 5- 8.0. Spectrum solution Qr / AOT / iso-octane - 0. The measurement was conducted immediately after the introduction of an aqueous salt solution AgNO_3 - a) 24 hours - b). $[\text{Qr}] = 103.6 \mu\text{M}$ $[\text{AOT}] = 0.15 \text{ M}$

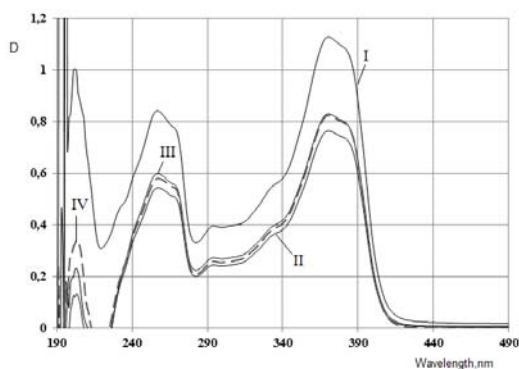


Fig. 3: Optical absorption spectra Qr 200 mM solution in 0.15 M solutions of AOT: Sigma ultra (99%) - I, Fluka (96%) - II, Sigma-Aldrich USP (99%) - III, Acros Organics (96%) - IV

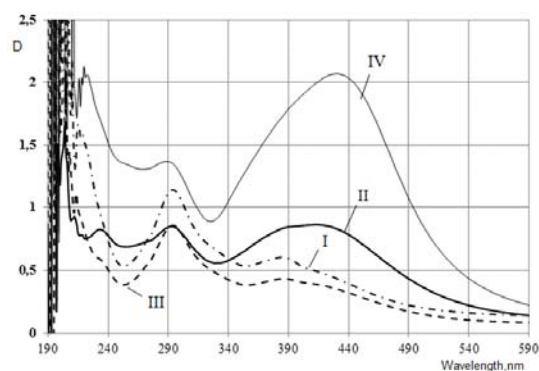


Fig. 4: Optical absorption spectra of solutions of silver nanoparticles, measured immediately after synthesis - Sigma Ultra, II-Fluka, III-Sigma USP, IV-Acros Organic

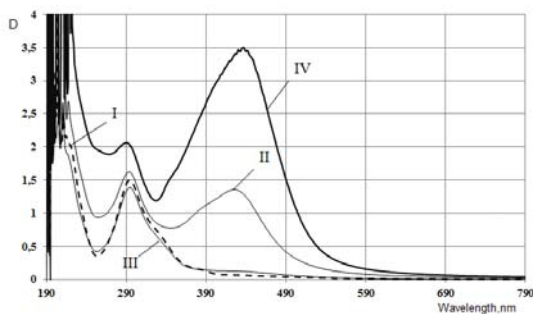


Fig. 5: Spectra of solutions of Ag NPs, 200 mMQR / 0.15 M AOT (i) after 2 days from the beginning of synthesis: I-Sigma Ultra 99%, II-Fluka 96%, III-Sigma USP 98%, IV-Acros Organic 96%

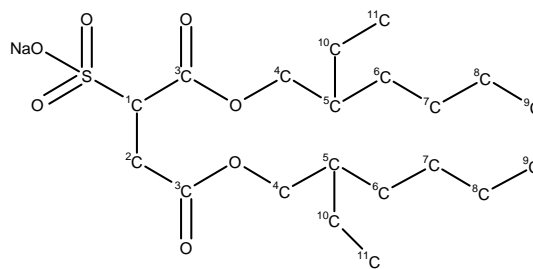


Fig. 6: Structural formula AOT with the numbering of the atoms

Table 2: Results of the study sample represented companies AOT

	IR cm^{-1}	NMR1H, ppm, solvent D_2O	Elemental analysis found, %
Sigma-Aldrich	2961, 2932, 2874 C-H st	0.76-0.90 m, 12H, CH_3 (9, 11)	C 53.2
	1737 C=O st	1.17-1.38 m, 16H, CH_2 (6, 7, 8, 9, 10)	H 8.5
	1465 CH_2 δ	1.45-1.54 m, 2H, CH (5)	S 7.4
	1249 C-O st	2.93-3.17 m, 2H, CH_2 (2)	
	1051 C-O st	3.84-4.11 m, 5H, CH + CH_2 (1, 4)	
		2.15 c, 0.02	
Fluka	2961, 2932, 2874 C-H st	0.76-0.90 m, 12H, CH_3 (9, 11)	C 52.6
	1737 C=O st	1.17-1.38 m, 16H, CH_2 (6, 7, 8, 9, 10)	H 8.5
	1465 CH_2 δ	1.45-1.54 m, 2H, CH (5)	S 7.4
	1251 C-O st	2.93-3.17 m, 2H, CH_2 (2)	
	1052 C-O st	3.84-4.11 m, 5H, CH + CH_2 (1, 4)	
		2.15 c, 1.33	
Sigma UPS	2961, 2932, 2874 C-H st	0.76-0.90 m, 12H, CH_3 (9, 11)	C 53.2
	1737 C=O st	1.17-1.38 m, 16H, CH_2 (6, 7, 8, 9, 10)	H 8.5
	1465 CH_2 δ	1.45-1.54 m, 2H, CH (5)	S 7.4
	1251 C-O st	2.93-3.17 m, 2H, CH_2 (2)	
	1052 C-O st	3.84-4.11 m, 5H, CH + CH_2 (1, 4)	
		2.15 c, 0.91	
Acros Organics	2961, 2932, 2874 C-H st	0.76-0.90 m, 12H, CH_3 (9, 11)	C 51.7
	1737 C=O st	1.17-1.38 m, 16H, CH_2 (6, 7, 8, 9, 10)	H 8.3
	1465 CH_2 δ	1.45-1.54 m, 2H, CH (5)	S 7.5
	1251 C-O st	2.93-3.17 m, 2H, CH_2 (2)	
	1052 C-O st	3.84-4.11 m, 5H, CH + CH_2 (1, 4)	
		2.16 c, 0.71	

plasmon resonance of nanoparticles Ag ($\lambda = 420$ nm) is the highest (top curve) for the solution of AOT (AcrosOrganics). Based on these data, we can conclude that the nature of AOT has a significant impact on the electronic levels, responsible for the light absorption of the solution components used.

Analysis of the spectra in Fig. 5 shows that when stored in air solutions of Ag nanoparticles intensity of the absorption bands -Sigma Ultra, II-Fluka, III-Sigma USP, IV-Acros Organic increases by 66.7, 40.1, 91.0 and 75.2% respectively, but the difference in the optical properties of the solutions on the basis of various AOT - persists. It is necessary to pay attention to the mechanism of formation of ions by a reduction reaction and evolution of Ag NPs in aerobic conditions. The explanation can be found in the works on the role of ideas about the early stages of activation of molecular oxygen in the theory peroxidation A.N. Bach (1987), in modern nanochemistry and nanobiotechnology¹⁴⁻¹⁶.

To determine the purity and identification of the impurities of AOT we conducted studies of the samples AOT produced by various companies using the methods of IR, NMR spectroscopy and elemental analysis. The results are shown in Table 2, the

structural formula of AOT with numbering of carbon atoms is shown in Figure 6.

CONCLUSION

Spectrophotometric investigations showed that the absorption spectra obtained by dissolving quercetin using different AOT (Sigma Ultra, Fluka, Sigma USP) were identical, but for the AOT Acros observed a significant increase in the intensity of the absorption band. Physico-chemical analysis (NMR, IR, elemental analysis) of the samples showed no obvious AOT differences. Due to the fact that manufacturers have used different methods of synthesis of AOT, it led to the production of substances of different structures, affecting the process of obtaining silver nanoparticles, which can serve as an indicator of the nature of AOT.

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