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Spectroscopic Study of Cationic Carbocyanine Dye Binding to $GdYVO_4$:Eu Nanoparticles

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The interaction of the inorganic nanoparticles ($GdYVO_4$:Eu, d = 2 nm) and organic carbocyanine dye 3,3' -diethyloxa-carbocyanine iodide ($DiOC_2$) has been studied spectrophotometrically. The formation of complexes of dye molecules with spherical nanoparticles $GdYVO_4$:Eu in aqueous solutions of cationic dye $DiOC_2$ was found. It is shown that nanoparticle $GdYVO_4$:Eu can form a complex with 5-10 molecules of the cationic dye $DiOC_2$ which leads to the decrease in the intensity of the absorption and luminescence spectra of the dye in aqueous solution.

Keywords: Dye, Nanoparticle, Complex «inorganic nanoparticle - organic molecule».

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1. INTRODUCTION

Modern scientific and technical progress is related to the development of new materials. In focus of new quickly developing scientific direction, which was nucleated on the joint of physics, chemistry, biology, electronic and computer technique and it is known under the name «nanotechnology», so-called, nano-scale objects are of specific interest. Recently, significant advances have led to a large variety of labeling reagents based on nanomaterials, such as quantum dots, magnetic nanoparticles, lanthanide doped-compounds, fluorophore-tagged latex/silica nanoparticles, fluorophore–labeled polymeric nanospheres etc. Strong interest in such objects is dictated also by the fact that nanoparticles have the potential to revolutionize the diagnosis and treatment of many diseases, for example cancer and infectious diseases.

In the work [1] it was shown that spheric nanoparticles $GdYVO_4$:Eu of 2 nm diameter have a tendency to be accumulated in the nucleus of living cell, that makes them very attractive for the use as nanocontainer for delivery of different substances inside of nucleus including for photodynamic therapy of the malignant tumor. The interaction of the nonorganic nanoparticles ($GdYVO_4$:Eu, d = 2 nm) and the organic carbocyanine dye 3,3' -diethyloxa-carbocyanine iodide ($DiOC_2$), which was used as a model system of active compounde, has been studied spectrophotometrically.

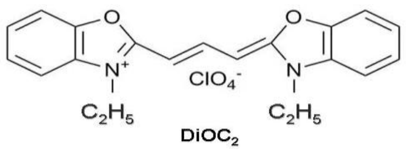

Fig. 1 – Structural formula of dye $DiOC_2$

2. MATERIALS AND METHODS

The carbocyanine dye $DiOC_2$ and nanoparticles $GdYVO_4$:Eu were synthesized in Institute for Scintillation Materials National Academy of Sciences of Ukraine. Chloroform (Sigma Aldrich) used to prepare stock solution of the dye was a spectroscopic grade product. To prepare aqueous solution of the dye with nanoparticles, doubly distilled water was used. The concentration of the dye in the solutions was in the range of 1×10^{-6}–2×10^{-4} M. The concentration of the nanoparticles in the solutions is varied within the 0,0005 g/l–2,95 g/l range.

Visible absorption spectra were recorded using spectrophotometer UV-Vis Specord 200 (Analitic, Jena). Solutions were placed in a quartz cuvette of 2 nm optical path length. Luminescent spectra were recorded using spectrofluorimeter Lumina (Thermo Scientific, USA).

3. RESULTS AND DISCUSSION

The process of co-operation of molecules of dye with nanoparticles can be described with a balanced reaction:

$$nD+NPs \rightarrow D(NPs)n,$$

where D, NPs and DNPs – dye, nanoparticle and complex of dye with nanoparticle respectively.

As we can see from the structural formula, $DiOC_2$ relates to salt dyes, so in polar solvents it dissociates with formation of cation and anion. Moreover, analysis of absorption spectra $DiOC_2$ in the range of concentrations from 1×10^{-6} to 2×10^{-4} M shows, that Bouguer-Lambert-Beer law is satisfied and the dye is situated in water solution in monomeric form. Maximum of absorption band is centered at 480 nm, luminescence maximum, at 498 nm.

At the investigation of process of complex formation of the system «nanoparticle-dye molecule» two approaches have been used.

It is known that binding of dye molecules to the particles is accompanied by changes in the absorption and luminescence spectrums [2]. In this paper we studied the effect of changes in $DiOC_2$ dye optical density as a function of $GdYVO_4$:Eu nanoparticles concentration in aqueous solutions. $DiOC_2$ concentration in solutions remained constant ($1,5\times10^{-5}$ M), the concentration of nanoparticles varied in the range of 0,0005 –2,95 g/l. It was found that the addition of nanoparticles to the solution leads to the changes in optical density of the solution, measured at the main at maximum. (Fig. 2). It is seen that in the concentration range 0,001 – 0,01 g/l occurs drop in the absorption intensity of the dye, which is associated with the interaction of the dye with the nanoparticle and the

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formation of complex «inorganic nanoparticle — organic molecule» [3]. In the absorption spectrum of the dye $DiOC_2$ is not observed the appearance of new bands, which suggests that the addition of nanoparticles does not lead to the dye aggregation on nanoparticle's surface. Further increase in the concentration of nanoparticles, as shown in Fig. 2, leads to a gradual increase in dye's optical density. At high concentrations of nanoparticles in the solution, the optical density of the solution does not change (Fig. 2). At the same time the addition of nanoparticles to the dye solution causes the same changes in the luminescence spectra (Fig. 3).

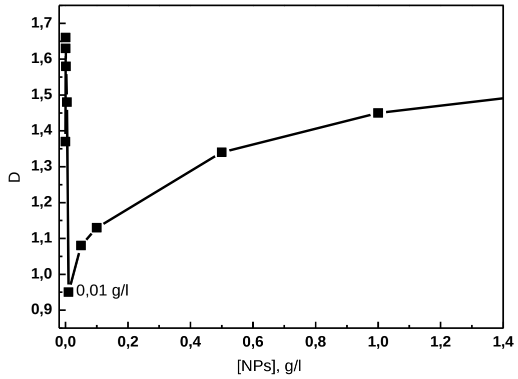

Fig. 2 – Changes in DiOC2 optical density as a function of NP_s concentration

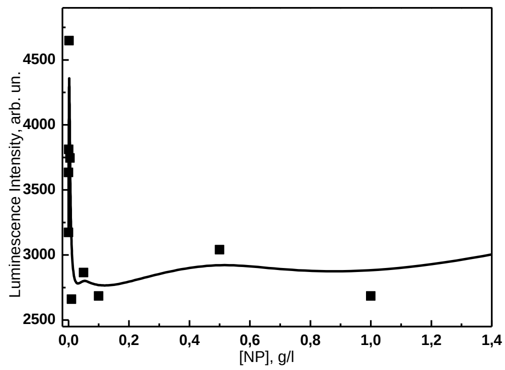

Fig. 3 – Dependence of the luminescence intensity of $DiOC_2$ dye on NP_s concentration

In the range of low concentrations of nanoparticles in solution (0,002 – 0,01 g/l) there is a reduction of the luminescence intensity of the dye measured at the main maximum. Further increase in nanoparticles concentration does not affect the intensity of the dye luminescence. Increasing the intensity of the absorption of $DiOC_2$ dye after a certain concentration of nanoparticles in solution (0,01 g/l) can be explained by agglomeration of the nanoparticles, increase due to their concentration in the solution and the release of dye molecules. However, this fact requires further study. However, the concentration of nanoparticles $GdYVO_4$:Eu 0,01 g/l can be taken as a kind of optimal concentration at which the formation of complexes «inorganic nanoparticle — organic molecule» with a maximum number of dye molecules per nanoparticle is observed. Using the mass of nanoparticles $GdYVO_4$:Eu which equal $9{,}6\times10^{-21}$ g [4], and the ratio of amounts of substances in solution, we obtain the composition 1:9.

As a second approach to the study «inorganic nanoparticle — organic molecule» complexes formation we have study the «sorption capacity» of the nanoparticles by varying the concentration of the $DiOC_2$ dye in the concentration range (1×10^{-6} — 2×10^{-4} M) in constant concentration of nanoparticles (0,01 g/l) (Fig. 4).

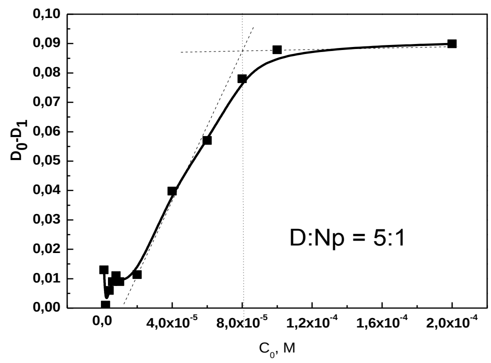

Fig. 4 – Dependence D_0-D_1 from the dye concentration (where D_0 and D_1 – optical density of the solution without and with NP_s)

The change in optical density of dye solutions with and without nanoparticles with increasing total concentration of the dye has been studied. As seen in Fig. 4, increasing concentrations of $DiOC_2$ leads to a gradual increase in the part of dye associated with the nanoparticle, followed by the saturation region. The point of intersection of two tangents, as shown in Fig. 4, give us the concentration at which the binding of the dye with nanoparticles is maximal (8×10^{-5} M). At this concentration $DiOC_2$ about 10% of the dye molecules bound to nanoparticles $GdYVO_4$:Eu, which corresponds to the concentration of $7{,}4\times10^{-6}$ M. Taking into account the weight of one nanoparticle which equal to $9{,}6\times10^{21}$ g, the ratio of nanoparticle:dye molecule is = 1:5.

4. CONCLUSION

Thus, using two approaches, the process of complex formation in the system «inorganic nanoparticle – organic molecule» has been studied spectrophotometrically. The formation of complexes of dye molecules with spherical nanoparticles $GdYVO_4$:Eu (d = 2 nm) in aqueous solutions of cationic dye $DiOC_2$ was found. It is shown that nanoparticle $GdYVO_4$:Eu can form a complex with 5-10 molecules of the cationic dye $DiOC_2$ which leads to the decrease in the intensity of the absorption and luminescence spectra of the dye in aqueous solution.

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