

Dye J-aggregate—semiconductor nanocrystal hybrid nanostructures in reverse micelles: an experimental study

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Reverse micelle solutions can be used for the assembly of hybrid nanostructures of the composition dye monomer—Ag₂S nanocrystal, dye J-aggregate—CuI nanocrystal, and dye J-aggregate—PbI₂ nanocrystal. The assembly is effected by means of adsorption of the dye (3,3'-di-(γ -sulfoethyl)-4,5,4',5'-dibenzo-9-ethylthiacarbocyanine betaine pyridinium salt) onto the nanocrystal surface. Factors responsible for the dye adsorption onto semiconductor nanocrystals in reverse micelle solutions are analyzed. It is suggested that adsorption can be the outcome of forces induced by both van der Waals and chemical interactions. The surfactants used for stabilization of reverse micelle solutions also influence the assembly of the hybrid nanostructures.

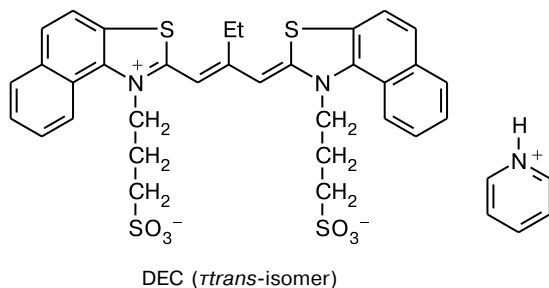
Key words: cyanine dyes, J-aggregates, semiconductor nanocrystals, hybrid nanostructures, reverse micelles.

Targeted design of nanosized objects with specified structure and properties is a key problem in modern materials science. Recently, increasing attention has been paid to complex nanostructures and ordered systems rather than unique properties of individual nanoparticles. Combining nanosized organic and inorganic components into common structures allows one to use the properties of both classes of materials and to fabricate nanostructures with new properties. Recent interest in hybrid organo-inorganic nanostructures (HOINs) is due to the possibility for photo-induced charge separation to occur in such systems (this phenomenon is basic to water photosplitting and converting light into electricity). The most striking example of using charge separation in hybrid nanostructures is provided by the Grätzel solar cells¹ prepared from titania nanoparticles bearing adsorbed sensitizer molecules. Owing to the combination of specific properties of two materials, such heterostructures convert sunlight into electricity, thus simulating photochemical sensitization occurring in the course of photosynthesis. The HOINs studied so far were based on nanocrystalline titania and cyanine dyes;^{2,3} merocyanine dye;⁴ alizarin;^{5,6} zinc(II) and magnesium(II) phthalocyanines;⁷ oxide nanoparticles (ZnO, Nb₂O₅, SnO₂, In₂O₃) and a ruthenium complex;⁸ Ag/titania core-shell nanoparticles and tricarbo-cyanine dye;⁹ CdS nanocrystals and copper tetrasulfophthalocyanine;¹⁰ CdSe, CdSe@ZnS nanocrystals and diazaperylene;¹¹ CdSe@ZnS nanocrystals and pyridyl-substituted porphyrins,¹² as well as SiO₂ and SnO₂ colloidal particles and rhodamine 6G;¹³ SnO₂ and Nile blue cationic dye;^{14,15} MoS₂ nanoclusters

and diethylcarbocyanine.¹⁶ Organic dyes in monomeric form usually act as sensitizers of inorganic nanoparticles. Meanwhile, some classes of dyes tend to form various ordered structures. Among them, of particular interest are dye J-aggregates, *i.e.*, highly ordered structures in which the dye molecules are stacked plane to plane. Similarly to natural light-harvesting photosynthetic complexes of plants, J-aggregates are characterized by high extinction coefficients. Optical excitations in such systems can coherently propagate over a large number of molecules in the form of excitons. These unique optical properties make the dye J-aggregates promising components of hybrid structures for light-harvesting antennas. The properties of a heterojunction formed by a nanocrystal and a dye J-aggregate were studied.¹⁷ The authors observed a resonance energy transfer between the dye J-aggregates and CdSe nanocrystals. The direction of energy transfer in this HOIN was controlled by changing the size of the nanocrystal.

Earlier,¹⁸ we have reported the self-assembly of organo-inorganic nanostructures "dye J-aggregate—AgI nanocrystals" in solutions of AOT—water—hexane reverse micelles (AOT is sodium bis(2-ethylhexyl)sulfosuccinate). Reverse micelles are widely used as nanoreactors to provide an appropriate environment for controlled nucleation and growth of nanoparticles.¹⁹ By varying the size of reverse micelles one can control the size of particles synthesized in the micelles. It was established that photoinitiated charge separation occurs in the AgI nanocrystals—dye J-aggregate hybrid nanostructures. Electrons transferred

from the sensitizer to AgI participate in the reduction of interstitial silver ions and formation of latent image centers. Therefore, the system promising for information storage applications appears to be inappropriate for being an element for converting sunlight into electricity. Hence the search for other compounds capable of acting as inorganic components of such hybrid systems becomes topical. Clearly, the first requirement for such compounds includes a specific pattern of mutual arrangement of the energy levels of the components. In addition, it was found that not all nanocrystals are suitable for forming HOINs. Adsorption of the carbocyanine dye DEC occurs efficiently on hexagonal β -AgI nanocrystals and is not observed on cubic γ -AgI nanocrystals.¹⁸ Also, we did not observe adsorption of DEC on cubic CdS, ZnS, CdSe, and PbS nanocrystals. We took into account the fact that the crystal lattice plays an important role in the assembly of HOINs and that adsorption of DEC occurs efficiently on β -AgI. Accordingly, in the present study copper iodide (CuI), lead iodide (PbI₂), and silver sulfide (Ag₂S) with lattice constants similar to those of β -AgI were chosen as inorganic components to synthesize HOIN.



The aim of the present study is to investigate the formation of hybrid nanostructures comprising an organic component (carbocyanine dye DEC) and semiconductor nanocrystals of different composition in reverse micelle solutions and to establish the principles for controlling their assembly.

Experimental

The substances used included potassium iodide (99%, Aldrich), 20% aqueous ammonium sulfide (Sigma), silver nitrate (chemically pure grade), lead nitrate (analytical grade, Spectrokhim), and copper sulfate (analytical grade, Spectrokhim). Two surfactants, sodium bis(2-ethylhexyl)sulfosuccinate C₂₀H₃₇SO₇Na (AOT, Sigma) and sodium dodecylsulfate C₁₂H₂₅SO₄Na (SDS, Sigma), as well as hexanol (chemically pure grade) were used to stabilize reverse micelles. Ethanol, distilled water, and *n*-hexane (99%, HPLC grade, Lab-scan) were used as solvents.

The cyanine dye DEC was kindly provided by Prof. B. I. Shapiro (M. V. Lomonosov Moscow State Academy of Fine Chemical Technology).

Lead nitrate and copper sulfate were purified by recrystallization. To remove water, AOT was predried at 40 °C *in vacuo* (10⁻³ Torr) until constant weight. Hexane and the AOT solu-

tions in hexane were kept in glass-stoppered flasks in a desiccator filled with a drying agent.

Nanocrystals were obtained following known procedures^{19,20} by mixing two microemulsions (1 : 1, v/v) whose aqueous phases contained the necessary reactants, *viz.*, AgNO₃ and (NH₄)₂S for Ag₂S nanocrystals; Pb(NO₃)₂ and KI for PbI₂ nanocrystals; and CuSO₄ and KI for CuI nanocrystals. Solutions of AOT reverse micelles containing salts solubilized in the aqueous phase were prepared by adding the AOT solutions in hexane to the aqueous solutions of the corresponding salt. Silver sulfide nanocrystals were obtained in solutions of SDS reverse micelles. The solutions of SDS reverse micelles containing AgNO₃ and (NH₄)₂S were prepared analogously using hexanol as co-surfactant to additionally stabilize the microemulsions.

Aqueous dye solutions were prepared from the dye solution in ethanol ($C = 1 \cdot 10^{-3}$ mol L⁻¹) because the dye occurs only as the *cis*-monomer even at high concentrations. To this end, a precalculated volume of the DEC solution in ethanol was evaporated to dryness on a water bath at 65–70 °C; then, the dye was dissolved in appropriate amount of water to obtain the desired concentration of the solution and kept on a water bath for 1 min at the same temperature. To prepare a reverse micelle solution, a solution of AOT in hexane was added to the aqueous dye solution at 65–70 °C. The mixture thus obtained was vigorously shaken until a transparent microemulsion was formed.

Reverse micelle solutions were prepared at different ratios of molar concentrations $W = [\text{H}_2\text{O}]/[\text{surfactant}]$. For AOT reverse micelles, the W values were varied by changing the AOT concentration in hexane at constant amount of the aqueous phase ($28 \cdot 10^{-3}$ mL of aqueous phase per millilitre of organic phase). The hydrodynamic radius of an AOT reverse micelle can be calculated using expression $R_h = 0.175W + 1.5$ (nm). Taking into account the thickness of the interfacial AOT layer (0.9 nm),²¹ one has $d = 0.35W + 1.2$ nm for the diameter of the water pool of AOT reverse micelles. For SDS reverse micelles, the diameter of the water pool was determined from empirical data obtained in Refs 22 and 23.

Absorption spectra were obtained with Perkin—Elmer Lambda EZ-210 and Shimadzu UV-3101PC spectrophotometers in quartz cells (optical path length was 10 mm) at 18–25 °C. The standard arm included the cell with the corresponding solvent or reference micelle solution.

Results and Discussion

CuI and PbI₂ nanocrystals. As far as we know, the synthesis of copper iodide nanoparticles in reverse micelles using Triton X-100 as surfactant is the one and only study on the subject.²⁴ In the present study, CuI nanocrystals were synthesized with AOT as surfactant. The synthesis was carried out at equimolar reactant ratio to exclude the effect of excess ions on the subsequent dye adsorption.

Copper iodide can exist as a number of polymorphs (Table 1) including cubic γ -CuI and a layered hexagonal structure (at room temperature), the wurtzite-type β -CuI (at $T > 643$ K), and the rock salt type α -CuI (at $T > 703$ K). The absorption bands of different CuI polymorphs were determined at 4 K.²⁵ The cubic structure is characterized by three bands with maxima at 337, 394, and 396 nm. The

hexagonal and wurtzite-type structures are characterized by two bands each, namely, the bands near 370 and 380 nm and those at 384 and 390 nm, respectively. On going from bulk to nanosized material the absorption bands may undergo some shift due to the quantum size effect. For instance, maxima of the absorption bands of cubic CuI nanocrystals obtained in colloidal solutions in the presence of polymers²⁶ are at 405 and 340 nm. Positions of maxima of the absorption bands of the hexagonal copper iodide nanocrystals remain nearly unchanged, namely, at 379 and 368 nm.²⁷ Figure 1 shows the absorption spectra of CuI nanocrystals obtained in AOT reverse micelles at $W = 10$. The absorption spectrum recorded immediately after preparation exhibits two strong bands with maxima at 320 and 347 nm. As time passes, they weaken and a band at 412 nm appears, which can unambiguously be ascribed to absorption of the cubic CuI nanocrystals. The band with the maximum at 347 nm can either be the second band of the cubic CuI polymorph or correspond to I^- ions characterized by absorption at 346 nm;²⁴ the absorption band at 320 nm corresponds to I_3^- ions.²⁸ Note that the spectrum recorded 25 min after the preparation (see the inset in Fig. 1) demonstrates a strong absorption peak of cubic CuI nanocrystals and a weak band near 380 nm, which can correspond to crystals of the wurtzite-type or hexagonal polymorphs. The existence of the high-temperature polymorph at room temperature is a well-known phenomenon for nanoparticles. It was shown that at room temperature, copper halide nanocrystals can also exist as a metastable β -polymorph.²⁹ As the particle size increases, the stable cubic phase is formed. The hexagonal phase of CuI per-

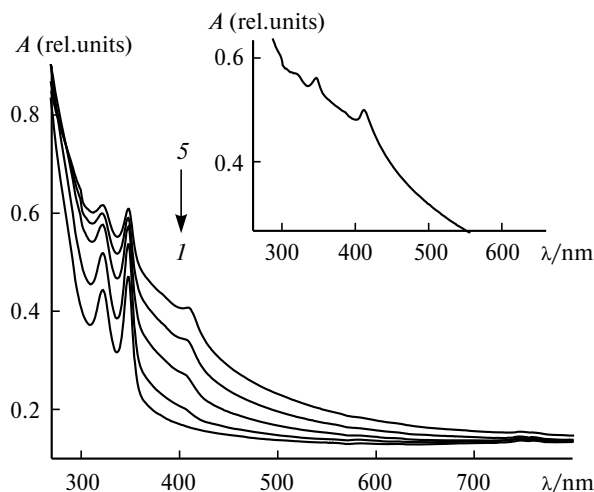


Fig. 1. Absorption spectra of solutions of reverse micelles containing CuI nanocrystals ($W = 10$) synthesized at equimolar reactant ratio, recorded immediately after mixing (1) and 5 (2), 10 (3), 15 (4), 20 (5) and 25 min (inset) after mixing.

sists up to a radius of 57 nm;³⁰ β -CuI nanocrystals were also obtained at room temperature.³¹ The possibility of formation of intermediate-type copper halide structures comprising hexagonal and cubic layers in nanosized samples cannot be ruled out too.²⁹ This suggests that CuI nanocrystals obtained in the present work comprise both cubic and hexagonal (or wurtzite-type) polymorphs, thus being an intermediate-type structure.

To obtain the HOIN, a freshly prepared solution of the DEC dye in reverse micelles was added to a solution of

Table 1. Data on the formation of hybrid nanostructures using nanocrystals of different composition and structure in AOT reverse micelles

Compound	Synthesis conditions of nanocrystals	Lattice symmetry	Lattice constants (\AA)	HOIN
AgI ¹⁸	Excess I^-	Hexagonal (β -AgI)	$a = 4.60, b = 7.5$	J-DEC*—HK AgI
	Excess Ag^+	Cubic (γ -AgI)	$a = 6.47$	—**
ZnS ¹⁸	Equimolar	Cubic (γ -AgI)	$a = 6.47$	—**
	Excess Zn^{2+}	Cubic	$a = 5.41$	—**
CdS ¹⁸	Excess S^{2-}	Cubic	$a = 5.41$	—**
	Excess Cd^{2+}	Cubic	$a = 5.832$	—**
PbS ¹⁸	Excess S^{2-}	Cubic	$a = 5.832$	—**
	Equimolar	Cubic	$a = 5.90$	—**
CdSe ¹⁸	Excess Cd^{2+}	Cubic (metastable)	$a = 6.05$	—**
	Excess Se^{2-}	Cubic (metastable)	$a = 6.05$	—**
α -Ag ₂ S	Excess Ag^+	Monoclinic	$a = 4.23, b = 6.91, c = 7.87$	—**
	Excess S^{2-}	Monoclinic	$a = 4.23, b = 6.91, c = 7.87$	—**
PbI ₂	Excess I^-	Hexagonal	$a = 4.557, c = 6.979$	J-DEC—HK PbI ₂
CuI	Excess Cu^+	Cubic (γ -CuI)	$a = 6.082$	J-DEC—HK CuI
	Excess I^-	Hexagonal (β -CuI)	$a = 4.451, c = 7.309$	J-DEC—HK CuI
AgBr ³⁶	Equimolar	Cubic	$a = 5.77$	Monomer DEC—HK AgBr

* J-DEC stands for J-aggregate of the carbocyanine dye DEC.

** No adsorption was observed.

CuI nanocrystals in reverse micelles in a 1 : 1 ratio 40 min after the preparation. The kinetic behavior of the absorption spectra of the mixture is shown in Fig. 2.

Mixing the solutions in reverse micelles is followed by a gradual decrease in the optical density in the J-aggregate band and by the appearance of a new long-wavelength band with the maximum at 677 nm; this maximum shifts to 683 nm with time. By analogy with the formation of the AgI nanocrystals—J-aggregate¹⁸ HOINs, we assign this band to the J-aggregate adsorbed on the CuI nanocrystals. In the present study, nanocrystals were synthesized at equimolar reactant ratio, but adsorption was also observed on the nanocrystals synthesized in the presence of a two-fold excess of copper ions.

The system under study behaves similarly to the AgI—J-aggregate system, *viz.*, after a certain time, the HOIN precipitates in the gravity field. Shaking the sample is followed by re-appearance of the absorption bands of CuI nanocrystals and the dye band at 683 nm. Centrifugation of the solution allows one to precipitate the HOINs, isolate them from the solution in reverse micelles, and then to disperse them in hexane without adding surfactants.

The results obtained confirm the assumption that the state of the dye aggregates is immediately related to nanocrystals, *i.e.*, the J-aggregates are adsorbed on their surface. The HOINs prepared are characterized by quenching of fluorescence of the J-aggregates. This is an indication of electron transfer from the aggregate to the conduction band of the crystal (sensitization phenomenon) and suggests the formation of the CuI nanocrystals—dye J-aggregate hybrid system in the micelle solution.

Mixing solutions of DEC and PbI₂ nanocrystals in reverse micelles was also followed by the appearance of the long-wavelength band with the maximum at 687 nm, which is red shifted relative to the J-band of the dye (Fig. 3).

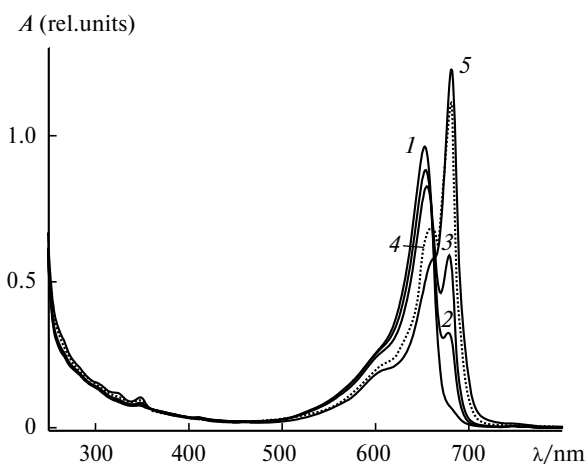


Fig. 2. Absorption spectra of a mixture of solutions of reverse micelles containing CuI nanocrystals ($W = 16$) and DEC ($W = 26$), recorded immediately after preparation (1) and 5 min (2), 30 min (3), 24 (4), and 48 h (5) after preparation.

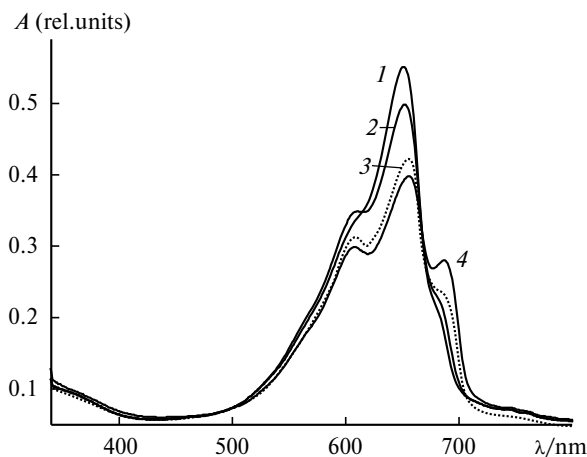


Fig. 3. Absorption spectra of a mixture of solutions of reverse micelles containing PbI₂ nanocrystals ($W = 6$) and DEC ($W = 26$), recorded immediately after preparation (1) and 5 min (2), 15 h (3), and 5 days (4) after preparation.

However, no complete transformation of the dye from a free aggregate to an adsorbed J-species occurs in this case. This behavior can be explained by the fact that the solution of reverse micelles contains a small amount of highly soluble (and, consequently, unstable) PbI₂ nanocrystals ($\lg PR = 8.06$). The lack of strong exciton peak seems to be due to the same reason. However, one can state with certainty that adsorption of dye J-aggregates onto PbI₂ nanocrystals does occur.

Ag₂S nanocrystals. Published data on the synthesis of Ag₂S nanocrystals in reverse micelles are scarce. These nanocrystals are synthesized using AOT³² or silver-functionalized AOT³³ as surfactants.

In this study, Ag₂S nanocrystals were synthesized using AOT. The absorption spectra of the Ag₂S nanocrystals obtained in AOT reverse micelles at $W = 6$ show no specific features (Fig. 4). Analogous spectra of Ag₂S nanocrystals at room temperature were obtained earlier.³³ Low-temperature synthesis usually results in monoclinic (rhombohedral) Ag₂S crystals (acanthite) (see Table 1). The Ag₂S nanocrystals synthesized in reverse micelles have the same crystal structure.³⁴

To prepare hybrid nanostructures, a solution of AOT reverse micelles containing Ag₂S nanocrystals ($W = 6$) was allowed to stay for 45 min and then a freshly prepared solution of AOT reverse micelles ($W = 26$) containing DEC (see Fig. 4) was added. The behavior of the dye in the mixture with Ag₂S nanocrystals is similar to its behavior in the presence of other sulfide nanocrystals,¹⁸ *viz.*, the J-aggregate is transformed to the *trans*-monomer (no new bands corresponding to the adsorbed dye aggregate are observed).

Factors affecting the assembly of hybrid nanostructures. The results of our experiments and the published data on the assembly of hybrid nanostructures are listed in Table 1.

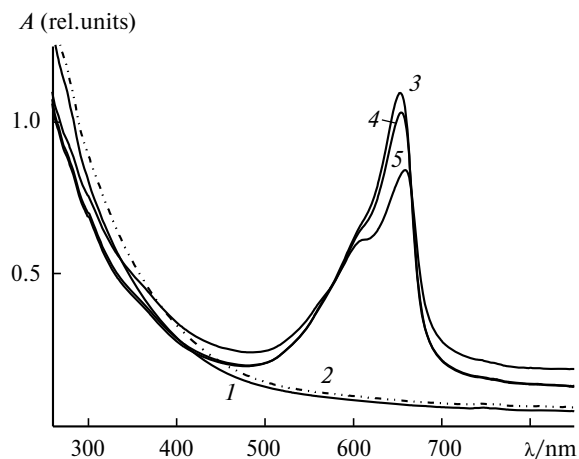


Fig. 4. Absorption spectra of solutions of reverse micelles containing Ag_2S nanocrystals, recorded immediately (1) and 40 min (2) after preparation and absorption spectra of a mixture of solutions of reverse micelles containing Ag_2S nanocrystals and DEC, recorded immediately after (3) and 20 min (4), and 24 h (5) after mixing.

The assembly of hybrid structures from dyes and nanoparticles can be controlled using electrostatic interactions between the ionic dye and the charged surface of the nanocrystal.^{14,15,35} In our case, electrostatic interactions between the surface of nanocrystals charged due to the presence of excess ions and the ionic dye are insignificant for the assembly of hybrid nanostructures.^{18,36}

Analysis of the data of Table 1 shows that DEC is adsorbed on halide nanocrystals ($\beta\text{-AgI}$, PbI_2 , CuI , AgBr) and indicates an important role played by the lattice symmetry and constants. According to published data,³⁷ thiocyanine dyes can interact with the surface of silver halide crystals through the formation of the sulfur—silver bond. It is assumed that both sulfur atoms are involved in adsorption. Now, suppose that adsorption is due to the formation of a chemical bond (chemical interaction) between the dye and nanocrystals. In this case, an important role is played by the crystal structure (in particular, lattice constants) of the nanocrystals. We have shown¹⁸ that the dye is adsorbed onto hexagonal AgI nanocrystals and does not adsorb onto cubic AgI nanocrystals. However, the dye is adsorbed not only onto wurtzite-type hexagonal nanocrystals, but also onto cubic AgBr nanocrystals.

Adsorption of dyes onto the surface can also be an outcome of other interactions. For instance, it is believed³⁸ that adsorption of a dye onto the surface of silver halide microcrystals is a result of van der Waals interactions between the π -conjugated system of the dye and the polarizable substrate. This provides an explanation for adsorption of the dye on various halides, because halide ions have high polarizability. The polarizabilities of sulfur and selenium ions are also high; however, experiments with chalcogenides (ZnS , CdS , PbS , CdSe) revealed no adsorption of DEC and formation of hybrid nanostructures.

Thus, adsorption of DEC on the surface of nanocrystals can be caused by both chemical and van der Waals interactions. To form DEC—nanocrystals hybrid nanostructures, the nanocrystals should contain readily polarizable ions (e.g., I^- and Br^-) and have a particular type of the crystal lattice and appropriate lattice constants (this holds for particles with the hexagonal lattice). However, the results obtained show some exceptions indicating that adsorption of dyes on the surface of nanocrystals is a complex process and, presumably, there exist some previously ignored factors affecting its efficiency.

One of them can be the effect of the surfactant that forms the micelle shell. We carried out experiments on the preparation of hybrid nanostructures with Ag_2S nanocrystals in SDS micelles. The HOINs were prepared by adding a freshly prepared solution of AOT reverse micelles ($W = 26$) containing DEC in 1 : 1, 1 : 2, and 1 : 8 (v/v) ratios to a solution of SDS reverse micelles containing Ag_2S nanocrystals ($W = 8$) stored for 30 min after preparation. The absorption spectra of the Ag_2S nanocrystals obtained in SDS reverse micelles at $W = 8$ (this corresponds to a water pool size of 3.7 nm) at twofold excess of sulfur ions match the spectra of the particles obtained in AOT reverse micelles.

Mixing the solutions of DEC and Ag_2S nanocrystals (1 : 1, v/v) in reverse micelles causes the equilibrium between the monomer and the dye aggregate to shift toward the *trans*-monomer due to the interaction of the dye with the surfactant, which leads to disaggregation (Fig. 5). In the subsequent periods of time, the optical density in the monomer and aggregate bands decreases after mixing and an absorption band at 640 nm appears (see Fig. 5, curve 4). After 48 h, the dye almost completely attains a new state characterized by $\lambda_{\text{max}} = 640$ nm (see Fig. 5, curve 5).

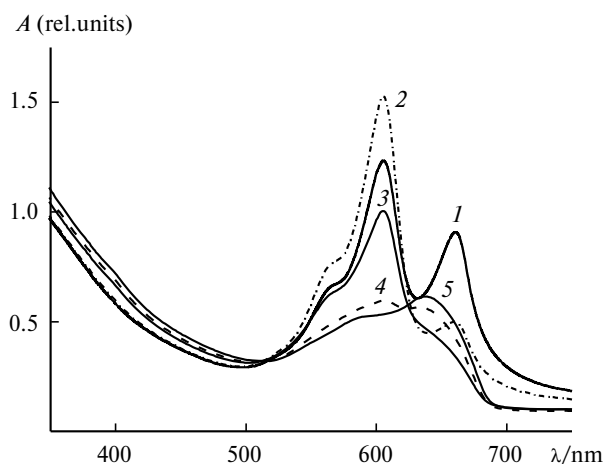


Fig. 5. Absorption spectra of a mixture of solutions of reverse micelles containing Ag_2S nanocrystals ($W = 8$) and reverse micelles containing DEC ($W = 26$) in a 1 : 1 ratio, recorded immediately after preparation (1) and 5 (2), 25 (3), and 55 min (4), and 48 h (5) after preparation.

It is known that adsorption onto silver iodide microcrystals can form two states of adsorbed dye, *viz.*, a planarly adsorbed monomer (M_a -state) characterized by the absorption maximum at 622 nm and a monomer adsorbed at the long edge (B_a -state, $\lambda_{\max} = 649$ nm). We believe that the state of the dye in the mixture with Ag_2S nanocrystals ($\lambda_{\max} = 640$ nm) corresponds to the dye monomer adsorbed on Ag_2S in the B_a -state.

At a 1 : 1 ratio, the number (n) of dye molecules per nanocrystal is estimated as two or three monomers. Since further increase in the dye concentration in the micelle solution is impossible, to increase the coverage density of the surface with the dye, the micelle solutions were mixed in 1 : 2 ($n = 5-6$) and 1 : 8 ($n = 16-25$) ratios. The behavior of the system was found to be similar to the case of mixing in the 1 : 1 ratio. The increase in the coverage density of the surface of nanocrystals causes no formation of the aggregated state of the dye. In both cases, adsorption results in Ag_2S nanocrystals—DEC monomer hybrid nanostructures.

Thus, in the present study we showed that the surfactant plays an important role in the formation of hybrid nanostructures in reverse micelles. The concept of reverse micelles as inert nanoreactors in which nanocrystals are surrounded by water and rigid surfactant shell is idealized. A reverse micelle with a growing nanocrystal does not necessarily contain free water at all; in this case, nanoparticles can be stabilized through adsorption of surfactant immediately onto the surface of nanocrystals. In this case, the possibility of dye adsorption is determined by the strength of adsorption of the surfactant on the surface of nanocrystals. In turn, this parameter depends on the surfactant structure, the surface state of nanocrystals, and on the presence of ions. As a consequence, control of the formation of various hybrid nanostructures with specified properties through adsorption of organic compounds on the surface of nanocrystals requires additional studies on the effect of the surfactant structure in reverse micelles on the dye adsorption onto nanocrystals.

In the present study we analyzed factors responsible for adsorption of the cyanine dye DEC on the surface of semiconductor nanocrystals in solutions of reverse micelles. Nanocrystals of different composition were used, including various metal halides, sulfides, and selenides. Solutions of reverse micelles can be used to assemble hybrid nanostructures through adsorption of the dye on the surface of nanocrystals and to obtain various structures including DEC J-aggregate— AgI nanocrystals, DEC monomer— Ag_2S nanocrystals, DEC J-aggregate— CuI nanocrystals, and DEC J-aggregate— PbI_2 nanocrystals. The use of CdS , ZnS , $CdSe$, and PbS nanocrystals as inorganic component did not lead to the formation of hybrid nanostructures. Analysis of the results obtained suggested that adsorption of the dye on the surface of nanocrystals can be due to both van der Waals and chemical

interactions. However, when using solutions of reverse micelles to prepare hybrid structures, one should consider yet another important factor, namely, the effect of the micelle solution *per se*. The surfactant used to stabilize the micelle solution can influence the assembly of hybrid structures. In particular, no formation of hybrid nanostructures with Ag_2S nanocrystals was observed in AOT reverse micelles, whereas the use of a mixture of the surfactants AOT and SDS made it possible to prepare a DEC monomer— Ag_2S nanocrystals hybrid structure. This fact can be explained by the ability of the surfactant molecules to adsorb on the surface of nanocrystals in reverse micelles. The strength of adsorption of the surfactant onto the surface of nanocrystals depends on various factors including the chemical composition of nanocrystals, the surfactant structure, and the presence of excess ions. It will thus influence subsequent adsorption of dye molecules on nanocrystals and determine the possibility to prepare dye—nanocrystals hybrid nanostructures.

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