Preparation of aqueous CdS colloids in the presence of cadmium complexonates: effect of complexonates on the size of CdS nanoparticles

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The results of a systematic study of the preparation of CdS colloids in aqueous solutions containing different Cd^{2+} complexonates are presented. The effects of the ratio of the reagents and the nature and concentration of various stabilizing surfactants and Cd^{2+} complexonates, including those of some sulfur-containing compounds, on the size of the colloidal particles have been studied. Thermodynamic calculation of the expected equilibrium size of the colloidal particles as a function of the solvent composition, taking into account the increase in the solubility of the CdS phase as the particle size decreases, has been performed. Comparison of the calculated results with the experimental data shows that the size of colloidal particles is determined to a great extent by kinetic factors of their growth rather than by thermodynamic factors. It has been established that when the size of colloidal particles is less than a critical value, their dissolution by adding strong compexing agents to the system does not result in a change in the observed mean-volume size of the particles.

Key words: cadmium sulfide, cadmium complexonates, colloids; nanoparticles, equilibrium size of particles, thermodynamic calculation.

Colloidal solutions of semiconducting particles attract the attention of researchers as photocatalysts of various processes.[1,2] So-called Q-particles of semiconductors (for CdS with a size $2r < 50$ Å), many properties of which can noticeably differ from those characteristic of three-dimensional semiconductors, are of special interest.[3,4] At the same time, comprehensive experimental study of physicochemical properties of semiconducting particles is retarded by the absence of simple and reliable methods for reproducible preparation of them. In addition, rather complete and noncontradictory quantitative theories that describe the growth of colloidal particles during their preparation, unfortunately are scarce to date, and only semiquantitative concepts based on the fact that the size of colloidal particles is determined mainly by the number of nuclei of their growth at the initial moment of formation of the colloid are used as a rule.

It is well known[5] that a strong supersaturation of a mother liquor accompanied by the simultaneous retardation of the growth rate of particles formed is necessary for preparing highly dispersed low-soluble substances. This can usually be reached when a relatively highly concentrated solution of one substance is mixed with a very dilute solution of another substance, with which the first substance forms a hardly soluble compound. A high concentration of the first substance provides the strong supersaturation of the solution and the higher nucleation rate, while the low concentration of the second substance restricts the growth rate of nuclei formed due to the slow diffusion of this component from the dilute solution.

In this work, the possibility of well controlled and reproducible synthesis of CdS colloids is studied. To control and retard the growth rate of CdS nanoparticles, the complex salt of one of colloid-forming components (Cd^{2+}) was used instead of its dilute solution. In this case, the rate of colloid growth can be limited by the rate of decomposition of the initial cadmium complex.

Experimental

Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), 2,2′-dipyridyl (DIP), and phenanthroline (PHEN) (all of them were of analytical grade), sodium sulfide ($Na_2S \cdot 9H_2O$), thiourea (THIO), sodium ethylenediaminetetraacetate ($Na_2(H_2edta)$), and cysteine (CYS) (all of them were of high-purity grade, Reakhim), and thioglycerol (Fluka) and 3-mercaptopropionic acid (MPA) (Sigma) were used without preliminary purification. A solution of sodium oxalate (SOX) was prepared from oxalic acid (high-purity grade) and sodium hydroxide (analytical grade, both of them from Reakhim). The following surfactants were used as stabilizing additives: polyacrylamide (PA), polyacrylic acid (PAA), polyvinylpyrrolidone (PVP), and sodium dodecyl sulfate (SDS) (Reakhim).

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Absorption spectra of colloidal CdS solutions were recorded at ~20 °C in quartz cells (l = 1 cm) on a Shimadzu UV-300 spectrophotometer. The size of particles formed was determined by the known correlation dependence[6] between the size of a particle and the edge of its optical absorption and by electron photomicrographs in some cases. For these measurements, an aqueous solution of colloidal CdS was applied to a copper grid covered with graphite and dried at a reduced pressure. Samples obtained were studied on a JEM 100 CX (JEOL, Japan) electron microscope.

Preparation of CdS colloids. A 10^{-3} M solution of $CdCl_2$ (10 mL) containing $2 \cdot 10^{-3}$ mol L^{-1} (with respect to the monomer) of a stabilizing surfactant and additions of necessary complexing agents was prepared in a 100-mL glass at ~20 °C. Then 10 mL of a $2 \cdot 10^{-3}$ M solution of Na_2S was added with vigorous stirring (the color of the colloidal CdS solution formed can change from yellow to colorless depending on the type and concentration of additives). These colloidal solutions are stable in some cases for more than 6 months.

Thermodynamic calculation of the equilibrium size of colloidal CdS particles in the presence of cadmium complexonates

During the formation of CdS colloids, at the instant when the growth of colloidal particles stops and the system reaches the quasi-equilibrium state, all of the cadmium is distributed between CdS particles and an aqueous phase of the solution, where it exists both as the aquated Cd^{2+} ion and compounds with complexing agents. It can be assumed that a thermodynamic equilibrium is established among the possible compounds containing cadmium. When one complexing agent L involved in the stepwise process of complex formation is present, the equilibrium mentioned can be described by the following system of equations:

$$\begin{cases} Cd^{2+} + L \rightleftharpoons CdL^{2+} & (K_1, \xi_1) \\ CdL_{n-1}{}^{2+} + L \rightleftharpoons CdL_n{}^{2+} & (K_n, \xi_n) \\ Cd^{2+} + S^{2-} \rightleftharpoons CdS & (SP, \xi_s) \end{cases} \tag{1}$$

Here ξ_i are the chemical variables of the indicated reactions, equal to the change in the initial concentration of the ith component divided by the stoichiometric coefficients; K_i and SP are the stability constants and the solubility product of the corresponding compounds.

It should be mentioned that the solubility product of a dispersion particle depends on its size,[7]

$$SP = SP_\infty \cdot \exp[2\sigma\bar{v}/(rRT)], \tag{2}$$

where SP_∞ is the solubility product of a bulky particle (for CdS at 298 K $SP_\infty = 1.6 \cdot 10^{-28}$ mol^2 L^{-2});[9] σ is the excessive surface energy (surface tension) at the solution—particle interface; $\bar{v}$ is the partial molar volume of the phase, which comprises a particle (for CdS $\bar{v}$ = 30.1 cm^3 mol^{-1}); r is the radius of a particle; R is the universal gas constant; T is the temperature (we will assume in further discussion that T = 298 K).

In the case when the cadmium salt, the sulfide ion, and the complexing agent L are initial compounds for the formation of the colloid, the following system of equations is valid:

$$\begin{cases} \dfrac{\{[Cd^0] - (\xi_1 + \ldots + \xi_n + \xi_s)\} \cdot \{[L^0] - (\xi_1 + \ldots + \xi_n)\}}{\xi_1} = K_1^{-1} \\ \ldots\ldots\ldots\ldots \\ \dfrac{\{[Cd^0] - (\xi_1 + \ldots + \xi_n + \xi_s)\} \cdot \{[L^0] - (\xi_1 + \ldots + \xi_n)\}^n}{\xi_n} = K_n^{-1} \\ \{[Cd^0] - (\xi_1 + \ldots + \xi_n + \xi_s)\} \cdot \{[S^0] - \xi_s)\} = \\ \qquad = SP_\infty \cdot \exp[2\sigma\bar{v}/(rRT)] \\ \dfrac{4}{3}\pi \cdot \dfrac{N}{\bar{v}} r^3 = \xi_s \end{cases} \tag{3}$$

Here $[Cd^0]$, $[L^0]$, and $[S^0]$ are the initial concentrations of the cadmium salt, the complexing agent, and the sulfide anion, respectively; N is the concentration of colloidal particles. This system of equations can be simplified by some assumptions, which do not change qualitatively the picture of the equilibriums. Let the whole process be described by the addition of only one ligand, and $[L^0]$, $[S^0] \gg [Cd^0]$. In this case, system (3) is reduced to one Eq. (4), which relates the radius of particles (r) and the stability constant of the complex (K_1),

$$\frac{4}{3}\pi \cdot \frac{N}{\bar{v}} r^3 + \left(1 + [L]K_1\right) \cdot \frac{SP_\infty}{[S]} \exp[2\sigma\bar{v}/(rRT)] = [Cd^0], \tag{4}$$

where [L] and [S] are the equilibrium concentrations, which are approximately equal to the initial concentrations of the ligand and the sulfide anion ($[L^0]$ and $[S^0]$) under the assumptions made. Specifying a reasonable value of N and using the value $\sigma \approx 1.09 \pm 0.24$ J m^{-2} estimated on the basis of the published[8] data,[*] the equilibrium size of a colloidal particle, which turns out to depend on the stability constant of the complex, can be found from Eq. (4).

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[*] The value was estimated in the following way: taking into account the dissolution of cadmium sulfide particles with $2r$ = 25 Å on the addition of $Na_2(H_2edta)$ and the simultaneous stability of these particles toward alkalization,[8] the range of values of the solubility product SP_{CdS} was found:

$$\frac{[Cd(H_2edta)]}{K_1[H_2edta]} < \frac{SP_{CdS}}{[S]} < \frac{SP_{Cd(OH)2}}{[OH]^2}$$

where $K_1 = 5 \cdot 10^{16}$ L mol^{-1} and $SP_{Cd(OH)_2} = 2 \cdot 10^{-14}$ mol^3 L^{-3} (see Ref. 9) are the stability constant of the cadmium complex with the ethylenediaminetetracetate ion and the solubility product of cadmium hydroxide, respectively; $[Cd(H_2edta)]$, $[S^{2-}]$, $[OH^-]$, and $[H_2edta]$ are the equilibrium concentrations of the reagents. Using the values of concentrations corresponding to experimental conditions,[8] we obtained $2 \cdot 10^{-21}$ mol^2 L^{-2} < SP_{CdS} < $2 \cdot 10^{-17}$ mol^2 L^{-2}. Then the range of σ values was established for the SP found by Eq. (2): 0.85 J m^{-2} < σ < 1.32 J m^{-2}. It should be mentioned that, generally speaking, the estimated value of σ is almost an order of magnitude greater than the known typical σ values for the aqueous phase—inorganic solid state interface. Nevertheless, we will use just this experimentally established value in further calculations.

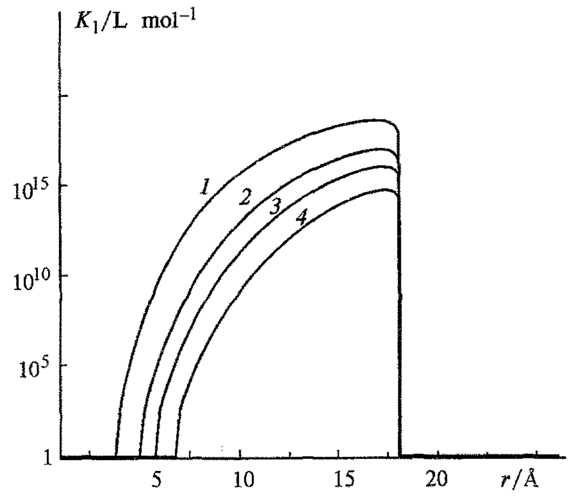

Fig. 1. Calculated dependences of the equilibrium size (r) of CdS particles on the stability constant (K_1) of the initial CdL complex at $[L^0] = [S^0] = 5 \cdot 10^{-3}$ mol L^{-1}, $[Cd^0] = 5 \cdot 10^{-4}$ mol L^{-1}, $N = 10^{-6}$ mol L^{-1}, and σ/J m^{-2}: 1.04 (*1*), 1.24 (*2*), 1.45 (*3*), and 1.66 (*4*).

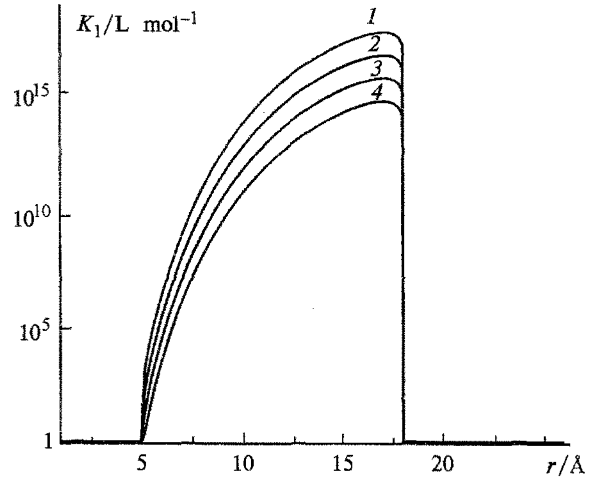

Fig. 2. Calculated dependences of the equilibrium size (r) of CdS particles on the stability constant (K_1) of the initial CdL complex at $[S^0] = 5 \cdot 10^{-3}$ mol L^{-1}, $[Cd^0] = 5 \cdot 10^{-4}$ mol L^{-1}, $\sigma = 1.53$ J m^{-2}, $N = 10^{-6}$ mol L^{-1}, and $[L^0]/[S^{2-}]$: 0.1 (*1*), 1.0 (*2*), 10 (*3*), and 100 (*4*).

Let us consider the effect of various parameters entering Eq. (4) on the dependence of the equilibrium size of CdS particles on the K_1 constant. For this purpose, we fix the magnitudes of all values used, except the parameter in which we are interested; the variation of this parameter results in a series of dependences of K_1 on r.

The dependences of the equilibrium size of CdS particles on the stability constant of the initial complex calculated by Eq. (4) at different excessive surface energies (σ) are presented in Fig. 1. The characteristic feature of these dependences is the region of existence of two solutions at the specified K_1. The solution with a lower r corresponds to particles (conventionally denoted as "first" particles), which are characterized by the fact that their size and the increased value of SP allow both nanoparticles of cadmium sulfide and the cadmuim complex to exist simultaneously in comparable fractions in an aqueous phase. Large ("second") particles correspond to the case when almost all of cadmium exists as sulfide and is distributed over N particles of the colloid.

As can be seen from Fig. 1, the size of the first particles increases, and that of the second particles remain unchanged as σ increases. In addition, the upper boundary of values of the stability constant of the complex, at which the existence of particles of the CdS colloid with the certain size (in this case, with $r = 18$ Å at $N = 10^{-6}$ mol L^{-1}) is possible, decreases. For example, when $\sigma = 1.04$ J m^{-2} the formation of particles with $r < 18$ Å is thermodynamically unfavorable, if it is possible to form the CdL complex with the stability constant $>10^{19}$ L mol^{-1}, and when $\sigma = 1.66$ J mol^{-2}, the formation of the same particles are thermodynamically forbidden already at $K_1 \geq 10^{15}$ L mol^{-1}.

The calculated dependences of the equilibrium size of a CdS particle on the stability constant of the initial complex are presented in Fig. 2 for various ratios of $[L^0]/[S^{2-}]$ and a fixed value of $[S^0]$. An increase in this ratio results in an increase in the size of particles corresponding to the first solution of Eq. (4), while the size of particles corresponding to the second solutions remains unchanged. The upper boundary of possible values of the stability constant, at which the existence of CdS colloidal particles of the certain size is possible, decreases simultaneously.

The calculated dependences of the equilibrium size of a CdS particle on the K_1 value at various concentrations of colloidal particles (nuclei) N are presented in Fig. 3. It is noteworthy that the size of the first type

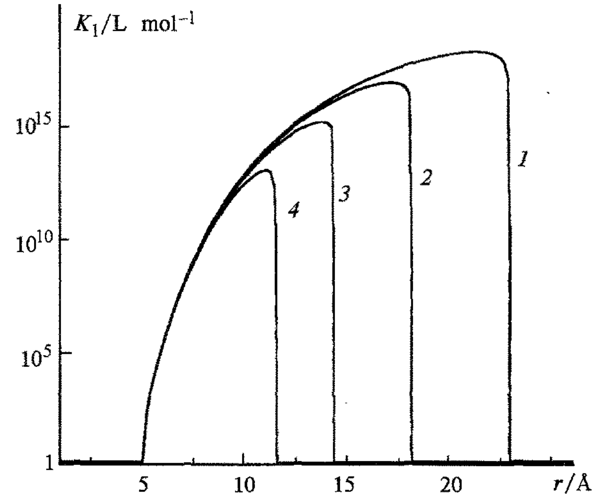

Fig. 3. Calculated dependences of the equilibrium size (r) of CdS particles on the stability constant (K_1) of the initial CdL complex at $[L^0] = [S^0] = 5 \cdot 10^{-3}$ mol L^{-1}, $[Cd^0] = 5 \cdot 10^{-4}$ mol L^{-1}, $\sigma = 1.53$ J m^{-2}, and N/mol L^{-1}: $5 \cdot 10^{-7}$ (*1*), 10^{-6} (*2*), $2 \cdot 10^{-6}$ (*3*), and $4 \cdot 10^{-6}$ (*4*).

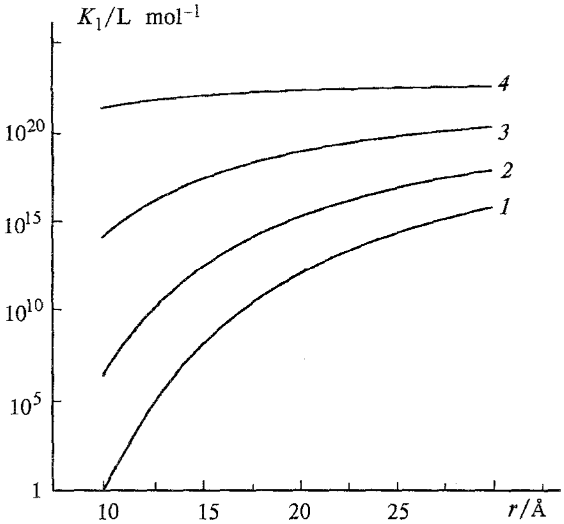

Fig. 4. Calculated upper boundaries of the stability constant K_1 at which the existence of a CdS particle with radius r is possible at $[L^0] = [S^0] = 5 \cdot 10^{-3}$ mol L^{-1}, $[Cd^0] = 5 \cdot 10^{-4}$ mol L^{-1}, and σ/J m^{-2}: 0.2 (*1*), 0.6 (*2*), 1.1 (*3*), and 2.0 (*4*).

particles remains unchanged and that of the second type particles, of course, decreases as the number of nuclei increases. This results in a decrease in the value of the upper boundary of admissible values of the stability constant K_1.

Unfortunately, the calculational scheme discussed does not allow one to determine *a priori* the equilibrium concentration of colloidal particles or, which is the same, the concentration of nuclei N, which is probably controlled not by the thermodynamics, but by the kinetics of the growth of colloidal particles. Nevertheless, even the simplified scheme shows that, first, their thermodynamically stable colloidal particles with smallest admissible sizes can be formed only in the presence of complexing agents, which are characterized by rather low values of stability constants. Second, at high concentrations of strong complexing agents only colloids with the particle size not smaller than that determined by specific values of stability constants of compounds, which are present in solution, are stable (Fig. 4). Thus, it becomes possible to answer the question: Can colloidal particles of a specified size exist in the presence of a fixed amount of the complexing agent with a known stability constant?

Results and Discussion

The results of experiments on preparing colloidal CdS solution under various conditions are briefly summarized in Tables 1—3. Comparison of theoretical (calculated) and experimental data allows us to draw the conclusion that only particles designated as "second" particles are formed in practice when colloids are prepared according to the procedure described above.

Indeed, first, it is impossible to prepare colloids with particles of the very small size comparable to that expected for the first type particles (r < 10 Å). Second, it is found experimentally (see Table 2) that an increase in the $[L^0]/[S^0]$ ratio results in a decrease in the size of colloidal particles, while it should increase for the "first" particles and remain unchanged for the "second" particles according to Eq. (4) (see Fig. 2). Because of the dependence of the size of the second type particles on the concentration of nuclei (see Fig. 3), this behavior can be explained by the fact that an increase in the $[L^0]/[S^0]$ ratio results in an increase in the number of nuclei (*i.e.*, N). Third, it is observed in practice that an increase in the stability constant K_1 of the CdL complex

Table 1. Effect of concentrations of initial reagents and various surfactants on the position of the absorption edge (λ) of the colloid and the average size ($\bar{r}$) of the CdS particles formed

Concentration, [X]/mol L^{-1}	λ/nm	$2\bar{r}$/Å	Concentration, [X]/mol L^{-1}	λ/nm	$2\bar{r}$/Å
$[X] = [PA]$, $[Cd^0] = 5 \cdot 10^{-4}$, $[S^0] = 10^{-3}$			$[X] = [S^0]$, $[Cd^0] = 5 \cdot 10^{-4}$, $[PA] = 10^{-3}$		
$5 \cdot 10^{-2}$	454	37.5	$2 \cdot 10^{-3}$	490	57
$3 \cdot 10^{-3}$	462	40	10^{-3}	495	62
$2 \cdot 10^{-3}$	470	43.5	$7 \cdot 10^{-4}$	500	>100
10^{-3}	506	>100	$6 \cdot 10^{-4}$	503	>100
$5 \cdot 10^{-4}$	502	>100			
$X = [Cd^0]$, $[PA] = 10^{-3}$, $[S^0] = 3 \cdot 10^{-3}$			$X = [PAA]$, $[Cd^0] = 5 \cdot 10^{-4}$, $[S^0] = 10^{-3}$		
$1.5 \cdot 10^{-3}$	510	>100	$1.4 \cdot 10^{-3}$	474	46
10^{-3}	509	>100	$6.9 \cdot 10^{-4}$	481	50
$7.5 \cdot 10^{-4}$	500	>100	$1.4 \cdot 10^{-4}$	498	>100
$X = [PVP]$, $[Cd^0] = 5 \cdot 10^{-4}$, $[S^0] = 10^{-3}$			$X = [SDS]$, $[Cd^0] = 5 \cdot 10^{-4}$, $[S^0] = 10^{-3}$		
$4.5 \cdot 10^{-2}$	508	100	10^{-2}	501	>100
$4.5 \cdot 10^{-3}$	512	>100	$5 \cdot 10^{-3}$	504	>100
$9 \cdot 10^{-4}$	513	>100	10^{-3}	514	>100
			$5 \cdot 10^{-4}$	514	>100
			$2 \cdot 10^{-4}$	514	>100

Table 2. Effect of concentrations of complexing agents L that do not contain sulfur on the position of the absorption edge (λ) of the colloid and the average size ($\bar{r}$) of CdS particles in a solution with $[Cd^0] = 5 \cdot 10^{-4}$ mol L^{-1}, $[S^0] = 10^{-3}$ mol L^{-1}, and $[PA] = 10^{-3}$ mol L^{-1}

[L] /mol L^{-1}	$\log\left[\frac{\sum CdL_i}{Cd^{2+}}\right]$	λ/nm	$2\bar{r}$/Å	[L] /mol L^{-1}	$\log\left[\frac{\sum CdL_i}{Cd^{2+}}\right]$	λ/nm	$2\bar{r}$/Å
	L = THIO				L = SOX		
$2 \cdot 10^{-2}$	−0.034	485	59	$2 \cdot 10^{-2}$	2.18	487	54.5
10^{-2}	−0.380	494	>100	10^{-2}	1.71	477	47.5
$5 \cdot 10^{-3}$	−0.700	505	>100	$5 \cdot 10^{-3}$	1.23	473	45.0
$2.5 \cdot 10^{-3}$	−1.010	505	>100	$2.5 \cdot 10^{-3}$	0.88	477	47.5
10^{-3}	−1.420	509	>100	10^{-3}	0.35	490	57.0
				$7.5 \cdot 10^{-4}$	0.18	496	>100.0
	L = DIP				L = PHEN		
10^{-2}	4.45	420	29.0	$5.5 \cdot 10^{-3}$	8.610	Turbid	—
$6 \cdot 10^{-3}$	3.75	419	29.0	$2.8 \cdot 10^{-3}$	7.130	~370	22.0
$2 \cdot 10^{-3}$	2.22	422	29.5	$1.4 \cdot 10^{-3}$	3.910	~380	23.0
10^{-3}	1.23	430	31.0	$1.1 \cdot 10^{-3}$	2.760	~380	23.0
$8 \cdot 10^{-4}$	0.94	440	33.5	$5.5 \cdot 10^{-4}$	0.820	~400	25.5
$5 \cdot 10^{-4}$	0.42	452	37.0	$2.7 \cdot 10^{-4}$	0.016	~430	31.0

Note. The values of the stability constants (K_1/L mol^{-1}) of Cd^{2+} complexes: with THIO, 40; with SOX, $3 \cdot 10^3$; with DIP, $3 \cdot 10^4$; and with PHEN, $2 \cdot 10^6$ (see Ref. 10).

Table 3. Effect of concentrations of sulfur-containing additives on the position of the absorption edge (λ) of the colloid and the average size ($\bar{r}$) of CdS particles in a solution with $[Cd^0] = 5 \cdot 10^{-4}$ mol L^{-1}, $[S^0] = 10^{-3}$ mol L^{-1}, and $[PA] = 10^{-3}$ mol L^{-1}

[THIO] /mol L^{-1}	λ/nm	$2\bar{r}$ /Å	[CYS] /mol L^{-1}	λ/nm	$2\bar{r}$ /Å	[MPA] mol L^{-1}	λ/nm	$2\bar{r}$ /Å
$5 \cdot 10^{-2}$	380	23.0	10^{-2}	400	25.5	10^{-1}	392	24.5
$5 \cdot 10^{-3}$	406	26.5	$5 \cdot 10^{-3}$	408	26.5	10^{-2}	416	28.0
$5 \cdot 10^{-4}$	415	28.0	10^{-3}	432	31.5	10^{-3}	433	32.0
$2.5 \cdot 10^{-4}$	477	47.5	$5 \cdot 10^{-4}$	451	36.5	$5 \cdot 10^{-4}$	464	41.0
$2.5 \cdot 10^{-5}$	508	>100.0	$2 \cdot 10^{-4}$	474	45.5			

results, as a rule, in a decrease in the size of CdS colloidal particles (the exception is only very stable complexes $Cd(H_2edta)$), while according to Eq. (4), one should expect that the size of the "first" particles should increase and that of the "second" particles remain unchanged (see Figs. 1—3). This apparent contradiction can be resolved, if it is assumed that the number of nuclei depends on K_1 and only the second type particles are formed in practice. Indeed, to increase the number of nuclei, the growth rate of the colloid should be limited, which can be done, for example, due to an increase in the stability of the complex.

The calculated dependences of the upper boundaries of the stability constant K_1, at which the existence of nanoparticles of cadmium sulfide with the specified radius r is possible, on σ are presented in Fig. 4. These curves are plotted for the second type particles. It can be seen from Fig. 3 that for these particles the certain concentration of nuclei $N(r)$ corresponds to the radius r, and each of them is characterized by the upper boundary of the stability constant $K_1(N)^{max}$ (the maximum on the $K_1(r)$ curve). Thus, the "second" particles with the r radius will be stable until the appearance of the complexing agent with the stability constant higher than $K_1(N(r))^{max}$. The curves in Fig. 4 are the most enveloping of these maxima obtained for the fixed σ value.

The theoretical conclusions are confirmed by experiments on dissolution of Q-colloids of CdS. Figure 5 shows the change in the absorption spectrum of a colloidal solution of CdS with the size of Q-particles with $2r <$ 23 Å after adding $Na_2(H_2edta)$, which forms a very stable complex with cadmium ions ($K_1 = 5 \cdot 10^{16}$ L mol^{-1})[9] and, as a result, dissolves colloidal particles. The unexpectedly constant shape of the absorption spectrum of the colloid during its dissolution have engaged our attention. Indeed, since the size of particles should decrease in the process of dissolution, the edge of the absorption of the CdS colloid observed in the spectrum should shift to the UV region according to the known correlation.[6] However, it is seen from Fig. 5 that in fact the absorption edge is not shifted, which formally means that the average particle size over the sample is constant.

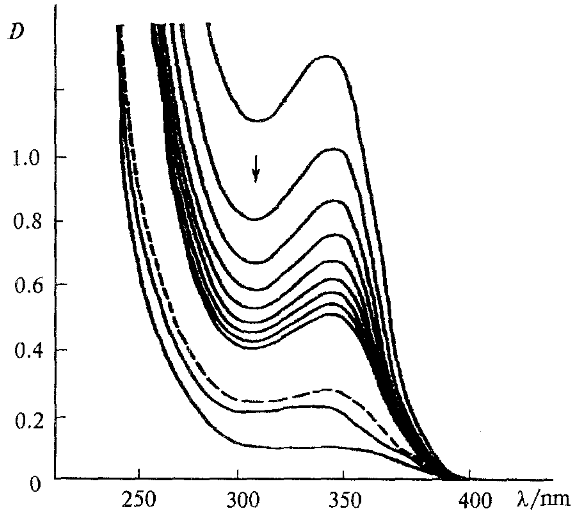

Fig. 5. Changes (points) in the absorption spectrum of a colloidal CdS solution ($5 \cdot 10^{-4}$ mol L^{-1}) with a particle size of $2r < 23$ Å prepared in the presence of $5 \cdot 10^{-2}$ mol L^{-1} of thioglycerol after the addition of $5 \cdot 10^{-3}$ mol L^{-1} of $Na_2(H_2edta)$ at ~20 °C (spectra were recorded at 5 min intervals).

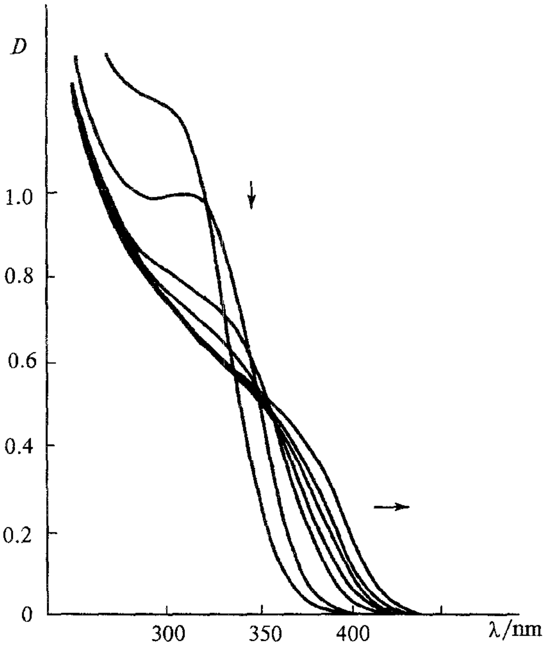

Fig. 6. Changes (points) in the absorption spectrum of a colloidal CdS solution ($5 \cdot 10^{-4}$ mol L^{-1}) with a particle size of $2r > 23$ Å prepared in the presence of $5 \cdot 10^{-3}$ mol L^{-1} of thioglycerol after the addition of $5 \cdot 10^{-3}$ mol L^{-1} of $Na_2(H_2edta)$ at ~20 °C (spectra were recorded at 5 min intervals).

Thus, the dissolution of very small colloidal particles under the action of the very strong complexing agent results only in a decrease in their number, but not in the average size. (It should be mentioned that the similar constant character of the shapes of absorption spectra was also observed for the slow growth of small ($2r \leq 30$ Å) CdS particles in inner cavities of lipid vesicles;[10,11] in this situation, the growth of colloidal particles was supported by sulfidizing of the $Cd(H_2edta)$ complex as well.) When Q-particles of CdS of a somewhat larger size ($2r \leq 23$ Å) are present in the solution, the addition of $Na_2(H_2edta)$ results in a smooth development of fine particles to large particles (Fig. 6), which is easily fixed by the shift in the absorption edge

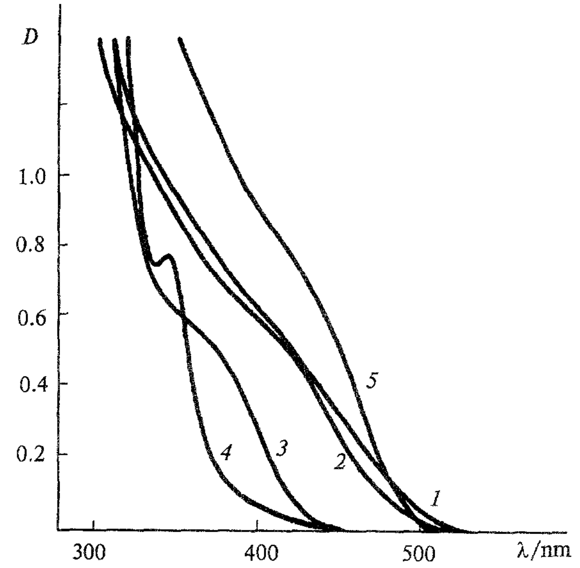

Fig. 7. Optical absorption spectra of a colloidal CdS solution ($5 \cdot 10^{-4}$ mol L^{-1}) prepared from a 10^{-3} *M* solution of $CdCl_2$ with various complexing agents at ~20 °C, $[S^0] = 2 \cdot 10^{-3}$ mol L^{-1}, and $[L^0] = 10^{-3}$ mol L^{-1}: *1*, THIO; *2*, SOX; *3*, DIP; *4*, PHEN; *5*, $Na_2(H_2edta)$.

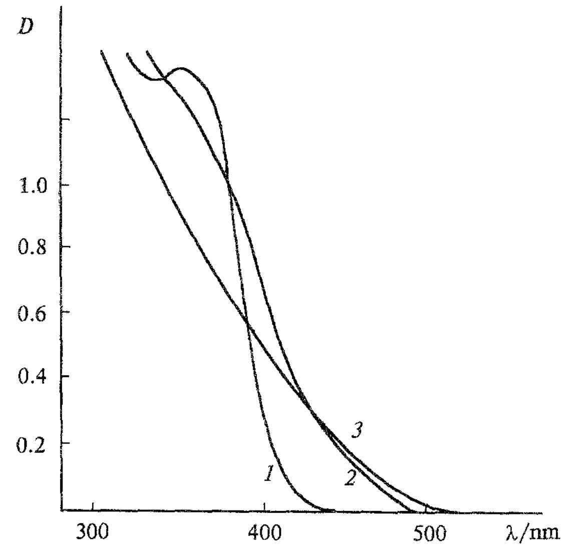

Fig. 8. Optical absorption spectra of a colloidal CdS solution ($5 \cdot 10^{-4}$ mol L^{-1}) prepared from a 10^{-3} *M* solution of $CdCl_2$ with various sulfur-containing ligands at $[S^0] = 2 \cdot 10^{-3}$ mol L^{-1} and $[L^0] = 5 \cdot 10^{-3}$ mol L^{-1}: *1*, thioglycerol; *2*, CYS; *3*, MPA.

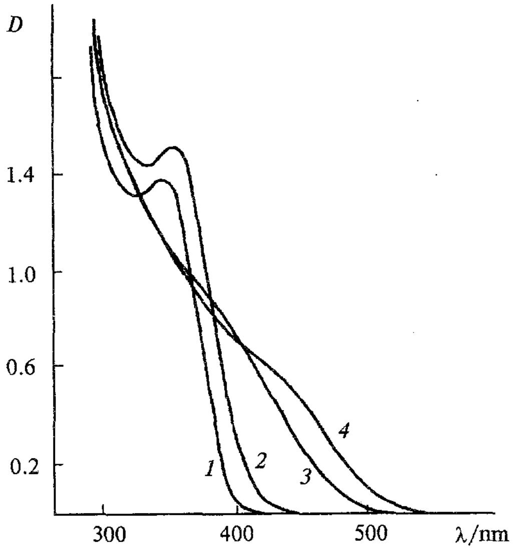

Fig. 9. Optical absorption spectra of a colloidal CdS solution ($5 \cdot 10^{-4}$ mol L^{-1}) prepared by the addition of thioglycerol to a 10^{-3} *M* solution of $CdCl_2$ to the concentration, *C*/mol L^{-1}: *1*, $5 \cdot 10^{-2}$; *2*, $5 \cdot 10^{-3}$; *3*, $2.5 \cdot 10^{-4}$; *4*, $2.5 \cdot 10^{-5}$ ($[S^0] = 2 \cdot 10^{-3}$ mol L^{-1}, ~20 °C).

to the visible region with time. It is of interest that additions of surfactants exert almost no effect on the observed picture of dissolution. This illustrates their rather weak effect on the surface tension σ, which determines the properties of CdS nanoparticles.

The absorption spectra of colloidal solutions of CdS obtained by our procedure in the presence of cadmium complexonates of various natures are presented in Fig. 7. The position of the absorption edge of the colloids shows that an increase in the stability constant of the complex results in a decrease in the equilibrium size of the colloidal particles. This is probably related to the fact that it is the decomposition rate of the cadmium complex that determines the number of nuclei and, hence, the size of the particles formed. The latter is confirmed by the fact that the sizes of colloidal particles differ for complexonates of the different natures at a fixed initial (*i.e.*, before adding the sulfide ion and after adding the ligand) concentration of activated Cd^{2+} ($\log([CdL]/[Cd^{2+}])$ = const and $[Cd^0]$ = const, see Table 2), and the stronger the initial complex, the smaller the size of the particles.

In the preparative aspect, some organic sulfur-containing compounds turned out to be the best complex forming additions, which regulate well the size of colloidal CdS particles. The absorption spectra of the colloidal CdS solution obtained on the addition of various organic sulfur-containing substances and without stabilizing surfactants are shown in Fig. 8. It should be mentioned that colloids prepared in the presence of sulfur-containing organic compounds are considerably more stable than those obtained with adding ligands, which do not contain sulfur. It is of interest that colloids of cadmium sulfide obtained in the presence of thioglycerol (Fig. 9) can be dried in the air to form solid films, which can be reversibly dissolved again. The size of colloidal particles remains almost unchanged after drying and dissolution.

Thus, the simplified thermodynamic calculation of the equilibrium size of the particles of CdS colloids from its dependence on the composition of the solution, which takes into account the sensitivity of the solubility product of CdS to the size of the particles, shows that stable colloids with extremely fine particles cannot be formed in the presence of strong complexonates of cadmium. This is caused by the fact that such complexons stronger bind cadmium than fine sulfide particles, whose solubility is considerably increased due to the size effect.

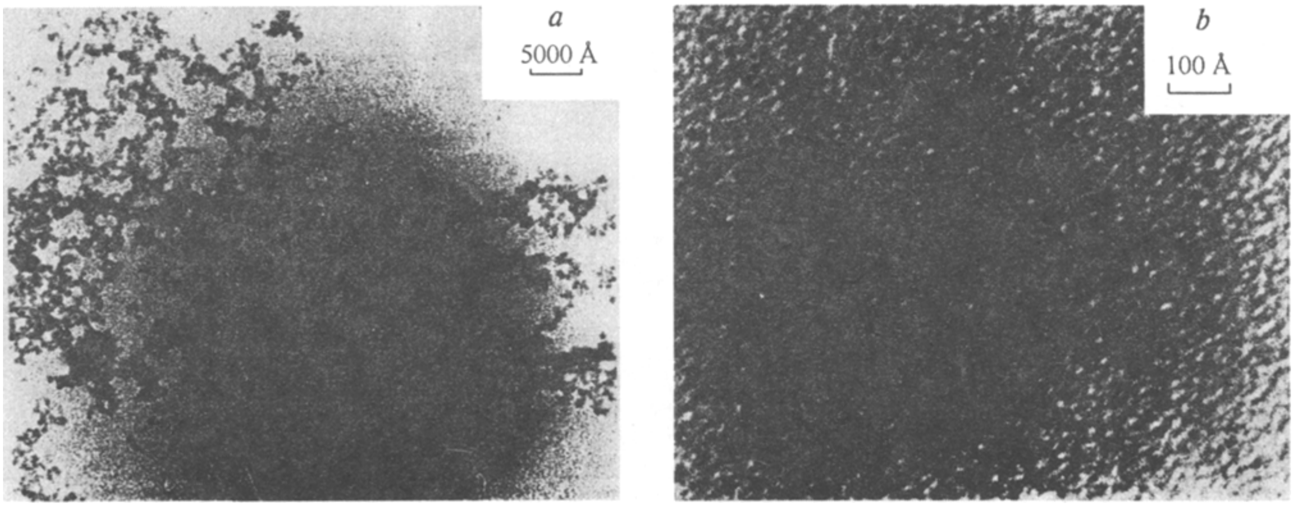

Fig. 10. Electron photomicrographs of specimens of colloidal CdS in the absence of thioglycerol (*a*) and in the presence of $5 \cdot 10^{-2}$ mol L^{-1} of thioglycerol (*b*) ($[CdS] = 5 \cdot 10^{-4}$ mol L^{-1}, $[S^0] = 1.5 \cdot 10^{-3}$ mol L^{-1} before drying).

The extremely dispersed solid phase is dissolved because of this. For example, CdS particles with $r < 18$ Å cannot be formed in the presence of an excess of complexing agents with $K_1 > 10^{16}$ L mol^{-1}.

Unexpected regularities of the dissolution of Q-colloids of CdS were also found when strong complexing agents were added to the solution: in some cases, only the number of CdS particles changed, but not the size. It is evident that this phenomenon is related to the self-acceleration (autocatalysis) during the dissolution of colloidal particles by strong complexing agents. In fact, one can expect (because of the dependence of SP on the size) that particles, which were first to decrease their size for some reason, will further be dissolved with the acceleration as well, because the smaller the particle, the less stable it to dissolution. Thus, the dissolution of colloidal particles should be heterogeneous. The observed maintenance of the average size of particles during their dissolution is caused by this fact.

At the same time, the use of milder cadmium complexonates allows one to obtain CdS colloids with a wide range of particle sizes. Thioglycerol seems to be the most interesting complexon-stabilizer. The preparation of the CdS colloid in an aqueous solution in the presence of thioglycerol is, first, simple, quick, and reproducible; second, the size of CdS particles can be easily controlled within the 25 to 200 Å range (Fig. 10); and, third, it does not require the addition of other stabilizing surfactants. Finally, the use of thioglycerol makes it possible to concentrate CdS colloids by drying solutions up to the formation of solid films.

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