

## MODEL OF SYNTHESIS OF ZNS NANOPARTICLES STABILIZED BY CETYLTRIMETHYLAMMONIUM BROMIDE

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A mathematical model of synthesis and stabilization of ZnS nanoparticles in aqueous solutions of cetyltrimethylammonium bromide (CTAB) is presented. ZnS nanoparticles precipitated by the reaction of sodium sulphide and zinc acetate are significantly influenced by CTAB both in a stage of nucleation and in a stage of growth and stabilization. The suggested model assumes a dominating influence of the nucleation stage on future properties of emerging ZnS nanoparticles. On the basis of a calculated nucleation rate depending on a degree of the ZnS supersaturation, the model adopts an approximate assumption that ZnS nuclei are formed all at one moment. Mathematical formulation of the nucleation model attempts to explain a recently observed relationship between ZnS nanoparticles radii and the CTAB concentration. The dependence of a surface tension of zinc acetate and CTAB aqueous solutions on the CTAB concentration was measured and further applied to obtain the relation between the CTAB monomer concentration and the CTAB total concentration. The nucleation model assumed a key role of CTAB monomers, which were considered as nucleation centres. The predicted radii of ZnS nanoparticles agreed with the measured data with a relative uncertainty of 0.34%.

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### 1. Introduction

A typical feature of nanomaterials is strong relation of their physical and chemical properties to their size. Their optical absorption, magnetization, resistivity as well as other useful qualities can be adjusted in this way. Fabrication of particles of the required size and with a narrow size distribution can be essential for their effective application. A large total surface area of nanoparticles results in their high adsorption and catalytic activity; moreover, the stability of the suspensions is affected by the size of the solid-phase components. Therefore, metal and semiconductor nanoparticles are often used as catalysts and photocatalysts in various reactions.

Nanoscale structures are prepared by top-down or bottom-up methods. Precipitation is an important bottom-up method, which enables using coincidental physical and chemical factors to effect size of nanoparticles. In general, a rapid nucleation period is followed by a slow growth of nanoparticles called Ostwald ripening.

Nowadays, the most often used photocatalyst is nanosized titanium dioxide, but in some recent works preparation and photocatalytic applications of ZnS nanoparticles have been studied [1-6]. For example, ZnS nanoparticles have been reported to have better photocatalytic activity than TiO<sub>2</sub> in case of carbon dioxide reduction [4-6]. Besides reverse microemulsion methods [7], the ZnS precipitation in aqueous solutions is mostly performed in the presence of stabilizing

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cationic surfactants, as referred in e.g. our recent papers [4,5]. Sodium sulphide was mixed with zinc acetate in an aqueous solution of CTAB, forming ZnS nanoparticles of wurtzite structure [4,8,9] with an average radius of about 2.0 nm. CTAB monomers were adsorbed on ZnS nanoparticles surface stabilizing their colloid dispersions and influencing their size.

The aim of this paper is to derive a theoretical model describing the relation between the typical radius of produced ZnS nanoparticles and the CTAB concentration, in order to clarify a nucleation role of this cationic surfactant. By our best knowledge, a similar theoretical model has not been published in the literature yet. Formulation of such nucleation model should bring deeper understanding an influence of cationic surfactants on nucleation and size of nanoparticles.

Diffusion and nucleation models were derived and tested on experimental data adopted from our recent paper.<sup>5</sup> Unlike the diffusion model, the nucleation model was in a good agreement with the experimental data and, therefore, was introduced in this paper.

## 2. Experimental

Cetytrimethylammonium bromide (Aldrich) and water deionized by reverse osmosis (Aqua Osmotic, Czech Republic) was used for preparation of all solutions. Dependence of surface tension of zinc acetate solution ( $2 \text{ mmol}\cdot\text{L}^{-1}$ ) on the CTAB concentration was determined by a standard method of capillary elevation using three independent glass capillaries with diameters of 0.275 mm, 0.325 mm and 0.400 mm. The preparation of ZnS nanoparticles was described in our paper:<sup>5</sup> 50 ml of the aqueous solution of  $\text{Na}_2\text{S}$  ( $15 \text{ mmol}\cdot\text{L}^{-1}$ ) was added drop-wise to 250 ml of the aqueous solution of zinc acetate (2 mM) under vigorous stirring in total concentrations of CTAB varied from  $0.1\text{--}5 \text{ mmol}\cdot\text{L}^{-1}$ .

## 3. Nucleation model and its verification

At first we tested a commonly used diffusion model based on the hypothetical assumption that a nucleation rate does not depend on the concentration of CTAB (this model is not discussed here in detail). The active reactive surface area of growing particles was gradually reduced by adsorption of CTAB and the diffusion growth terminated after reaching adsorption equilibrium. However, obtained theoretical results disagreed with the experimental data [5]. Therefore, we propose a new nucleation model, which is described in the following text.

Depending on the CTAB concentration, the reaction aqueous medium of ZnS precipitation contained varying ratios of CTAB monomers and micelles. In the nucleation model, we considered the concentrations of CTAB monomers and micelles that were much higher than the concentrations of natural nucleation centres, and they increased a nucleation rate. This substantially affects the size of the produced ZnS nanoparticles.

The nucleation model is based on the assumption of a very fast nucleation process connected with a significant decrease of supersaturation of ZnS, precipitated by zinc and sulphide ions in the concentrations of  $1.7 \text{ mmol}\cdot\text{L}^{-1}$  and  $2.5 \text{ mmol}\cdot\text{L}^{-1}$ , respectively. First we examined if CTAB monomers or micelles act as the nucleation centres.

The concentration of CTAB monomers  $c_1$  depending on the CTAB concentration  $c$  follows the relationship, [10,11] demonstrated in Fig. 1

$$c_1(c) = c_{\text{cmc}} - \frac{\sqrt{\frac{2}{\pi}} \sigma e^{-\left(\frac{c-c_{\text{cmc}}}{\sqrt{2}\sigma}\right)^2} + (c - c_{\text{cmc}}) \left( \text{erf}\left(\frac{c - c_{\text{cmc}}}{\sqrt{2}\sigma}\right) - 1 \right)}{\sqrt{\frac{2}{\pi}} \frac{\sigma}{c_{\text{cmc}}} e^{-\left(\frac{c_{\text{cmc}}}{\sqrt{2}\sigma}\right)^2} + \text{erf}\left(\frac{c_{\text{cmc}}}{\sqrt{2}\sigma}\right) + 1}, \quad (1)$$

where  $c_{\text{cmc}}$  is the critical micellar concentration (CMC) and the parameter  $\sigma$  characterizes the speed of change of the function  $c_1(c)$  from a linear dependence to a constant value. The critical micellar concentration of CTAB in water is about  $1 \text{ mmol}\cdot\text{L}^{-1}$ . The experimental dependence of ZnS nanoparticles radii on the CTAB concentration [5] demonstrated the influence of CTAB at the CTAB concentration of about  $0.5 \text{ mmol}\cdot\text{L}^{-1}$ , at which the concentration of micelles is negligible. For these reasons, we further considered only the monomers as nucleation centres.

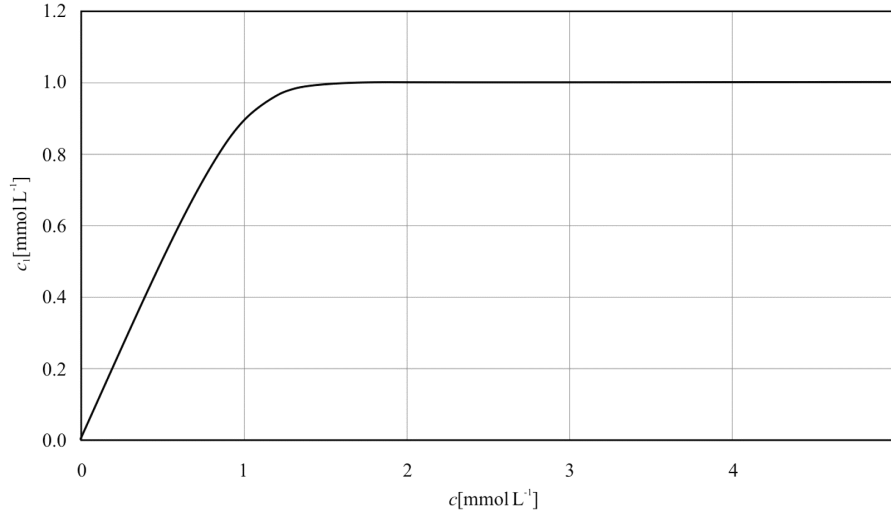


Fig. 1 Concentration of monomers  $c_1(c)$  on CTAB concentration  $c$ . This curve was constructed for  $\sigma = 0.28 \text{ mmol}\cdot\text{L}^{-1}$ , obtained by fitting experimental data (see below)

The assumption of extremely fast nucleation was approximated in this model by simultaneous nucleation of all nuclei, resulting in an instantaneous decrease of ZnS supersaturation to values, at which production of other nuclei is negligible. In order to confirm such an assumption, it was necessary to determine the ZnS nucleation rate as a function of the CTAB concentration.

On the basis of the standard nucleation theory [12-15] the nucleation rate, which is a number of created nuclei per unite volume and time, can be expressed as a function  $\theta(c,S)$  of the CTAB monomer concentration  $c_1(c)$  and a degree of ZnS supersaturation  $S = C/C_s$ , where  $C$  and  $C_s$  are ZnS actual and saturation concentrations, respectively. In our model, the values of  $\theta(c,S)$  are equal to the product of a monomer concentration  $c_1(c)$  and a probability of nucleation  $P(c,S)$ , which is the function of a CTAB concentration and a degree of supersaturation, as follows

$$\theta(c,S) = c_1(c) \cdot P(c,S). \quad (2)$$

From the nucleation theory, a final formula for the probability of homogeneous nucleation can be expressed as

$$P(c,S) = \exp\left(-\frac{16\pi\Omega^2}{3(kT)^3(\ln S)^2} \gamma(c)^3\right), \quad (3)$$

which is lower than here assumed pseudo-heterogeneous nucleation on CTAB monomer centres. The parameter  $\Omega \approx M_{\text{ZnS}}/\rho_{\text{ZnS}} = 39.4 \cdot 10^{-30} \text{ m}^3$  is the volume of a ZnS (wurtzite) molecule in a ZnS nanoparticle ( $M_{\text{ZnS}}$  and  $\rho_{\text{ZnS}}$  are the molar mass and the density of ZnS). The function  $\gamma(c)$  is the

interfacial energy between a solid ZnS nanoparticle and the supersaturated ZnS solution with zinc acetate ( $\leq 2 \text{ mmol L}^{-1}$ ) and the CTAB concentration  $c$ .

This model assumed that water molecules were removed from a volume of a future nucleus during the nucleation, and  $\text{Zn}^{2+}$  and  $\text{S}^{2-}$  ions re-configured as a result of ZnS crystallization, which caused only a minimal relative change of the nucleus volume. This model also assumed that the spatial area of fluctuation increase of the ZnS molecule concentration  $C$  was higher than the ZnS critical nuclei size. Under these conditions, there is no significant discontinuity of the ZnS concentration on nuclei. In this approach, the interfacial energy  $\gamma(c)$  in Eq. (3) represents only the work necessary to remove water molecules from the nucleus volume. In this approximation its value equals to the surface tension of water with zinc acetate ( $\leq 2 \text{ mmol L}^{-1}$ ) at a CTAB concentration  $c$ . The dependence of the surface tension on the CTAB concentration in Fig. 2, measured by the method of capillary elevation, demonstrated the characteristic influence of CTAB. Fig. 2 also shows a fitted curve derived theoretically in the following text.

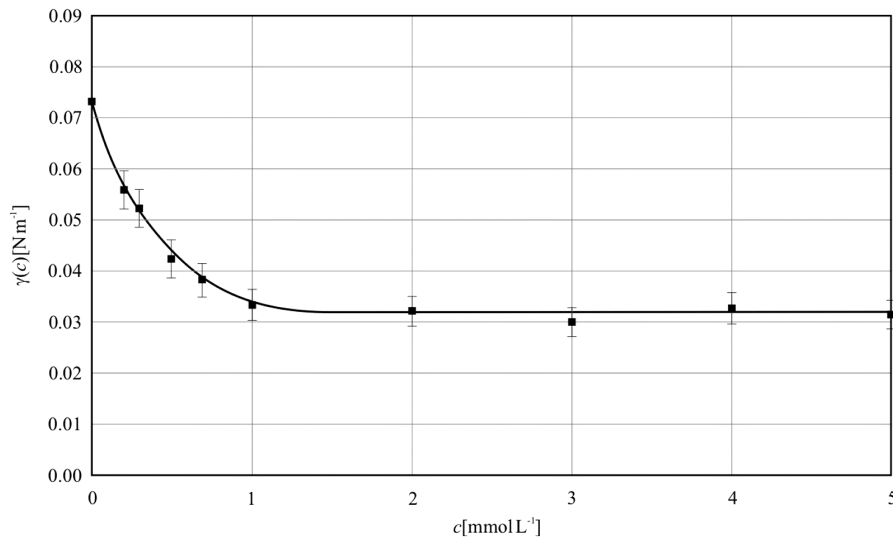


Fig. 2 Experimental dependence of surface tension of zinc acetate ( $2 \text{ mmol L}^{-1}$ ) and CTAB on the CTAB concentrations. Each point was measured using three independent capillaries with different radii. The solid line represents the fit according to the model equation (6) below

Even at CTAB concentrations above CMC, mostly free CTAB monomers bind to the ZnS interfacial boundary. The monomer concentration  $c_1(c)$  is a crucial parameter for the calculation of the surface tension of CTAB solutions using the Langmuir-Szyskowski equation [16,17]:

$$\gamma(c) = \gamma(0) - RT\Gamma_{\infty} \ln(1 + K_L c_1(c)), \quad (4)$$

where  $\gamma(0)$  is the surface tension of water,  $K_L$  is the Langmuir constant of adsorption equilibrium, and  $\Gamma_{\infty}$  is the maximal adsorption density of a surfactant on the interfacial boundary.

Combining Eqs. (1), (2) and (3) we obtained the nucleation rate  $\theta(c, S)$  for  $c > 0$  as

$$\theta(c, S) = c_1(c) \cdot \exp \left\{ - \frac{16\pi\Omega^2}{3(kT)^3 (\ln S)^2} [\gamma(0) - RT\Gamma_{\infty} \ln(1 + K_L c_1(c))]^3 \right\}. \quad (5)$$

A problem of the relationship between monomer and total surfactant concentrations, i.e.  $c_1(c)$  vs.  $c$  in Eq.(1), have been addressed in the above mentioned papers [10,11]. By substitution of Eq.(1) to

Eq.(4) we got a theoretical function of the concentration  $c$  as follows

$$\gamma(c) = \gamma(0) - RT\Gamma_{\infty} \ln \left[ 1 + K_L \left( c_{\text{cmc}} - \frac{\sqrt{\frac{2}{\pi}} \sigma e^{-\left(\frac{c-c_{\text{cmc}}}{\sqrt{2}\sigma}\right)^2} + (c - c_{\text{cmc}}) \left( \text{erf}\left(\frac{c - c_{\text{cmc}}}{\sqrt{2}\sigma}\right) - 1 \right)}{\sqrt{\frac{2}{\pi}} \frac{\sigma}{c_{\text{cmc}}} e^{-\left(\frac{c_{\text{cmc}}}{\sqrt{2}\sigma}\right)^2} + \text{erf}\left(\frac{c_{\text{cmc}}}{\sqrt{2}\sigma}\right) + 1}} \right) \right], \quad (6)$$

with the parameters  $\Gamma_{\infty}$ ,  $K_L$  and  $\sigma$ . In Fig. 2. there are displayed the experimental data and their theoretical fit curve based on the function (6) with  $\Gamma_{\infty} = 8.66 \cdot 10^{-6} \text{ mol} \cdot \text{m}^{-2}$ ,  $K_L = 3 \text{ L} \cdot \text{mmol}^{-1}$ ,  $\sigma = 0.28 \text{ mmol} \cdot \text{L}^{-1}$  and  $c_{\text{cmc}} = 1 \text{ mmol} \cdot \text{L}^{-1}$ . Now the function  $c_1(c)$  and the value  $\gamma(0)$  could be used to calculate the nucleation rate  $\theta(c, S)$  according to Eq.(5) for various CTAB concentrations, as demonstrated in Fig. 3.

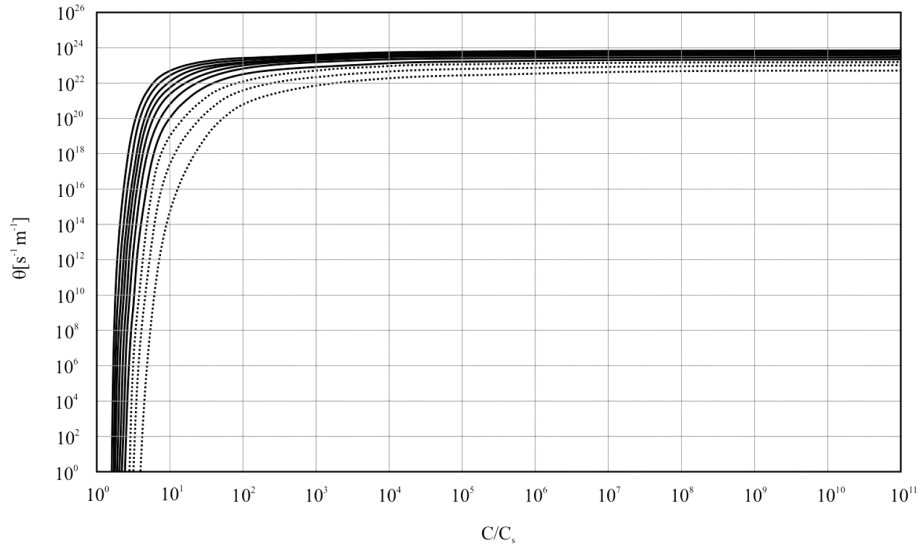


Fig. 3 Dependence of nucleation rate  $\theta(c, S)$  on a degree of supersaturation  $S$  for various CTAB concentrations  $c$  according to Eq. (5). Dotted curves correspond to low concentrations  $c = 0.1 \text{ mmol} \cdot \text{L}^{-1}$ ,  $0.2 \text{ mmol} \cdot \text{L}^{-1}$  and  $0.3 \text{ mmol} \cdot \text{L}^{-1}$  (bottom-up). Solid curves, corresponding to higher concentrations  $c$ , gradually increased to their maximal values.

For higher concentrations  $c$  and  $S > 100$  (in the range of 9 orders of magnitude), the nucleation rate  $\theta(c, S)$  can be approximated by a constant with the characteristic value of about  $\theta_{\text{max}} \approx 10^{23} \text{ s}^{-1} \text{ m}^{-3}$ . On the basis of Eq. (5), a time dependence of the degree of supersaturation  $S(t)$  evolution was derived/found via a simple balance differential equation

$$\left. \begin{aligned} N_A \frac{dC}{dt} &= -N \cdot \theta_{\text{max}} \\ S &= \frac{C}{C_s} \end{aligned} \right\} \rightarrow S(t) = S(0) - \left( \frac{N \theta_{\text{max}}}{C_s N_A} \right) t, \quad (7)$$

where  $N_A$  is the Avogadro's number, and  $N = 13$  is an estimate of a number of ZnS molecules in a critical nucleus of  $r_{\text{crit}} \approx 0.5 \text{ nm}$  in aqueous media with no surfactant [18]. By substitution of the initial degree of supersaturation  $S(0) = 1.262 \cdot 10^{11}$  and the ZnS (wurtzite) saturation concentration  $C_s = 1.585 \cdot 10^{-11} \text{ mol} \cdot \text{L}^{-1}$  to Eq. (7), we found that  $S(t)$  decreased to the value of 100 in  $t \approx 0.9 \text{ s}$ . In

a region of a low degree of supersaturation  $1 < S(t) < 100$ , a number of newly formed/emerging nuclei can be neglected in comparison with their total number. With regard to significantly longer times of measurable diffusion growth, the short characteristic time of nucleation (see Eq. (7)) can be considered as a confirmation of the basic assumption of immediate formation of all nuclei. At the residual supersaturation, a relatively slow additional growth occurred at every concentration of CTAB.

A critical nucleus with radius  $r_{\text{crit}}(c)$  formed at time  $t = 0$  subsequently grows for a period  $t$  to reach the radius  $r(c, t)$ . Experimental determination of the ZnS nanoparticles size [5] after 24 h confirmed a multiplicative character of an additional diffusion growth as

$$r(c, t) = \Lambda_D(t) \cdot r_{\text{crit}}(c, 0). \quad (8)$$

The multiplicative factor  $\Lambda_D(t)$  with a relative uncertainty of 2 % is independent of the CTAB concentration  $c$ , and converges to a constant value for  $t \rightarrow \infty$ . According to the standard nucleation theory, a critical nucleus radius is proportional to the interfacial energy  $\gamma(c)$

$$r_{\text{crit}}(c) = \left( -\frac{2}{\Delta G_V} \right) \cdot \gamma(c). \quad (9)$$

In a simple model approximation ( $c_1 \leq c_{\text{cmc}} \ll C$ ), we assume that the change of the Gibbs energy  $\Delta G_V$  in ZnS nucleation is independent of the monomer concentration  $c_1$ . Thus a nanoparticle radius can be expressed using the multiplicative factor  $\Lambda(t)$  as follows

$$r(c, t) = \Lambda(t) \cdot \gamma(c). \quad (10)$$

The factor  $\Lambda$  is a simple product of a time dependent diffusion factor  $\Lambda_D(t)$  and a constant ZnS nucleation factor  $\Lambda_N = -2/\Delta G_V$ . The fit to the experimental data [5] based on the relation (10) is shown in Fig. 4. The theoretical model (10) for  $\Lambda = 65.5 \text{ m}^2 \cdot \text{N}^{-1}$  exhibited an optimal agreement with the experimental data, expressed by a relative uncertainty of 0.37 %.

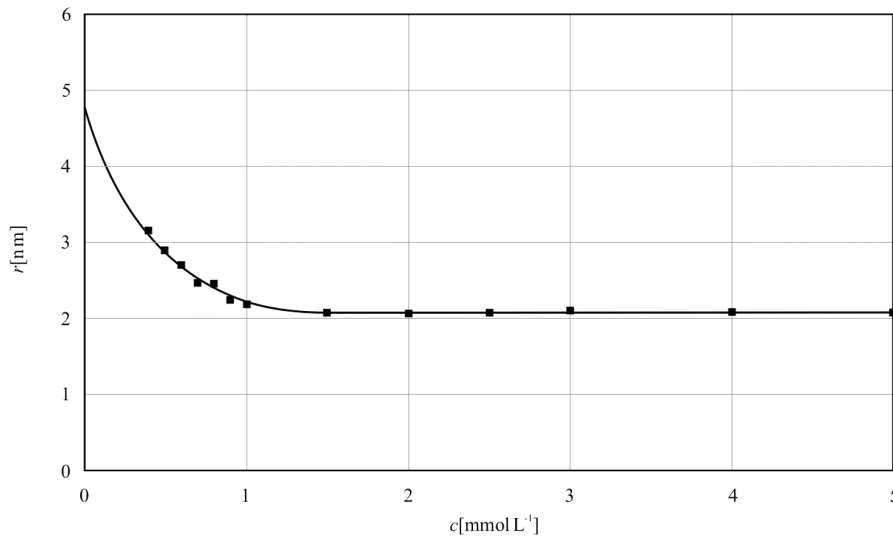


Fig. 4 Experimental data of ZnS nanoparticle radii at different CTAB concentrations fitted with the function  $r(c, t)$  at  $t = 180 \text{ s}$  after precipitation

#### 4. Conclusions

In our previous study [5] we found that the CTAB concentration significantly influenced the radii of synthesized ZnS nanoparticles. In this work, the mathematical model of nucleation and growth of CTAB-stabilized ZnS nanoparticles was developed to verify and interpret the previously obtained experimental data. The dominating influence of a nucleation phase on properties of formed ZnS nanoparticles was assumed to be a basic characteristic of the ZnS nanoparticle synthesis. Finding decisive parameters like the CTAB concentration enables preparation of nanoparticles size on demand for various applications. This assumption, based on the simplifying condition that nuclei were formed all at one time, was verified by the formulated dependence of a ZnS nucleation rate on a degree of supersaturation.

Nucleation in the presence of surfactants was confirmed to be more intensive than without them. The nucleation rate was assumed to increase due to i) the increase of the density of nucleation centres – CTAB monomers and ii) the decrease of a surface tension of the surrounding liquid phase. To verify this, a surface tension of aqueous solutions of zinc acetate ( $2 \text{ mmol L}^{-1}$ ) and CTAB depending on the CTAB concentration was measured, and the relationship between the CTAB monomer and the total CTAB concentrations was obtained. Finally, the mathematical dependence of the ZnS nanoparticle radius on the CTAB concentration was derived. An agreement of this theoretical model with the experimental data was expressed by a relative uncertainty of 0.34 %.

To summarize, the theoretical model derivation was based on the assumptions that the nucleation rate depends on the concentration of CTAB monomers and leads to a supersaturation drop in a very short time. The CTAB concentration influences surface tension and thus radii of critical nuclei and resultant nanoparticles. The validity of these assumptions was confirmed by a good agreement of this model with the experimental results [5].

To the best of our knowledge, a similar physical model which could explain the observed dependence of ZnS nanoparticles radii on the CTAB concentration has not been published yet. Till this time, the published papers devoted to this topic [19-21] mostly focused on laboratory experiments and already known models [22,23] and have not explained the discussed relationship.

The practical meaning of the presented model can be seen in possibility to control the size of synthesized nanoparticles by surfactant concentrations. Preparation of nanoparticles in the presence of surfactants and some additives for significant modification of their critical micellar concentrations [24] will be investigated in the future.

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