

# Synthesis of Zinc-Sulfate Nano Particles and Detection of Their Induction Time, Nucleation Rate and Interfacial Tension

**Jahangiri, Ali Reza\***<sup>†</sup>

*Faculty of Engineering, Shahrekord University, Shahrekord, I.R. IRAN*

**Sedighi, Mehdi**

*Department of Chemical Engineering, University of Qom, Qom, I.R. IRAN*

**Salimi, Farhad**

*Department of Chemical Engineering, Kermanshah Branch, Islamic Azad University, Kermanshah, I.R. IRAN*

**ABSTRACT:** *The production of zinc sulfate is important both medically and agriculturally. If zinc sulfate is produced without agglomeration at the nanoscale, its absorption in the body is more and faster. In this research, the induction time parameter is assessed for nucleation of zinc sulfate nanoparticles at room temperature and various supersaturations using acetone (as anti-solvent) in the presence of sodium dodecyl sulfate surfactant (SDS). The nucleation mechanism of zinc sulfate nanoparticles altered from primary to secondary by adding SDS surfactant in solution. The morphology of the zinc sulfate nanoparticles was analyzed by a Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM) tests. The TEM results revealed that the size of the nanoparticles is between 30 and 35 nm in the presence of SDS surfactant. The experimental data proved that the induction time reduces and improves with increasing supersaturation and SDS concentration, respectively. Meanwhile, the nucleation rate increases with the decrease in the interfacial tension of the zinc sulfate particles. The experimental results were also compared with the predictions of classical nucleation theory and the results proved good agreement between them.*

**KEYWORDS:** *Nucleation; Induction time; Supersaturation; SDS; Zinc-Sulfate nano particles.*

## INTRODUCTION

Recently, the production of nanoscale materials has been of great importance to researchers [1-3]. By reducing the particle size at the nanoscale and increasing the ratio of surface to volume in solution, the properties of the solution such as solubility, transparency and

colloidal stability were upgraded [4]. There are several methods for preparing nanoparticles in solution. Most of them are not cost-effective because of the high cost of raw materials, the complexity of the technique, the particle size, as well as low purity [5]. More recently,

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\* To whom correspondence should be addressed.

† E-mail: jahangiritmu@yahoo.com

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a special route called "bottom-up technology" has attracted researchers' interest in nanoparticle production. In this method, instead of producing the desired material by breaking bulk material into smaller pieces, the material is synthesized from atomic or molecular species. This differs from ordinary processes. In common methods; many materials are disposed as waste. There is no problem with the bottom-up method and also the stability of the synthesized material is higher because of the stronger bonds between the constituent atoms [6, 7]. The production of zinc sulfate at the nanoscale is important in the medical, industrial and agricultural sectors. In the medical field, zinc sulfate is used to accelerate wound healing, treat anorexia nervosa, release growth hormone. From the industry's point of view, that is useful in art silk fabrication as a coagulator. In agriculture industry, it is utilized as a nutrient particles for zinc deficiency in the soil. Therefore, when dissolved zinc sulfate is stored in nanoscale and avoids agglomeration, its absorption in body and soil has more effects [8, 9]. In the crystallization system, the induction time is defined as the time elapsed between the generation of supersaturation and the first changes in the physical properties of the system due to the appearance of new particles. In other words, the induction time is the sum of the time required to obtain a semi-stable state for the distribution of the clusters, the time required for the creation of a stable nucleus, and the time required for the growth of the nucleus to the desired size [10, 11]. By identifying the induction time, beneficial information can be obtained on nucleation rate and nucleation kinetic. Supersaturation levels and surfactants are two key factors in determining induction time [12-14]. Surfactants are useful to prevent the agglomeration of nanoparticles. In this study, zinc sulfate nanoparticles are prepared by bottom-up method in the presence of SDS as a surfactant to evaluate nucleation rate, induction time, and interfacial tension at various supersaturations.

## THEORITICAL SECTION

The classical nucleation theory presumes that the clusters are generated in a solution until the particle size attains a critical size. The amount of nuclei produced by this mechanism is as follows [15]:

$$B = B^0 \exp\left(-\frac{\Delta G}{kT}\right) \quad (1)$$

Based on the maximum amount of  $\Delta G$  (free Gibbs energy) in critical nuclei, which depends on the minimum size of stable nuclei and clusters (Gibbs-Thompson equation), the nucleation amount is as follows [16]:

$$B = B^0 \exp\left(-\frac{16\pi\gamma^3 V_m^2}{3(kT)^3 (\ln S)^2}\right) \quad (2)$$

In Eq.2,  $S = C/C^*$ ,  $V_m$ ,  $k$ ,  $T$  are supersaturation, molecular volume, Boltzmann constant and temperature respectively. The induction time has a reverse relationship to the nucleation rate, so:

$$t_{\text{ind}} \propto 1/B \quad (3)$$

$$t_{\text{ind}} = K \exp\left(\frac{16\pi\gamma^3 V_m^2}{3(kT)^3 (\ln S)^2}\right) \quad (4)$$

By getting logarithm on both sides of Equation (4):

$$\ln t_{\text{ind}} = \ln K + \left(\frac{16\pi\gamma^3 V_m^2}{3(kT)^3 (\ln S)^2}\right) \quad (5)$$

So for a given temperature, the diagram of  $\ln(t_{\text{ind}})$  Vs.  $1/T^3 (\ln s)^2$  is a straight line with a slope of A:

$$A = \frac{16\pi\gamma^3 V_m^2}{3k^3} \quad (6)$$

This method can be used to calculate the interfacial tension and to evaluate the effects of temperature [17, 18]

## EXPERIMENTAL SECTION

### Methods

In these series of experiments, zinc sulfate ( $\text{ZnSO}_4$ , Merck 99%), acetone ( $\text{C}_3\text{H}_6\text{O}$ , Merck 98%) as anti-solvent, SDS ( $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$ , Merck 98.5%) as surfactant, methanol (Aldrich, 98%) and distilled water was utilized.

### Production of Zinc-Sulfate nano particles without SDS surfactant

Taking into account all available options, the effects of the amount of anti-solvent and mixing time factors were investigated to obtain the best conditions of production of zinc sulfate crystal. In the first stage, to measure the desired amount of zinc sulfate for

the experiment, the zinc sulfate necessary to make a saturated methanol solution was determined using 0.7 g of zinc sulfate in 20 mL of methanol. Subsequently, different amounts of zinc sulfate (0.1, 0.2, 0.3, 0.4 g) in 20 mL methanol solutions were chosen for these series experiments. Samples containing a methanol solution and zinc sulfate were stirred for 10 minutes at 100 rpm on a magnetic stirrer and then slowly increased to 230 rpm. The concentration of this solution is equal to C. In the following stage, an anti-solvent (acetone) was added to the solution of methanol and zinc sulfate (one drop of acetone every 5 minutes). This process continued until the solution became cloudy. The color change of the solution shows the induction time. After the color change of the methanol and zinc sulfate solution and the recording of the induction time, the suspension was covered with a paraffin film and kept at room temperature (25 °C) for 6 hours. After this time, the suspension separates into two phases, with the clear phase (liquid) on the agglomerated (solid) phase.

A clear phase sample (5 cc) was obtained and weighed and placed in an oven at 100 ° C. After drying the sample, the pure amount of zinc sulfate was by weight and C\* (zinc sulfate saturation concentration) was evaluated.

#### *Production of Zinc-Sulfate nano particles with surfactant*

In this method, 0.2 g SDS were dissolved in 500 mL of a methanol solution. A sample of this solution was taken. A zinc sulfate solution was prepared as before with various concentrations of SDS and zinc sulfate. According to the previous method, the experiment was continued until the solution color changed and dried, but the time required to reach the clear phase was 10 hours. In this series of experiments, a transmission electron microscope (Zeiss EM10C-80KV) was used to ensure the formation of zinc sulfate nanoparticles by the addition of SDS surfactant.

## RESULTS AND DISCUSSION

### *The results related to the induced crystallization process without SDS*

The results of induction time ( $t_{ind}$ ) and dimensionless supersaturation (S) measurements are shown in Table 1.

In order to identify the dominant nucleation mechanism, the results of the experiment must conform

to classical nucleation theory. According to the theory of classical nucleation, if  $\ln t_{ind}$  Vs.  $1/(\ln S)^2$  diagram is a straight line, then the homogeneous nucleation mechanism is primary and if  $\ln t_{ind}$  Vs.  $\ln S$  diagram is a straight line, then the nucleation mechanism is secondary. The two diagrams are in Fig. 1.

The value  $R^2$  for the diagram (1 (A)) is 0.8862 and for (1 (B)) is 0.9599. Based on the results, homogeneous primary nucleation dominates over secondary nucleation under these conditions.

### *The results related to the induced crystallization process with SDS*

SDS surfactant was used to study the effect of surfactant addition on the induction time of zinc sulfate nanoparticle formation and nucleation parameters. The results are shown in Tables 2 and 3.

In order to identify the dominant nucleation mechanism according to section (3-1),  $\ln t_{ind}$  Vs.  $1/(\ln S)^2$  and  $\ln t_{ind}$  Vs.  $\ln S$  diagrams are plotted. Both diagrams are in in Fig. 2.

In general, the presence of contaminants in the system can affect the induction time, but the results are unpredictable. The impurity causes a change in solution structure or solubility equilibrium resulting from a change in chemical adsorption on the nucleus. According to the Fig. 2, induction time decreased by increasing the supersaturation concentration in presence of SDS as a surfactant. SDS prevents zinc sulfate from binding to the crystalline surface of the zinc sulfate particles.

Tai *et al.* [18] and Xu *et al.* [19] achieved similar results when studying the  $\text{NaCO}_3\text{-CaCl}_2$  systems in the presence of magnesium chloride and  $\text{MgSO}_4\text{-NaOH}$  system in the presence of EDTA. On the other hand, the induction time increases by increasing the supersaturation (the driving force of penetration from solution to crystal surface). The same results were reported by Manteghian *et al.* in preparation of nanoparticles of potassium chloride and barium chromate [20, 21].

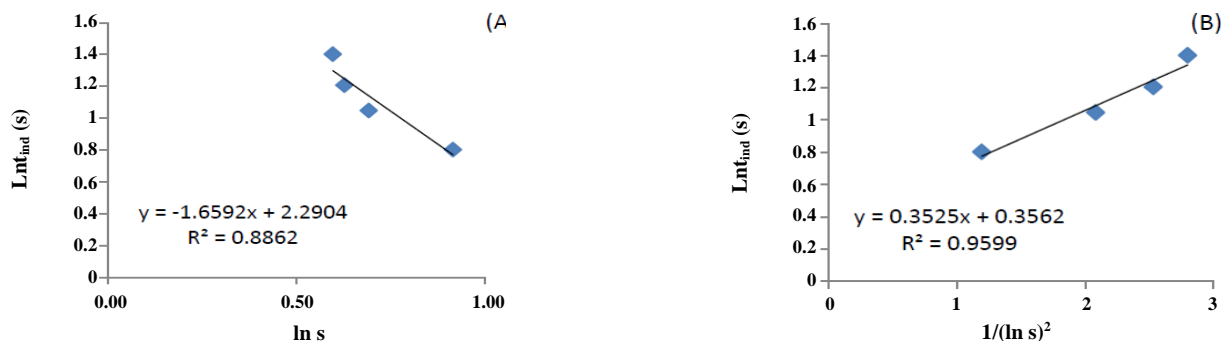
According to classical nucleation theory, while the secondary nucleation value of  $R^2$  is greater than the primary nucleation, secondary nucleation dominates the primary nucleation in experiments with SDS surfactants. The maximum  $R^2$  value of the linear regression was 0.9995, which refers to part D of the diagram. According to the TEM and SEM images (Fig. 3), the surfactant SDS

**Table 1: The induction time ( $t_{ind}$ ), supersaturation concentrations ( $C^*$ ), dimensionless supersaturation concentrations ( $S$ ) and the used amount of Acetone ( $V$ ) for different concentrations of Zinc-Sulfate solution ( $C$ ).**

C(g/cc)	V(cc)	$t_{ind}$ (s)	$C^*$ (g/cc)	S	Lnt(s)	Lns	$1/(Lns)^2$
0.4	7.9	4	0.22	1.82	1.401	0.598	2.798
0.3	9	3	0.16	1.88	1.205	0.629	2.531
0.2	10.5	3	0.10	2	1.047	0.693	2.081
0.1	12.1	2	0.04	2.5	0.802	0.916	1.191

**Table 2: The induction time, supersaturation and the used amount of Acetone by adding SDS surfactant for 0.1 and 0.2 g Zinc-Sulfate.**

Zinc-Sulfate (g)	0.1				0.2				
	$V_{SDS}$ (cc)	$V_{Acetone}$ (cc)	$t_{ind}$ (s)	$C^*$ (g/cc)	S	V(cc)	$t_{ind}$ (s)	$C^*$ (g/cc)	S
1		15.7	14	0.08	1.25	13.1	18	0.163	1.23
0.9		15.6	13	0.076	1.32	12.94	16	0.154	1.3
0.8		15.5	12	0.072	1.39	12.78	15	0.148	1.35
0.7		15.4	11	0.068	1.47	12.62	13	0.142	1.41
0.6		15.3	9	0.064	1.56	12.64	12	0.136	1.47
0.5		15.2	8	0.06	1.67	12.3	10	0.130	1.54
0.4		15.1	7	0.056	1.79	12.14	9	0.124	1.61
0.3		15	6	0.052	1.92	11.98	7	0.118	1.69



**Fig. 1: (A)  $Lnt_{ind}$  Vs.  $\ln S$  diagram, (B)  $Lnt_{ind}$  Vs.  $1/(\ln S)^2$  diagram without surfactant.**

avoids the agglomeration of the zinc sulfate nanoparticles. The solutions containing the SDS surfactant are amphiphilic, which means that one end adheres to the zinc sulfate particles and covers the surface, and the other end adheres to the methanol-acetone solution.

In fact, the solution of methanol and acetone surrounds with SDS-coated zinc sulfate nanoparticles. The ends adhering to the methanol-acetone solution have the same charge, i.e. the zinc sulfate particles (SDS-coated)

repel each other. That is why it avoids their agglomeration.

The nucleation power can be calculated using induction time data. If the nucleation rate is Eq. (7):

$$B = K_b S^n \quad (7)$$

Taking into account the inverse relationship of the induction time to the nucleation rate:

$$\ln t_{ind} = \ln K_b - n \ln S \quad (8)$$

**Table 3: The induction time, supersaturation and the used amount of Acetone by adding SDS surfactant for 0.3 and 0.4 g Zinc-Sulfate.**

Zinc-Sulfate (g)	0.4				0.3				
	V <sub>SDS</sub> (cc)	V <sub>Acetone</sub> (cc)	t <sub>ind</sub> (s)	C*(g/cc)	S	V(cc)	t <sub>ind</sub> (s)	C*(g/cc)	S
1		9.3	25	0.38	1.052	11.3	21	0.220	1.36
0.9		9.1	23	0.376	1.064	11.11	20	0.214	1.4
0.8		8.9	21	0.372	1.075	10.9	18	0.208	1.44
0.7		8.7	19	0.368	1.087	10.7	16	0.202	1.49
0.6		8.5	17	0.364	1.099	10.5	14	0.196	1.53
0.5		8.3	15	0.36	1.111	10.3	12	0.190	1.58
0.4		8.1	13	0.356	1.123	10.1	11	0.184	1.63
0.3		7.9	11	0.352	1.136	9.9	9	0.178	1.69

And then, depending on the slope of the line drawn between  $\ln t_{ind}$  and  $\ln s$ , nucleation power ( $n$ ) is calculated. The nucleation power obtained by varying concentrations of zinc sulfate nanoparticles in secondary nucleation is shown in the Table 4.

The crystal growth mechanism is influenced by the presence of surfactants. Surfactants can affect the stage of completion of the crystal growth level by adsorbing on the surface of the crystals and reducing the space of the crystals growth. *Isopesuca et al.* [22] realized the same study in research about Calcium carbonate solution.

#### Calculating interfacial tension

According to the classical nucleation theory and considering equation (4), the interfacial tension could be calculated on the basis of the linear relationship between  $\ln(t_{ind})$  and  $1/T^3(\ln s)^2$ . In this study, the interfacial tension is determined by slope  $A$  from Eq.(5) and substituting in Eq. (6) at 25°C:

$$\gamma = k \left( \frac{3}{16\pi V_m^2} \right)^{\frac{1}{3}} \quad (9)$$

Constants of Eq.(9) are:

Boltzman constant

$$k = 1.3805 \times 10^{-23} \text{ J K}^{-1}$$

Molecular volume of Zinc-Sulfate [16]

$$V_m = \frac{M_w}{\rho N_A}; M_w = 161.4426 \frac{\text{g}}{\text{mol}}; \rho = 3.8 \frac{\text{g}}{\text{cm}^3}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

The calculated interfacial tensions of the zinc sulfate nanoparticles are shown in Table 5. The results obtained are in good agreement with the result of *Durairajan et al.* [23].

The interfacial tension of zinc sulfate nanoparticles reduces in the presence of SDS and, as the interfacial tension of the solution decreases, the nucleation power improves considerably. These results are in agreement to the studies of *Flaten et al.* [24] and *Manteghian et al.* [11] in preparation of calcium carbonate and copper nanoparticles respectively.

#### CONCLUSIONS

In this study, the induction time of the prepared zinc sulfate nanoparticles by induced crystallization was measured by different concentrations. The addition of a saturated solution of anti-solvent (acetone) to zinc sulfate reduces the solubility. SEM and TEM images confirmed the production of zinc sulfate nanoparticles. Increasing supersaturation decreases the induction time and the amount of acetone used, which is consistent with conventional nucleation theory. Also, addition of SDS as a surfactant to acetone and zinc sulfate solution resulted in zinc sulfate nanoparticles by a secondary nucleation mechanism. Finally, it found that by decreasing interfacial tension, the nucleation rate increased.

#### Symbols

C	Initial concentration, g/mol
C*	Supersaturation concentration, g/mol
A	line Slope in constant temperature

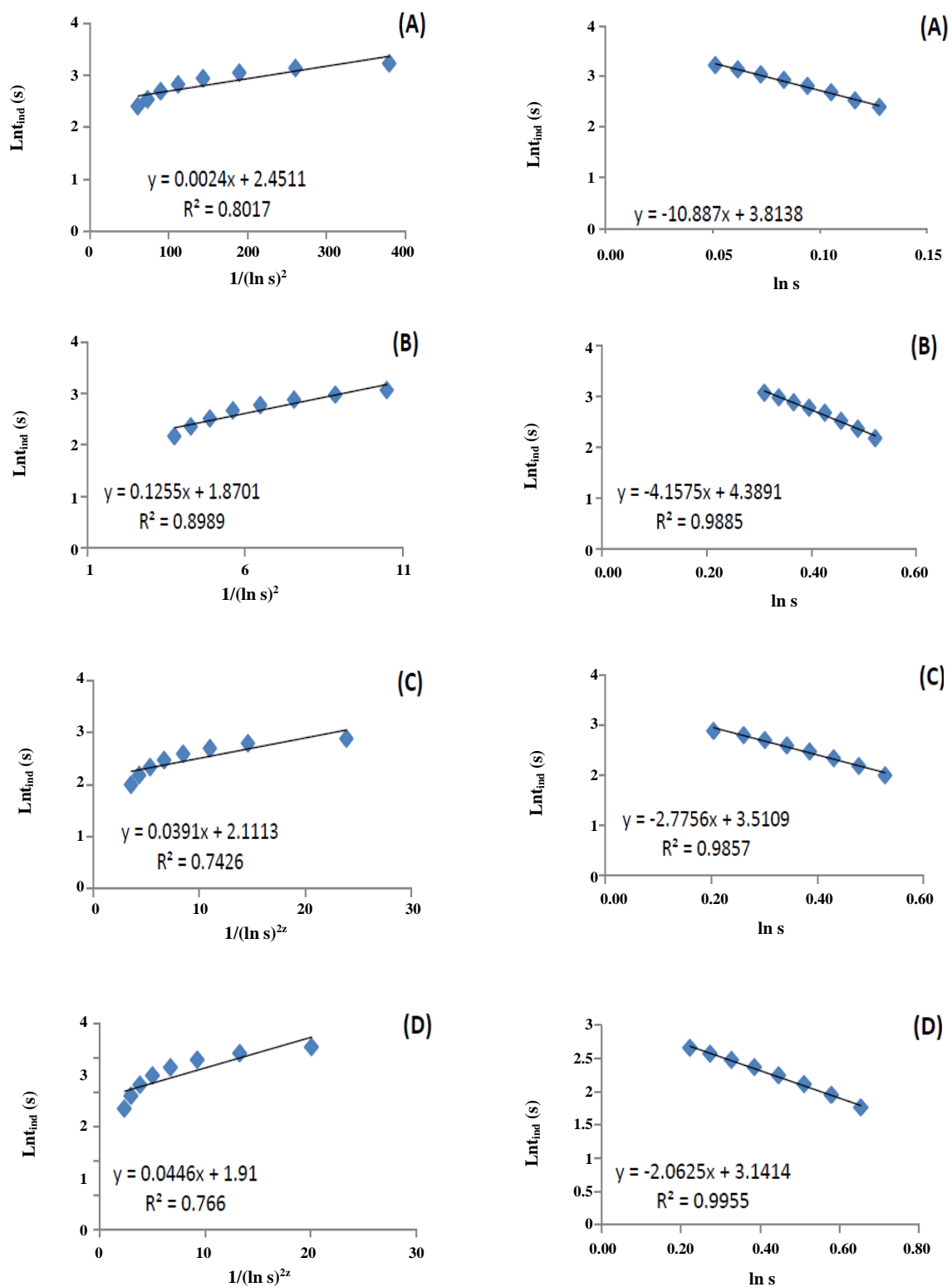


Fig. 2: (A)  $Lnt_{ind}$  Vs.  $\ln s$  diagram and  $Lnt_{ind}$  Vs.  $1/(\ln s)^2$  diagram with SDS surfactant in 25 °C Amount of Zinc-Sulfate: (A): 0.4g, (B): 0.3g, (C): 0.2g, (D): 0.1g.

Table 4: Nucleation power in presence of SDS.

Zinc-Sulfate (g)	n
0.4	10.8870
0.3	4.1575
0.2	2.7756
0.1	2.0625

Table 5: The interfacial tension of Zinc-Sulfate nanoparticles in 25°C.

Without SDS	
Without SDS	4.133
SDS+ 0.1g	1.704
SDS+0.2g	2.028
SDS+0.3g	2.936
SDS+0.4g	0.792

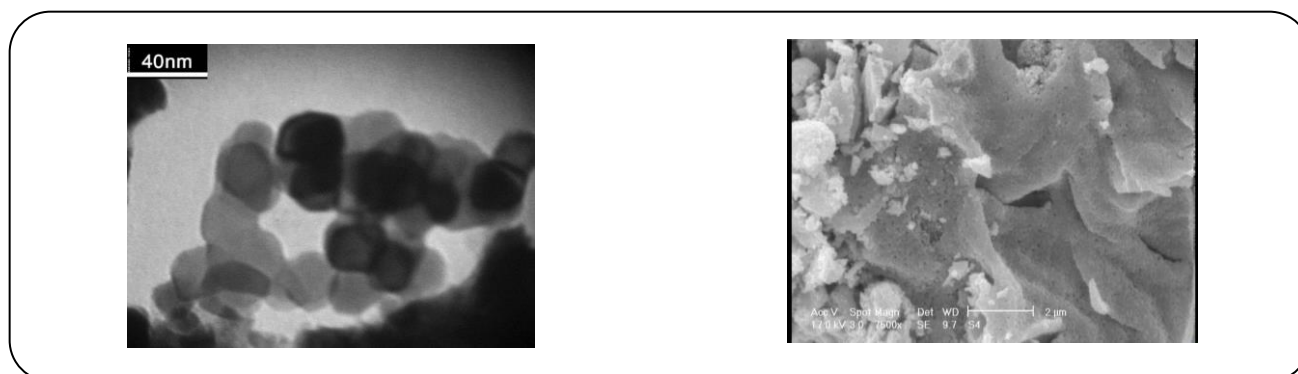


Fig. 3: The TEM and SEM images of Zinc-Sulfate particles in presence of SDS surfactant.

$K_b$	Stephan-Boltzmann constant
$\gamma$	Interfacial tension, $\text{mJ}/\text{m}^2$
$P$	Density, $\text{kg}/\text{m}^3$
$V_m$	Volume, $\text{m}^3$
$t_{\text{ind}}$	Induction time, s
$S$	Dimensionless Supersaturation
$M$	Molecular mass, $\text{g}/\text{mol}$
$N_A$	Avogadro constant, $\text{no.}/\text{mol}$

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