Determining the Stability of Potassium Sulfate Nanoparticles Influence of Mineral and Organic Additives

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ABSTRACT

In this study, the induction time of potassium sulfate Nano particles was measured at 25 ° C and different super saturation in order to nucleation, by Acetone   anti solvent, Also, the consuming volume of Acetone for nucleation, examined singly and at the presence of the superficial active material of cetyl tri methyl ammonium bromide(CTAB) and sodium citrate. Additionally, the surface tension of potassium sulfate nano particles has calculated at the presence of CTAB surfactant, by use of classic theory of nucleation. The results acquired that, at the presence of Acetone, the induction time rises by increasing the amount of super saturation, But at the presence of surfactant, the induction time is decreased by increasing of super saturation. In relation with the surface tension and also at the presence of CTAB, the surface tension decreased by increasing of potassium sulfate concentration.   Generally, by evaluating of done studies, we can say that, eventually, the presence of additives, has shown to changing in the main elements that is super saturation and the surface tension and leads to change the induction time. Also, by use of Transition Electronic Microscope (TEM), the sample was taken a photograph at the presence of CTAB surfactant and was determined that the nano particle is formed.

Keywords: Nucleation, Induction time, super saturation, surfactant, potassium Sulfate.

1. Introduction

Nano particles, are particles in 1- 100 nanometer dimensions and has different properties with respect to micro particles or particles in the bigger size. With decreasing the size of particles to nano scale and as a result, increasing level ratio to volume, different qualities increases such as bio accessibility, solubility in water, colloidal stability and the limpidity of solutions containing nanoparticles. Among various metal material, potassium nanoparticles have considered attention due to catalytic, optical, electric absorption and another properties. Potassium sulfate is formed Commonly from water and acid which is soluble in potassium. The ingredients of sulfate are salts and or asters of sulfuric acid that compose by replacing of one or two hydrogen to a metal. Most of metal sulfates ingredients, are soluble in water. Contrary to fluorides and oxides that have a tendency to dissolve in water[1]. In fact, when a material prepared in nano scale, its physical qualities

changed. This properties is valuable, in relation to size of different nano structures. Nano particles contain extensive spectrum, include of mineral and organic materials, shapeless or crystal particles, spread particles or powder in a matrix, in the form of single or isolated particles or in the clod, colloidal, suspension and emulsional solution states and…[2].In this investigation, by adding of CTAB surfactant and sodium citrate to the potassium sulfate particles, we would like examine that, adding the materials, how much change the induction time of nano particles forming and their stability range.

2. Theoretical
2.1. Primary nucleation
The classic theory of homogeneous primary nucleation supposes that clusters in a solution, are constituted by increasing mechanism, when critical size to be gained. The extent of nucleus formation with this mechanism is:

$$B = B' exp\left(-\frac{\Delta G}{KT}\right)$$

(1)

Basis on maximum degree ΔG (Gibbs free energy) in critical nucleus that found on minimum degree of stable nucleus and growth of clusters which under the Gibbs – Thomson equation, in equation (1), the rate of nucleation is following way:

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

(2)

$S=c/c*$ is super saturation. V_m is molecular volume, K is Boltzmann constant and T is temperature. As we know, the induction time contains information about kinetics of nucleation and it can has a reverse ratio with rate of nucleation, we have:

$$t_{ind} = K exp\left(\frac{16\pi\gamma^3 V_M^2}{3(KT)^3 (\ln S)^2}\right)$$

(3)

To get normal logarithm from the 2 sides of the equation (3):

$$lnt_{ind} = \ln K + \left(\frac{16\pi\gamma^3 V_M^2}{3(KT)^3 (\ln S)^2}\right)$$

(4)

So, for a certain temperature, graph of lnt_{ind} in front of $1/\ln s^2$ is right line with A gradient[3].

$$A=\left(\frac{16\pi\gamma^3 V_M^2}{3(KT)^3}\right)$$

(5)

2.2. Secondary nucleation
In secondary nucleation, nucleus is created near and at the presence crystals of solute material .In following equation, b, is lab order of nucleation and estimates.

$$B = K_b (s)^b$$

(6)

According to equation (6), $S=c/c*$ is super saturation, b is order of nucleation and k is

Boltzmann constant. As we said, the induction time is the content of information about kinetics of nucleation and it can has a reverse ratio with rate of nucleation.

$$t_{ind} = K_b(s)^{-b}$$

(7)

To get normal logarithm from (7)

$$lnt_{ind} = lnK_b - bln(s)$$

(8)

This equation shows the order of nucleation in a narrow part of super saturation. Therefore, at a certain temperature, graph of lnt_{ind} In front of lns is right line with b gradient[4].

3. Empirical activities
3.1. Materials
The matters used in the laboratory, are potassium sulfate ($k_2 So_4$), mineral and organic additives such as sodium citrate($C_2H_5Na_3O_72H_2O$), CTAB surfactant($CH_3(CH_2)15N$ $(CH_3)Br$) and Acetone anti solvent(C_3H_6O).

3.2. Test explanation
the experiments divided into three groups: first test is related to adding the Acetone anti solvent. Second is adding the CTAB surfactant additive and the third is adding the sodium citrate additive. Firstly, we begin with adding the acetone anti solvent on potassium sulfate. In this process to determine the amount of salt in doing test, we gain the saturation solvation for potassium sulfate, that this amount is 0.7 gram. Then we weigh the different amounts of potassium sulfate by scale, and solve it in 10 cc of distilled water and show it to C (salt concentration, according to g / cc of solution) and use it in the calculations. After we solve the salt in 10 cc of distilled water, mix the solution by magnetic mixer, with 2 cm in magnet's size and 230 rpm, until it solve very well. Now, we pour some acetone in the buret and then open the faucet and adds the acetone to salt solution drop by drop. And at the same time, measure the time with chronometer, so that after each drop, we wait almost 5 minutes, to dull the solution. When the solution to be dull, we write the time of dulling. This time is induction time. By doing of Batch crystallization process, we can decrease the solvation of potassium sulfate in the water. Using a anti solvent, cause to decrease the solvation of solute material, and as a result to be deposit, that is acetone consider as a anti solvent for potassium sulfate solution in water, and on the other side, water and acetone solve to each other in any ratio. According to volatile solution, the limitation of increasing the mixture rotation, prevent to increase the mechanical power, so mixture rotation is constant for all of the samples. In tests, we cannot increase the rotation of mixture due to vapor, in determination of solvation test, so the mixture rotation is constant in the inductive crystallization and other stages. However, the temperature increasing and solvent extent help to resolve the potassium sulfate in the water, but in this way, both of these quantities are constant. The effective element that is the extent of anti solvent remained. And we can access to the best conditions to produce crystal according to present facilities with changing this element. So, we write the consuming volume of acetone anti solvent until the solution to be dull. It should be care, doesn't change the environment temperature

during the test and that's better is worked at 25-26° C temperature ranges. Now, we pour the dull solution in the sampling dish and wait until the dull solution become transparent. Almost after 6 hours, it is clear that solution become transparent. Now, we take almost 5 cc of this transparent solution and put it on the heater at 100° C. After heating, we measure pure amount of remainder salt on basis gram and show it by C* (saturation concentration of remainder salt results of transparent solution according to g / cc of solution) and we use it in the calculations. This concentration is the same saturation concentration that we can determine the amount of super saturation by use of concentration and solvation. In the next experiment, we solve the 0.7 gram from sodium citrate and CTAB surfactant additives in 1 liter distilled water and take the different amounts of them from this solution and add to salt solution in different concentrations that we use the salt solution as C (salt concentration according to g / cc of solution) in the calculations. So, we use it by acetone anti solvent and determine the consuming volume and also the time dulling or induction time in solution. Next, similar to last test, we put the dull solution in the sampling dish. After passing 13 hours for surfactant and 11 hours for sodium citrate,   the solution is transparent and then put the solution on the heater and measure the remainder salt in results of vapor and use it as C* (saturation concentration of remainder salt result of vapor on   g / cc of solution) in the calculation. Additionally to make sure from the formation of potassium sulfate nano particles in result of adding the cetyl tri methyl ammonium bromide surfactant, has been taken a photograph from considering sample, by use of Transmission Electronic Microscope.
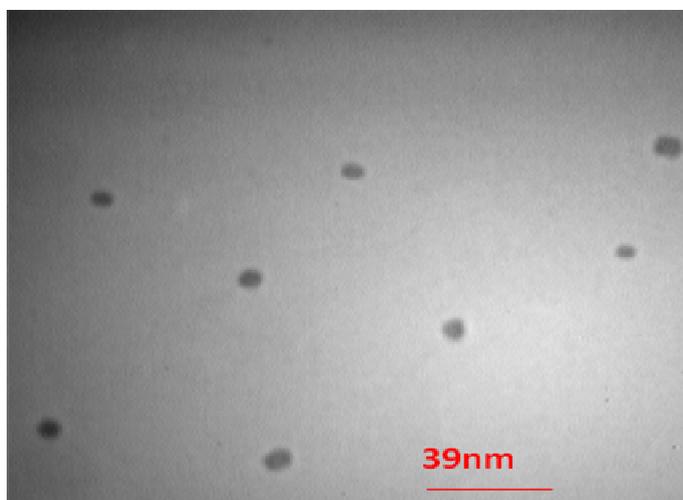
Figure 1.   The pictures of TEM formatted nano particles at 25° C at the presence of cetyl tri methyl ammonium bromide surfactant

## 4. Results
4.1. Measuring the induction time
We measured the induction time for potassium sulfate nano particles at 25° C and different super saturation Also, the related graphs, are drawn according to classic theory of nucleation.
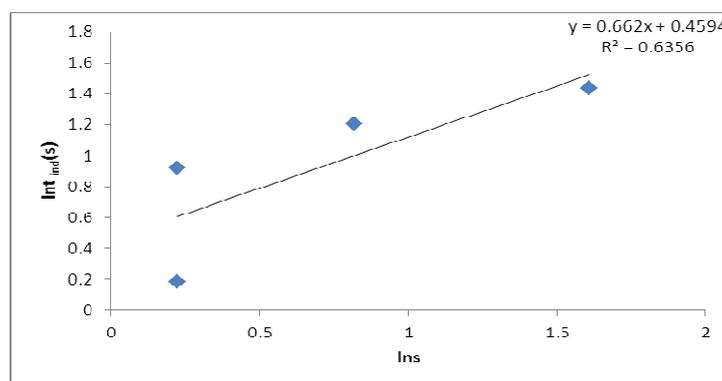
Table 1. The amounts of induction time, super saturation and consuming volume of acetone anti solvent for different concentrations of potassium sulfate

$C(\frac{g}{cc})$ concentration of solution	$t_{ind}(s)$ induction time	$C^*(\frac{g}{cc})$ solvation	$V(cc)$ Consuming volume	$S= \frac{C}{C^*}$ Super saturation
0.7	1.20	0.56	1.2	1.25
0.6	2.50	0.48	1.6	1.25
0.5	3.34	0.22	1.9	2.27
0.4	4.21	0.08	2.7	5

The following graphs, has been drawn according to gained data in table (1) to determine the nucleation.
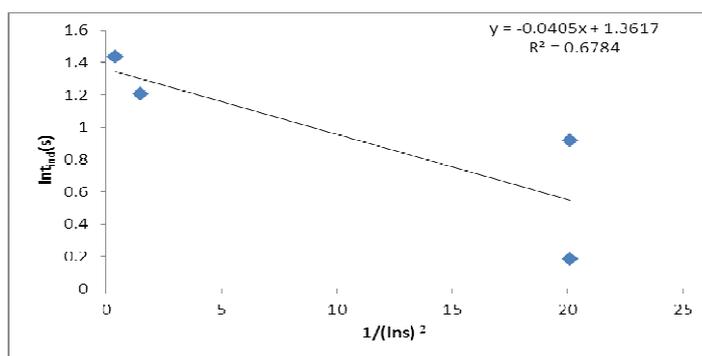
Figure 2. drawing of lnt_{ind}, in front of $1/(lns)^2$ at 25° C

Figure 3. drawing of lnt_{ind}, in front of lns at 25° C
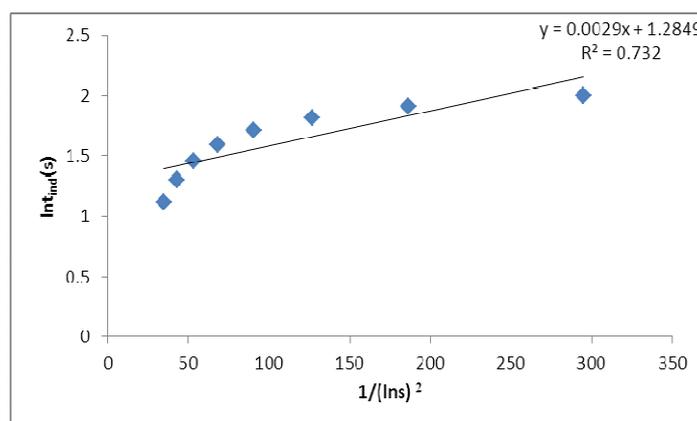
Considering to table(1), when super saturation increased, the induction time increased too,

and while the salt concentration   of   potassium sulfate decreased and the induction time increased, adding to consuming volume of acetone for nucleation. we can conclude from above graphs that they don't follow from classic theory of nucleation and probably, the nucleation occurs simultaneously.

Table 2. The amounts of induction time, super saturation and consuming volume of acetone anti solvent by adding of cetyl tri methyl ammonium bromide surfactant for different concentrations of potassium sulfate solution

$C(\frac{g}{cc})$ concentration of solution	$t_{ind}(s)$ induction time	$C^*(\frac{g}{cc})$ solvati on	$V(cc)$ Consuming volume	$S= \frac{C}{C^*}$ Super saturation
1	7.4	0.66	2.1	1.060
0.9	6.78	0.65	2.01	1.076
0.8	6.16	0.64	1.92	1.093
0.7	5.54	0.63	1.83	1.111
0.6	4.92	0.62	1.74	1.129
0.5	4.3	0.61	1.65	1.147
0.4	3.68	0.6	1.56	1.166
0.3	3.06	0.59	1.47	1.186

The following graphs, has been drawn according to gained data in table (2) to determine the nucleation.

Figure 4. drawing of lnt_{ind} in front of $1/(lns)^2$ at 25 ° C for different concentrations of potassium sulfate
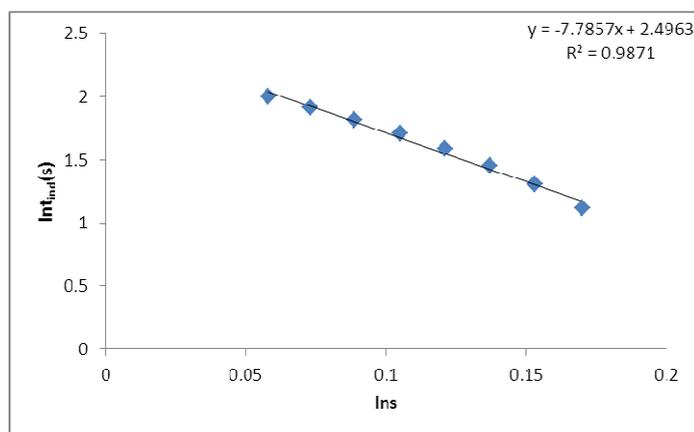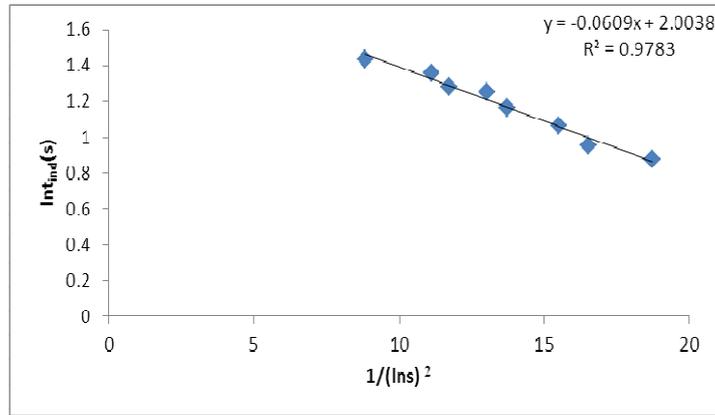
Figure 5. drawing of $\ln t_{ind}$ in front of lns at 25 ° C for different concentrations of potassium sulfate

According to table (2), when super saturation increased, the induction time decreased and the above graphs, indicating that, there is possibility to form of nucleus in mixing stage of nucleation and to anticipate the classic theory of nucleation very well. According to the correlation coefficient results of above graphs, due to the amount of coefficient in graph related to secondary nucleation is more than primary nucleation, so we may conclude this way that, secondary nucleation overcomes upon primary nucleation.

Table 3. The amount of induction time, super saturation and consuming volume of acetone anti solvent by adding of sodium citrate for different concentrations of potassium sulfate solution

$C(\frac{g}{cc})$ concentration of solution	$t_{ind}(s)$ induction time	$C^*(\frac{g}{cc})$ solvation	$V(cc)$ Consuming volume	$S= \frac{C}{C^*}$ Super saturation
1	4.20	0.5	4	1.4
0.9	3.9	0.516	3.7	1.35
0.8	3.6	0.522	3.5	1.34
0.7	3.5	0.528	3.2	1.32
0.6	3.2	0.534	2.8	1.31
0.5	2.9	0.54	2.6	1.29
0.4	2.6	0.546	2.3	1.28
0.3	2.4	0.552	2.1	1.26

The following graph, has been drawn according to gained data in table (3), to determine the nucleation.

Figure 6. Drawing of $\ln t_{ind}$ in front of $1/(\ln s)^2$ at 25 ° C for different concentrations of potassium sulfate
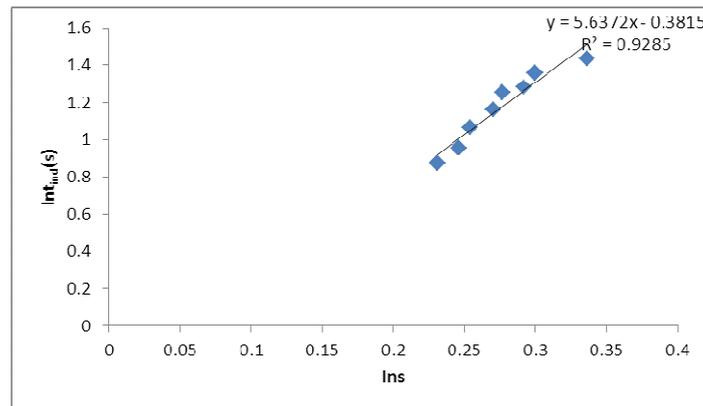
Figure 7. drawing of $\ln t_{ind}$ in front of $\ln s$ at 25 ° C for different concentrations of potassium sulfate

According to above graphs, we can understand that, the gained results is not according to classic theory of nucleation and may not distinguish which type of the nucleation overcomes on each other.

5. The effect of super saturation on the induction time

In the study of the induction time in production site of potassium sulfate nano particles, there are laboratory results of the induction time in different super saturation and at 25 ° C at the presence of cetyl tri methyl ammonium bromide surfactant and sodium citrate in above graphs. Graph of $\ln t_{ind}$ in front of $1/(\ln s)^2$ drew in order to comparison the laboratory results of induction time by model predictions. The results indicating that, when CTAB surfactant used, the induction time decreased by adding the amount of super saturation and the induction time decreased by reducing the amount of super saturation at the presence of sodium citrate. So, we can conclude that the presence of additives can

change the induction time by influence on the super saturation. The possible reason of the observations is the way of additives relation with the crystal surface of potassium sulfate. It seems how to cover the surfactant, don't prevent to join the sulfate solution to crystal surface of this material, and this event accelerate by adding super saturation (driving force of penetration of solution to crystal surface), and decreased the induction time. But about sodium citrate, there is some relations of the solution phase between sodium citrate and potassium sulfate probably, which its result is formation of complex in solution. This complex doesn't have enough penetration speed due to heaviness and a lot volume and by increasing the sulfate concentration of solution, more amount of the complex is formed and lead to Increasing the penetration hardness and decreasing the induction time. Contrary, by decreasing the concentration of sulfate in solution, the complex amount is less and sulfate of solution displaced in form of non-complexity and by more penetration speed and decrease the induction time. Also, the results of measuring the induction time show that, at the presence of CTAB and sodium citrate additives, The scope of induction time whether in the high super saturation or low super saturation is higher than in the position that don't use the additives . Also, the above tables, indicating that, by decreasing the additives concentration, decline the induction time and consuming volume of acetone for nucleation. Additionally have seen by increasing of consuming volume of acetone anti solvent, the induction time is higher and the time used from CTAB surfactant and sodium citrate additives, the induction time decrease by decline the volume of acetone consumption. Apparently, if the anti solvent adds to solvent, the size of particles will be large, due to low speed of nucleation. Also the mixture speed has a great effect on the particles size. The high speed of mixture caused to decrease the particles size and collecting them [5].
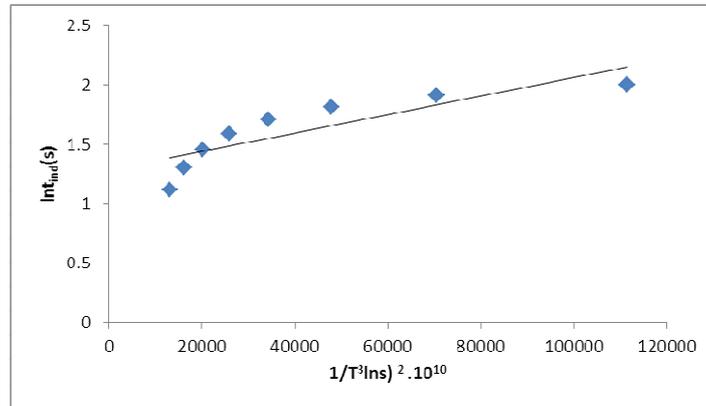
6. The calculation of surface tension
We can calculate the surface tension of the particles by measuring the induction time. In this test, the surface tension of particles at 25 ° C, calculated by use of lines gradient for graph of $\ln t_{ind}$ in front of $1/T^3 (\ln s)^2$, according to following equation:

$$\gamma = k \left(\frac{3A_1}{16\pi V_m^2} \right)^{\frac{1}{3}} \tag{9}$$

In equation (9), Boltzmann constant is k= 1.3805 ×10 [-23] J/k, A is the lines gradient of graph and atomic volume of potassium sulfate is V_m=1.087×10 [-28] m^3, that calculated from $V_m = \frac{M}{\rho N_A}$ equation. N_A= 6.023×10^{23} no./mol is Avogadro number, ρ = 2660 kg/m^3 equal to the density of potassium sulfate and M= 0.1742 kg/ mol is molecular mass.

Absolutely, the surface tension of the low solution salts is at the range 10-200 mJ / m^2. The amounts that gain for surface tension in potassium sulfate nano particles is smaller than this values. However, the results expected, because we know that potassium sulfate has a high solvation and the surface tension in this kinds of salts is less than 10-200 mJ / m^2. For example, the amount of 580 mJ / m^2, suggested for surface tension of gold nanoparticles, that shows its low salvation [6].

Figure 8. The measuring data of $\ln t_{ind}$ in front of $1/T^3(\ln s)^2$ at 25 ° C at the presence of surfactant

Table 4. The calculated amounts in surface tension of potassium sulfate nano particles at the presence of surfactant at 25 ° C according to mJ /m^2

$C(\frac{g}{cc})$ concentration of solution	$\gamma(mJ/m^2)$ Surface tension
0.7	0.657
0.6	1.708
0.5	1.711
0.4	2.97

7. Conclusion

Whereas in the present studies, always more care was about the nucleation to factors like super saturation and surface tension, in this research the induction time of potassium sulfate nano   particles was measured   at 25 ° C and different super saturation .Also the surface tension of potassium sulfate nano particles,   measured by use of classic theory of nucleation. According to the results of measuring the induction time and the calculation of surface tension we would have:

Application of acetone anti solvent in the production of potassium sulfate particles:

. The induction time increases, by adding the amount of super saturation.
.The consuming volume of acetone for nucleation, increases by decrease the concentration of potassium sulfate salt.
. Comparison of the results with models show that, the primary and secondary nucleation happen simultaneously and is not accordance with classic theory of nucleation.
The induction time increases, by adding the consuming volume of acetone.

Application of CTAB surfactant in different concentrations of potassium sulfate:

.The induction time decreases by increasing the amount of super saturation.

.The induction time and the consuming volume of acetone for nucleation decrease, by lowing   the additives concentration.

. Comparison   of   results with models shows that, there is possibility to primary and secondary nucleation continuously and predict the classic theory of nucleation very well.

. By considering to observations result of experiments, we defined that the solution remains dull in a long time at the presence of surfactant which it indicating the more stability of nano particles with respect to other additives.

.By researching on potassium sulfate particles and CTAB surfactant additive in primary nucleation and calculation the surface tension of them, determined that the surface tension decreased, by adding the surfactant in the more concentrations of potassium sulfate that indicating the rate of nucleation increases.

Application of sodium citrate additive in different concentrations of potassium sulfate:

. The induction time decreases, by lowing   the   amount of super saturation.

. The induction time decreases, by lowing   the   consuming volume of acetone.

.Comparison of results with models show that the primary and secondary   nucleation happen   simultaneously   and is not accordance with the classic theory of nucleation.

. The induction time decreases, by lowing the additives concentrations.

.According to experiments, we can conclude that, the stability of nano particles at the presence of sodium citrate is more than the position without additives.

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