Original Research Article

An empirical technique for prediction of nucleation mechanism and interfacial tension of potassium chloride nanoparticles

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ABSTRACT

Prediction of the nucleation mechanism is one of the most critical factors in the design of a crystallization system. Information about the nucleation mechanism helps to control the size, shape, size distribution, and purity of the produced crystals. When the crystallization method is used for producing nanoparticles, the nucleation mechanism should be predicted. In this study, an empirical correlation based on the induction time, classical nucleation theory, and Kashchive model is used to determine the nucleation mechanism. Nanoparticles are produced in the presence of Cetyl Trimethyl Ammonium Bromide (CTAB) and the effect of CTAB on the induction time and the interfacial tensions of potassium chloride nanoparticles have been investigated. The obtained results demonstrated that the nucleation mechanism of potassium chloride nanoparticles is heterogeneous. This method is simple and can be applied at ambient

conditions for synthesis other mineral nanoparticles. It can also be applied to study the induction time with high accuracy.

Keywords: Nucleation mechanism, Potassium chloride, Nanoparticles, Induction time, Interfacial tension

Introduction

Among the numerous ways of producing nanoparticles, one of the important methods is the precipitation from the liquid phase, which is based on crystallization. This method is very common due to the easier control of the size and the morphology of the produced nanoparticles [1]. The induced crystallization is a well-established precipitation method, which has been known for decades. In this process, a solute precipitates from a primary solvent, by adding a second solvent (anti-solvent), in which the solute is relatively insoluble. The anti-solvent is miscible with the primary solvent and decreases the solubility of the solute in the binary mixture, which ultimately leads to precipitation [2].

In crystallization processes, the induction time is an empirical approach to study the nucleation kinetics. It can be defined as the time between the achievement of supersaturation and the appearance of detectable changes in the physical properties of the solution due to the formation of the new nucleus. This change can occur in the colour, conductivity, or viscosity of the solution [3].

The induction time consists of three parts as follows: 1. The relaxation time (tr), which is the required time to achieve a quasi-steady-state distribution of molecular clusters; 2. The time needed for the formation of stable nuclei (t_n); 3. The time required for the growth of the nuclei (tg) and appearance of detectable changes in the system. In a low-viscous aqueous solution, the relaxation time is very short [4] and therefore, the induction time is expressed as below:

$$t_{ind} = t_n + t_g \tag{1}$$

The application of the induction time for expressing the nucleation was first done by Nielsen [5]. Following him, many other surveys have been so far carried out on the effect of the operating parameters, including supersaturation ratio [6], temperature [7], seed , mixing [8], solvent [9], and additive[10]. The conducted investigations have demonstrated that the increase of supersaturation can cause decrease the induction time and therefore, creating a long induction time will need a low supersaturation. Using a long induction time minimizes the calculation errors in the nucleation relations. It should be indicated that the induced crystallization with a good control, in addition to anti-solvent, is the best method for creating a low supersaturation. The effect of the supersaturation ratio and temperature on the induction time of the formation of Ag nanoparticles was studied by Ghader and Manteghian [7]. They used a scattered-light method to determine the induction time. In a similar study, the induction times of the nucleation of calcium carbonate were measured by the conductivity method; in their research, the cluster coagulation model and the classical nucleation theory were employed for the prediction of the interfacial tension [6]. In addition, the induction time has been so far applied for determining the kinetics of the nucleation of gas hydrates. Kashchiev and Firoozabadi studied the effect of additive on the nucleation of methane, ethane, and cyclopropane hydrates using an empirical model [11].

The aim of the current paper is to study the nucleation mechanism of the formation of potassium chloride nanoparticles in the presence of a stabilizing agent. The supersaturation is created by induced crystallization and the induction time is measured by changing the conductivity of the solution. This method can be used to determine the nucleation mechanism and the interfacial tension of nanoparticles. Furthermore, a good control on the addition of the anti-solvent can provide an opportunity for an exact observation, which will significantly reduce the measured error of the induction time. Mineral nanoparticles can be produced by this innovative technique with the least expenditure of energy. Finally, the results of this research can be applied in the design of crystallization system for producing nanoparticles on industrial scale.

Theory

Generally, there are two types of nucleation in crystallization systems. The "primary nucleation" occurs without the presence of crystals in the supersaturated system. On the other side, the nuclei

are often generated in the vicinity of the crystals, present in a supersaturated solution. This behavior is referred to as the "secondary nucleation" [3].

According to the classical nucleation theory, if the nucleation mechanism is the homogeneous primary, the nucleation rate will be expressed as follows:

$$J = K \exp\left(-\frac{16\pi\gamma^3 v_m^2}{3(kT)^3 (\ln S)^2}\right) \qquad (2)$$

Where K is the nucleation constant, S is the supersaturation ratio, γ is the interfacial tension, T is the temperature, and k is the Boltzmann constant. V_m is the molecular volume calculated from $V_m = M / (\rho N_A)$, where M is the molecular weight, ρ is the density of particles, and N_A is the Avogadro number.

The induction time is assumed to be inversely proportional to the nucleation rate; hence:

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

Thus, if the nucleation is the homogeneous primary, the plot of ln (tind) against $1/(\ln S)^2$ should yield a straight line. If "A" is the slope of the line of ln (tind) plotted against $1/(T^3 \ln^2 S)$, the interfacial tension can be calculated by the following relation:

$$\gamma = k\left(\frac{3A}{16\pi v_m^2}\right)^{\frac{1}{3}} \qquad (4)$$

Kashchiev and Firoozabadi developed a relation for the heterogeneous nucleation, based on the induction time, which can be expressed with the following form [11]:

$$t_{ind} = K\left[S(S-1)^{3m}\right]^{-\frac{1}{1+3m}} \exp\left[\frac{Y}{(1+3m)\ln^2 S}\right] \qquad (5)$$

Where "m" is the parameter, expressing the relationship between the radius of the primary nuclei and time ($t = r^m$), and "Y" is as below:

$$Y = \frac{4c^3 v^2 \gamma^3}{27(kT)^3} \qquad (6)$$

Where "c" is the shape factor and is equal to 36π for spherical nuclei. Kashchiev reported the value of "m", as a result of the growth of the nuclei, either 1, 1/2, or 1/3. If we assume m =1, Eq. 5 can be expressed as below:

$$\ln\left[t_{ind}S^{\frac{1}{4}}(S-1)^{\frac{3}{4}}\right] = \ln K + \frac{Y}{4\ln^2 S} \tag{7}$$

And with m=1/2:

$$\ln\left[t_{ind}S^{\frac{2}{5}}(S-1)^{\frac{3}{5}}\right] = \ln K + \frac{2Y}{5\ln^2 S} \tag{8}$$

And When m=1/3,

$$\ln\left[t_{ind}S^{\frac{1}{2}}(S-1)^{\frac{1}{2}}\right] = \ln K + \frac{Y}{2\ln^2 S} \tag{9}$$

The best value of "m" can be achieved by the best fitting of the experimental data on these relations. Subsequently, "Y" can be calculated from the slope of the specified plot. But if the nucleation mechanism is the secondary, the nucleation rate will be expressed by the following empirical formula[12]:

$$J=KS^n \tag{10}$$

Where K is constant and "n" is the nucleation order. This relation for the induction time is as follows:

$$t_{ind}=KS^{-n} \tag{11}$$

Therefore, the plot of ln (t_{ind}) against ln S yields a straight line, if the secondary nucleation occurs. Then, the nucleation order can be calculated from the slope of this plot. In a crystallization system, all of the nucleation mechanisms are involved. In order to determine the dominant nucleation mechanism, all the described plots are drawn and the one with a better fitting on the experimental data will be selected as the dominant mechanism of nucleation.
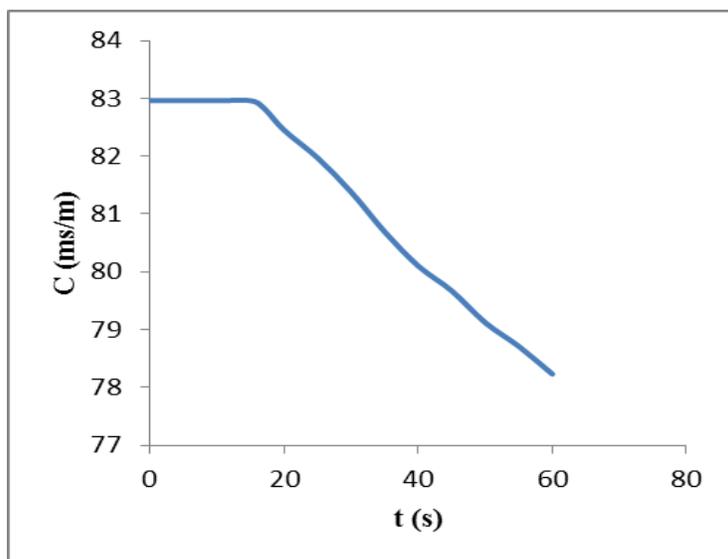
Experimental

General

For the induced crystallization, the anti-solvent should be soluble in the solvent and the solute is dissolved in it. In this study, acetone and water were respectively selected as the solvent and anti-solvent. Therefore, 0.2 g of potassium chloride was dissolved in 10 ml water and the solution was stirred for 10 minutes at 500 rpm. Then, a drop of acetone (anti-solvent) was added and the chronometer was activated. By the addition of acetone to the aqueous solution, the solubility of potassium chloride was reduced and it was removed from the solution phase. After 5 minutes, when no change appeared in the solution conductivity, the chronometer was reset and another drop of acetone was added. Thus, the chronometer got started.

In practice, the above-described process must be repeated until a change in the solution conductivity is detected. A change in the conductivity of the solution indicates that the particles have been removed from the solution phase and nanoparticles have been created. The time period elapsed from the moment of the last drop addition is reported as the induction time. In addition, the initial concentration (C) is determined by dividing the weight of potassium chloride, initially added to the container, to the final solution volume (Water + Acetone). The equilibrium concentration (C*) of potassium chloride solution is also measured by the titration method with silver nitrate, in the presence of potassium chromate as the detector. During the test, the temperature of the solution was kept constant at 25 °C. This process was repeated in the range of 0.4-1 g of the initial weight of potassium chloride.

Due to the high surface energy, nanoparticles were agglomerated. In the next step, Cetyl Trimethyl Ammonium Bromide (CTAB) was used for the stabilization of nanoparticles. For this purpose, 1 mM aqueous solution of CTAB was prepared and a specific volume of this solution was added to the main container. Potassium chloride, actone and CTAB were supplied by Merck..

Results and discussion

Reducing the solution conductivity at the time of nanoparticles formation has been shown in Figure 1.


Figure 1. Conductivity-time curve of potassium chloride solution at S=1.13

Results show induction time increase with decreasing supersaturation. The obtained experimental results of induction time in various supersaturation ratios have been demonstrated in Figure 2. For determination of nucleation mechanism, experimental results have been drawn based on Eq. (3) , (5) and (6).
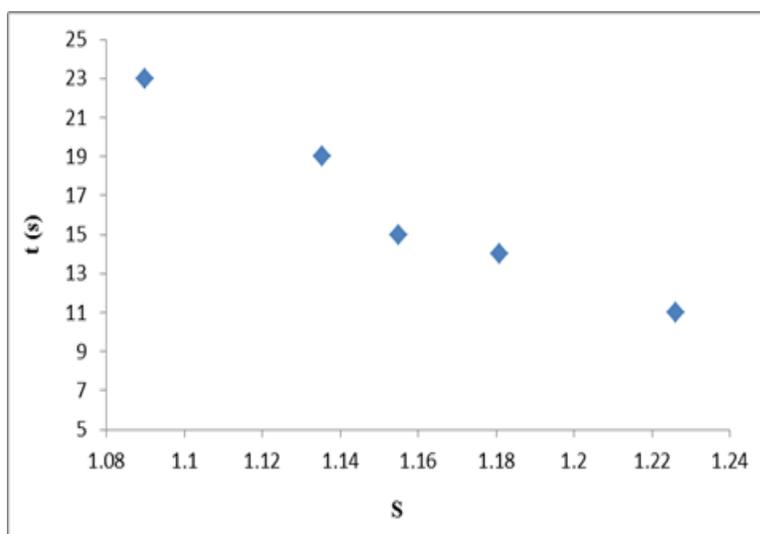
Figure 2. Experimental data of induction time of potassium chloride nanoparticles at 25°C

To determine the homogeneous nucleation the plot of $\ln(t_{ind})$ against $1/(\ln^2 S)$ has been drawn.
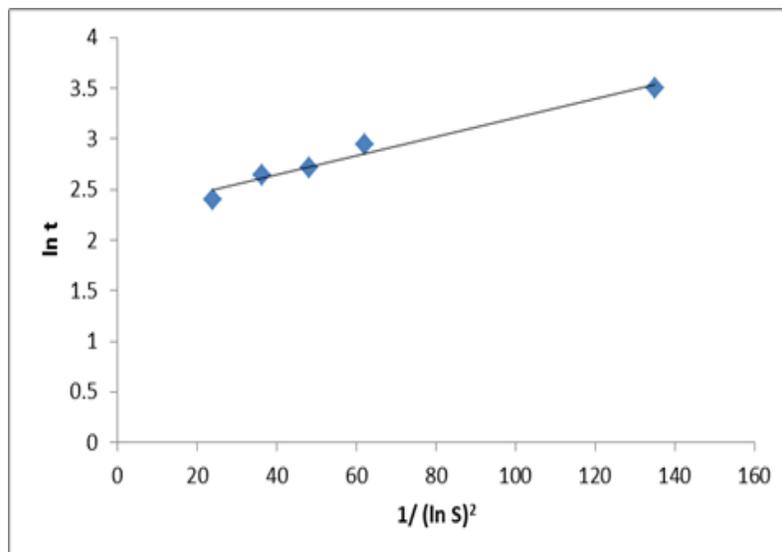
Figure 3. Measured data of ln t_{ind} vs $1/(\ln S)^2$ at 25°C

To use relation (5), the best value of "m" should be determined. So, the plot of ln[tind S1/4(S-1)3/4], ln[tind S2/5(S-1)3/5] and ln[tind S1/2(S-1)1/2] against 1/ ln2S have been drawn and the results show best fitting achieve when m=1/3.

**Table 1**. correlation coefficient to find growth factor in Kashchive model

m	R^2
1	0.945
$\dfrac{1}{2}$	0.9687
$\dfrac{1}{3}$	0.9746

To investigate the secondary nucleation mechanism, the plot of ln(tind) against ln S has been drawn. The R2 values of these liner correlations have been shown in table 2. Compares data of the correlation coefficient and better fitting on the Kashchive model show that heterogeneous nucleation is the dominant mechanism in potassium chloride nanoparticles formation. Due to dust particles in the environment that act as nucleation centers, the dominance of heterogeneous nucleation is explainable.

Table 2. Correlation coefficient to find growth factor in Kashchive model

Nucleation mechanism	R^2
Primary homogenous	0.9705
Primary heterogeneous	0.9746
Secondary	0.9337

After determining of nucleation mechanism interfacial tension of potassium chloride nanoparticles can be calculated. There are very little data for interfacial tension of potassium chloride particles. Figure 4, represents plot of $\ln[t_{ind} S^{1/2}(S-1)^{1/2}]$ against $1/\ln^2 S$ that used to calculate interfacial tension.
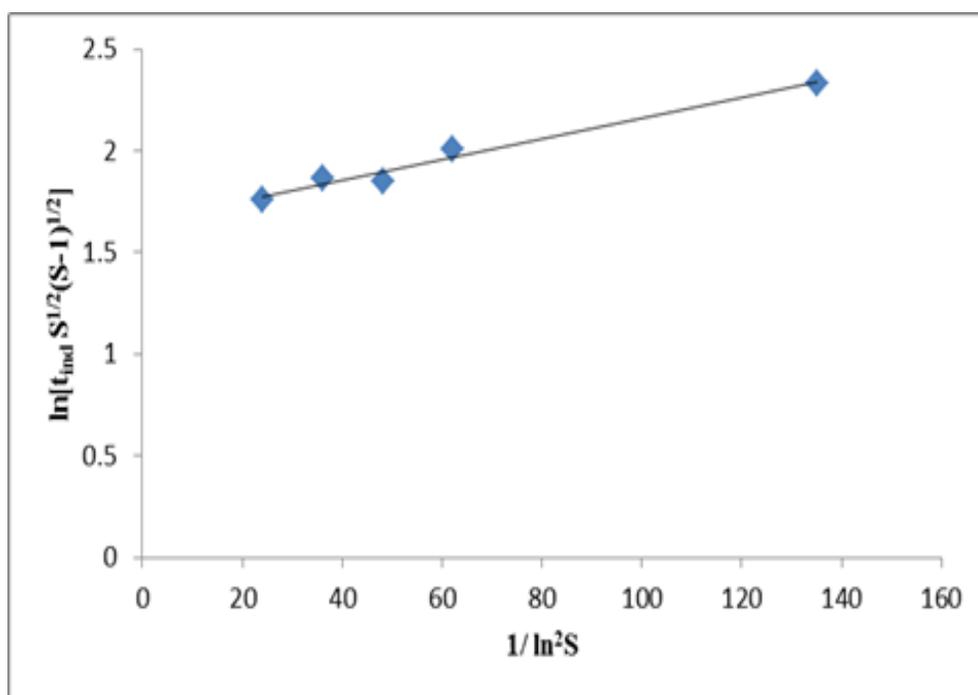
Figure 4. Experimental data for Kashchive model with m=1/3

The slope of this line is 51*10-4. To calculate interfacial tension from Eq.5 the following values have been used: M =74.55*10-3 kg/mol, ρ=1990 kg/m3, k=1.38*10-23J/k , V_m=6.22*10-29. The estimated value of interfacial tension is 2.22 mJ.m^{-2}. Considering high solubility of potassium chloride in water, the result of this study seems reasonable. For calculating interfacial tension a correlation is represented by Bennema(Bennema and Sohnel):

$$\gamma = kTV_m^{-2/3}0.25(0.7 - \ln x^*) \tag{12}$$

And Mersmann [14]:

$$\gamma = 0.414kT(C_sN_A)^{2/3}\ln\frac{C_s}{C^*} \tag{13}$$

In the calculation of the interfacial tension, x* is the solubility mole fraction and Cs is the molar concentration of the solute in solid. Furthermore, Alexander [15] and Sohnel [16] reported a value for the interfacial tension of potassium chloride in aqueous solution.

The results are shown in Table 3 for comparison purposes.

Table 3. Interfacial tension estimated by this work and other researchers

Interfacial tension (mJ.m^{-2})	Experimental
2.22	This work
21.15	Eq.12
18.69	Eq.13
2.19	Alexander et al, 2008
2.73	Bennema & Söhnel,1990

The value estimated in the present work is smaller than the value estimated in Eq. 12 and Eq. 13. However, it is very close to the value, reported by other researchers.

CTAB is a surfactant that electrostatically stabilizes nanoparticles. In this study, the effect of the CTAB concentration on the interfacial tension of nanoparticles was investigated. Therefore, different concentrations of the substance were added to the solution. The induction time and the supersaturation were measured the same as the previous step. Table 4 presents the estimated interfacial tension of the experimental data for various CTAB concentrations.

Table 4. Estimated interfacial tension in the presence of CTAB

Concentration of CTAB (mM)	Interfacial tension (mJ.m^{-2})
0.2	2.13
0.4	1.96
0.6	1.81
0.8	1.73
1	1.32

The results disclosed that by increasing the CTAB concentration, the interfacial tension of nanoparticles was reduced. According the fact that the reduction of the interfacial tension is a feature of surfactants [17], increasing the CTAB concentration can cause to increase the number of molecules of this surfactant (surrounding the nanoparticles), which consequently reduces the interfacial tension between the nanoparticles and the solvent.

In order to measure the interfacial tension of potassium chloride nanoparticles, a good correlation was presented in relation (14) based on the experimental data.

$$\gamma = -0.9225 C_{CTAB} + 2.3477 \qquad (14)$$

In this relation, the correlation coefficient (R^2) was 0.927.

According to the definition, the induction time is generally determined as soon as a detectable physical change in the solution occurs. In the visual determination of the induction time, the turbidity of the solution was the criterion. In fact, by adding the anti-solvent to the aqueous solution of potassium chloride, the solution was supersaturated and after a certain period of time,

the nanoparticles were created and the solution became turbid. The comparison data for the visual and conductivity-based determination of the induction time are shown in Figure 5.
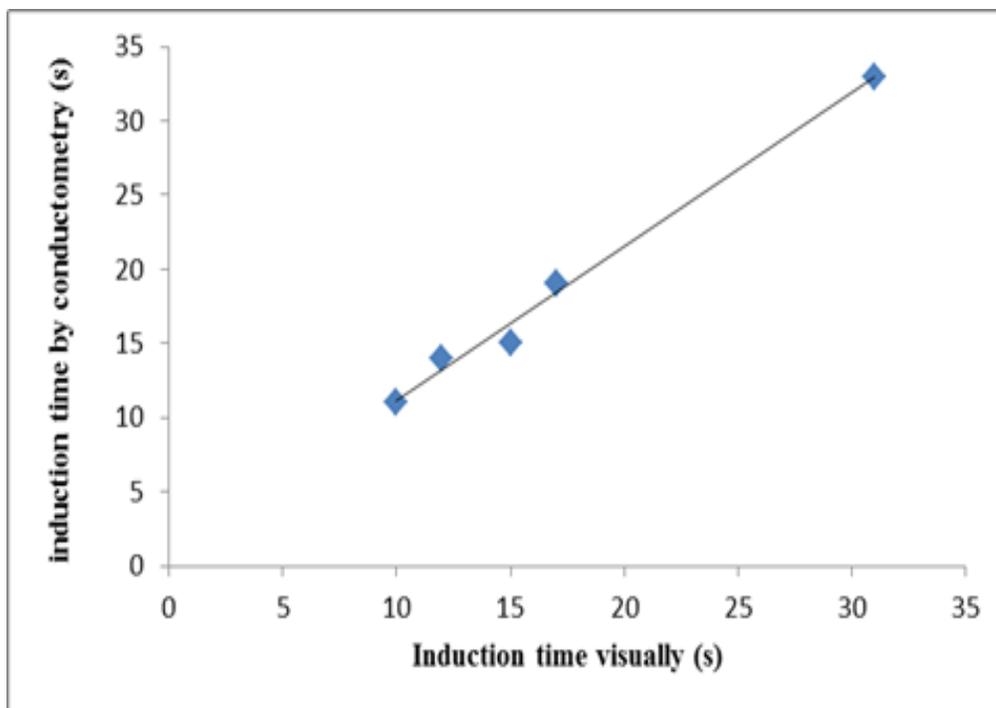
**Figure 5.** Compared data in visually and conductometry method

The results obtained from the visual measurement and conductivity were very close, but the slope of the curve was greater than 1 (Slope = 1.04). This slope implies that the formation of nanoparticles can be detected earlier using conductivity and a short period should elapse until the particles reach to a detectable size.

The formed nanoparticles were characterized by Dynamic Light Scattering (DLS) and Field-emission Scanning Electron Microscope (FESEM) in the presence of CTAB.The achieved result indicated that the mean size of the nanoparticles formed was approximately 30-40 nm in diameter, and the nanoparticles had a spherical shape.
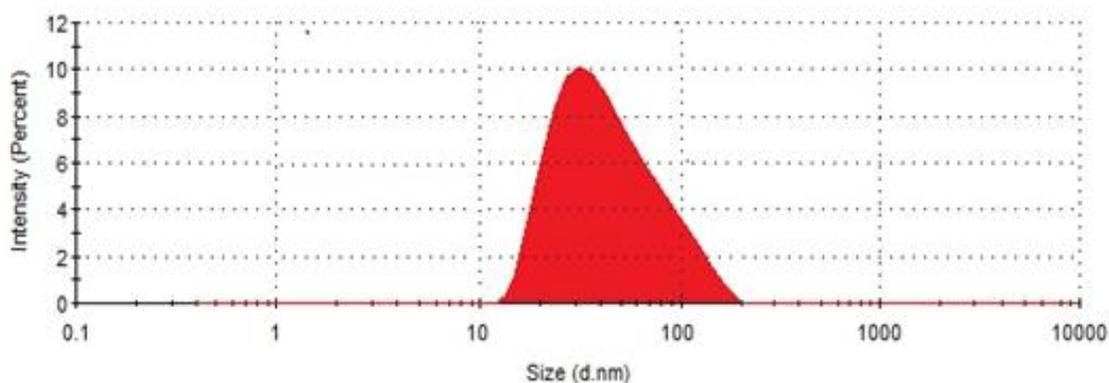
Figure 6. Distribution size curve of the potassium chloride noparticles

The distribution of particles was sharp and their shape was uniform.
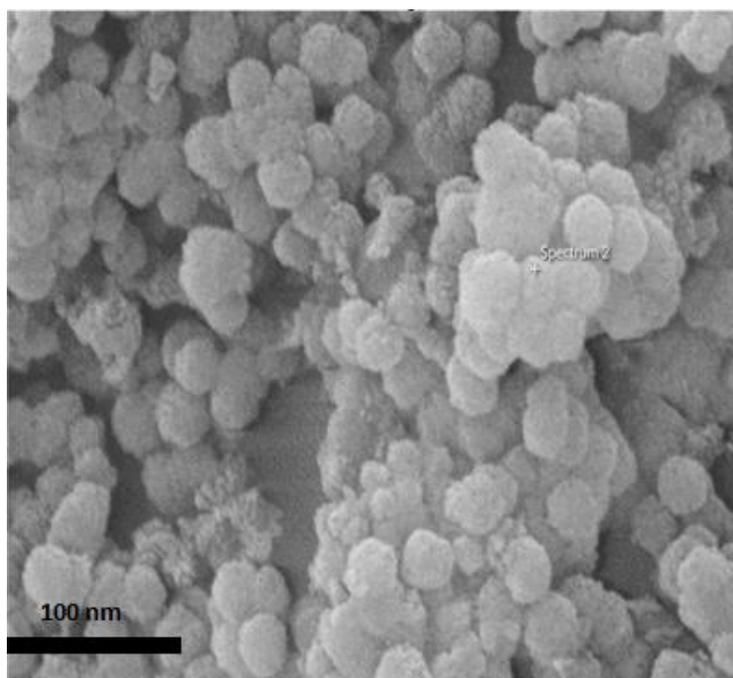
Figure 7. FESEM view of potassium chloride nanoparticles

CTAB was an appropriate surfactant for the synthesis of potassium chloride nanoparticles

Conclusion

In this research, potassium chloride nanoparticles were synthesized by the anti-solvent-induced precipitation. This method is very simple and can be applied for the nanoparticle synthesis of

other salts. In this study, an empirical approach based on the induction time was employed to determine the nucleation mechanism. The obtained results demonstrated that the nucleation mechanism of potassium chloride nanoparticles is heterogeneous and the interfacial tension of particles is 2.22 mJ.m-2. Moreover, it was realized that increasing the concentration of CTAB decreases the interfacial tension. Furthermore, this method can be used to determine the nucleation mechanism and the interfacial tension of nanoparticles, for which there are no research data.

Acknowledgments

References

[1]   E. L. Wolf, Nanophysics and nanotechnology: An introduction to modern concepts in nanoscience. John Wiley & Sons, (2008).

[2]   A. Myerson, Handbook of industrial crystallization. Butterworth-Heinemann, (2002).

[3]   J. W. Mullin, Crystallization. Butterworth-Heinemann, (2001).

[4]   J. Sohnel, O. Mullin, *Colloids. Surf. A.*, 123, 43 (1998).

[5]   A. E. Nielsen, O. Söhnel, *J. Cryst. Growth.*, 11, 242 (1971).

[6]   C. Y. Tai, W. C. Chien, *Chem. Eng. Sci.*, 58, 3233 (2003).

[7]   S. Ghader, M. Manteghian, M. Kokabi, R. S. Mamoory, *Chem. eng. technol.*, 30, 1129 (2003).

[8]   C. Xu, D. Liu, W. Chen, *J. Cryst. Growth.*, 310, 4138 (2008).

[9]   W. J. HAN Jiabin, *Chinese. J. Chem. Eng.*, 18, 767 (2010).

[10]   M. C. van der Leeden, D. Kashchiev, G. M. van Rosmalen, *J. Cryst. Growth.,* 130, 221 (1993).

[11]   D. Kashchiev, A. Firoozabadi, *J. Cryst. Growth.*, 250, 499 (2003).

[12]   A. Mersmann, *Dry. Technol.*, 13, 1037, (1995).

[13]   J. Sohnel, O and Mullin, *J. Cryst. Growth.*, 44,377 (1978).

[14]   A. Mersmann, *Chem. Eng. Process.*, 38, 345 (1999).

[15]   A. J. Alexander, P. J. Camp, *Cryst. Growth. Des.*, 9. 958 (2008).

[16]   P. Bennema, O. Söhnel, *J. cryst. Growth.*, 102, 547 (1990).

[17]   R. J. Farn, Chemistry and technology of surfactants. John Wiley & Sons (2008).