Kinetics of first stage of formation magnetite nanoparticles prepared by chemical precipitation method

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Abstract. First stage of formation magnetite nanoparticles is described by kinetics equation. Solution of kinetics equation is Gauss function. Mean value and standard deviation of Gauss function are \( x = \frac{Kt}{4r_0} \), \( \sigma = \frac{Dt}{2r_0} \). Critical size, determinant of collapse and growth of nanoparticles are determined. It’s showed nanoparticles less critical size may be is collapsed, bigger – grow. The dependence of the size and speed of the growth size on time are determined.

1. Introduction
Investigation of growth mechanism of nanoparticles is present large scientific and practical interest. As, nanoparticles with given size and characteristics are required in nanotechnology. Nanoparticles growth mechanism determines distribution function of nanoparticles on size, physical-chemical properties of nanoparticles medium and etc. Because of, known of growth mechanism give possibility control of preparation of nanoparticles and to obtain nanoparticles with given parameters (mean diameter, standard deviation, coefficient polydispersity and other) and characteristics (magnetic moment).
Nanoparticles growth mechanism is enough complex process and depended from many conditions (temperature, viscosity, concentration of medium and etc.). Conditions determinant of nanoparticle growth are changed in the dependence on method preparation of nanoparticles. Mechanisms of formation of nanoparticles, preparation by chemical precipitation, laser photolysis, and condensation metal atoms method are different [1-5].
Two stages of nanoparticles growth are suggested in preparation of nanoparticles by chemical precipitation method [1-3,7-12]. In the first stage, nanoparticles growth to occur due to sequent joining of atoms or molecules to nucleus. In the second stage to occur coagulation of formatted nanoparticles. In the literature, in base second stage of nanoparticle (water drop, aerosol, gel and etc.) growth is described [1-3,7-12]. Second stage of nanoparticles growth is described by diffusion equation and it is solved at different boundary conditions. Authors of works [1-3,7-11] obtained results, matched with experiment. Moreover, is having without coagulation growth model of nanoparticles for description second stage of growth [10]. This model is different tradition diffusion model and also gives asymmetric distribution function nanoparticles on size.

1 Rasim A.Ali-zasde.
At presented work, we described first stage of formation nanoparticles prepared by chemical precipitation method with kinetic equation. It has been showed that solution of equation is Gauss function and mean value and standard deviation of function are $\bar{x} = \frac{Kt}{4r_0}$, $\sigma = \sqrt{\frac{Dt}{2r_0}}$. Critical size, determinant of collapse and growth of nanoparticles are determined. It’s showed nanoparticles less critical size may be is collapsed, bigger – grow. The dependence of the size and speed of the growth size on time are determined.

2. Kinetics of the first stage of nanoparticles growth.

One of wide used magnetite nanoparticles preparation method is chemical precipitation of two 2 and 3 valent iron salts by alkali [13-15]. We determined also two stages of formation of nanoparticles, prepared by this method [1-3,9,16,17]. Stages of nanoparticles formation has been determined on the base of analysis of distribution function nanoparticles on size [16,17]. Analysis showed, distribution function is asymmetric and is flat to the big sizes. It’s has been showed initial part of distribution may be described by normal function, final- by logarithmic normal function [16,17]. It’s known, these function described different mechanisms of nanoparticles growth. In the first stage, nanoparticles are formatted from saturated solution. Growth of nanoparticles occurs due to consecutive jointing of molecules to the nucleus. In the second stage, nanoparticles have enough big size and growth from saturated solution is impossible. In this stage, coagulation of nanoparticles dominates. Transition diameter of between these two stages has been determined. Mean and transition diameters for magnetite nanoparticles samples I-VI are: (9.5; 9.3), (7.7; 7.5), (7.3; 7.2), (5.4; 5.3), (10.2; 10.1), (4.8; 3.4) nm, respectively [16,17].

In the first stage, in addition to nanoparticles growth its melting is possible, with small probability. It’s related with no stability of nanoparticles (superfluous of surfaces energy) [18,19]. Thus, take into account above indicating, the first stage formation of nanoparticles may be described by follow differential equation:

$$\frac{\partial \rho(r,t)}{\partial t} = D \frac{\partial^2 \rho(r,t)}{\partial r^2} - K \frac{\partial \rho(r,t)}{\partial r}$$

Change of density state on time may be occurs consecutive jointing molecules to the nucleus $\left(K \frac{\partial \rho(r,t)}{\partial r}\right)$, and melting of nanoparticles big size $\left(D \frac{\partial^2 \rho(r,t)}{\partial r^2}\right)$. Introduce non dimensional parameter $x=r/r_{max}$, where $r_{max}$ is maximum diameter of nanoparticles in the first stage (or transition diameter of between different growth mechanisms). Kinetic equation of the first stage of nanoparticles growth is written in non dimensional value as:

$$\frac{\partial \rho(x,t)}{\partial t} = D \frac{x^2}{r_0^2} \frac{\partial^2 \rho(x,t)}{\partial x^2} - K \frac{\partial \rho(x,t)}{r_0 \partial x}$$

(1)

Take into account above indicating, function of density state must satisfy following boundary conditions:

$$\rho(x,t)\big|_{t=0,x=0} = 1; \quad \rho(x,t)\big|_{t=0,x=1} = 0; \quad \rho(x,t)\big|_{x \to \infty,x=0} = 0; \quad \rho(x,t)\big|_{x \to \infty,x=1} = 1$$

Solution this equation will take as:

$$\rho(x,t) = e^{mx+nt} \cdot p(x,t)$$

where $m = \frac{K}{x_0^2 2D}, \quad n = -\frac{K^2}{x_0^4 4D}, \quad p(x,t) = \frac{Kx_0}{2x_0^2}$
Then equation (1) transformed to:
\[
\frac{\partial p(x,t)}{\partial t} = \frac{D}{r_0^2} \frac{\partial^2 p(x,t)}{\partial x^2}
\]

Solution of last equation will take as multiplication of two functions \( p(x,t) = R(x) \cdot S(t) \) [20].

We obtain after division both sides of last equation to \( R(x) \cdot S(t) \):

\[
\begin{cases}
\frac{r_0^2}{D} \frac{1}{S(t)} \frac{\partial S(t)}{\partial t} = -\lambda^2 \\
1 \frac{\partial^2 R(x)}{\partial x^2} = -\lambda^2
\end{cases}
\]

Solutions of these equations are:

\[
S(t) = e^{-\frac{D}{r_0^2} t}, \quad R(x) = e^{i\lambda x}
\]

Thus, we obtain one quotient solution of equation (1)

\[
\rho_A(x,t) = e^{-\frac{(D)}{r_0^2} - \lambda t} e^{(m+i\lambda x)}
\]

We obtain full solution of equation by integration of quotient solution on \( \lambda \)

\[
\rho(x,t) = \int A(\lambda) \rho_A(x,t) d\lambda
\]

We obtain \( A(\lambda) = \frac{1}{\pi} \) use boundary conditions. After integration we obtain

\[
\rho(x,t) = \frac{1}{\sqrt{2\pi} \sigma} e^{-\frac{(x-\bar{x})^2}{2\sigma^2}}
\]

As see \( \rho(x,t) \) is normal function with mean value \( \bar{x} = \frac{Kt}{4r_0} \), and standard deviate \( \sigma = \sqrt{\frac{D}{2} \frac{1}{r_0}} \), which depended on time.

3. Determination of coefficients \( K \) and \( D \)

Value of \( K \) has been calculated by formula in [21, 22].

\[
K = N_A \sigma_{AB}^2 \left[ 8\pi RT \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \right]^{1/2} e^{-E_a/RT}
\]

where \( N_A \) is Avogadro number, \( \sigma_{AB} \) - effective section of collision of molecule \( A \) and \( B \) (\( \sigma_{AB} = \sigma_A^2 + \sigma_B^2 \)). \( M_A \) and \( M_B \) - molecular mass (\( M_A \)-molecular mass of magnetic molecule is equal to 231.54, \( M_B \)-molecular mass of formatted nanoparticles, \( M_B=nM_A \), \( n \) - number of molecules), \( E_a \)-activation energy (\( \approx 2-5 \text{eV} \)) [23]. Evaluation of geometrical size of stable configuration of nanoparticles showed that at increasing number of molecules up 1 to 10, value of \( r_B \) is changed at interval \( r_A(1\pm2.8) \). Thus, evaluation of mean value of \( K \) with above indicated formula is: 1.58 \( 10^{-8} \text{m/c} \).

Value \( D \) is determined from determination of distribution parameter [24-26].

\[
\sigma^2 = \bar{x}^2 - \bar{x}^2
\]

Where \( \bar{x} \) and \( \bar{x}^2 \) are determined as:

\[
\bar{x}^m = \int x^m \cdot \rho(x,t) \cdot dx
\]
Result of integration substituted to determination of $\sigma$ and we obtain.

$$\left( \sqrt{D} \right)^2 + \left( \sqrt{D} \right)^2 \frac{r_0}{\sqrt{t}} - \sqrt{D} \frac{K^2t}{2} + K \frac{r_0^2}{2\sqrt{t}} = 0$$

Solution of cubic equation, don’t take into account term with ($<10^{-18}$) is [27]:

$$D = \frac{r_0^2}{t} \left( 0.167 \frac{Kt}{r_0} \right)^{2/3}, \quad \sigma = \frac{1}{\sqrt{2}} \left( 0.167 \frac{Kt}{r_0} \right)^{1/3}$$

All figures have been plotted by ORIGIN-7 on the base of data obtained by porogram written by FORTAN algorithmic langnguage.

In the figures 1, 2 the curves $x(t), \sigma(t)$ are presented for samples magnetic nanoparticles.

As see figures 1, 2 mean diameter and standard deviation are increased with increasing time. There value is agreed to value obtained by histogram distribution nanoparticles [16, 17]. In the figure 3 are presented the dependence of coefficient diffusion on time for nanoparticles samples VI, III and VI. As see coefficient of diffusion is decreased on time. This is related with increasing nanoparticle size on time, when diffusion is decreased. This is agreeing with result of work [28].

### 4. Results and discussion

In the figure 4 are presented curves of distributions nanoparticles on size. Curves 1, 2 and 3 obtained at different time of growth. As see for all cases distribution is gauss. Mean value and standard deviation of distribution are increased with increased time. This distribution not changed to transient diameter of nanoparticles (figure 4).
Growth and collapse of nanoparticles are determined from relations \( \frac{\partial \rho(x,t)}{\partial t} < 0 \) and \( \frac{\partial \rho(x,t)}{\partial t} > 0 \).

This obtained, that at \( x > \frac{Kt}{4r_{0}} \) growth, and at \( 0 < x < \frac{Kt}{4r_{0}} \) collapse of nanoparticles is possible. Growth of nanoparticles may be occurs by jointing molecules of collapsed nanoparticles. Collapse of nanoparticles is related superfluous energy of nanoparticles [18,19].

Stationary state of nanoparticles formatting is determined from condition \( \frac{\partial \rho(x,t)}{\partial t} = 0 \). Stabilise time is equal \( t = \frac{4r_{0}}{K}(x + 0.52) \). Evaluations of time showed, that it approximately are equal to time necessary for formatting transition diameter for every sample of nanoparticles. As see all expressions depended on transition diameter of nanoparticles.

The dependence of nanoparticles size on time formation of nanoparticles may be obtain from accumulation of mass at formatting of nanoparticles

\[
M(t) = \int \rho_{0} \cdot 4\pi r^{2} \rho(x,t) dx
\]

where \( \rho_{0} \) - is density of magnetite (5.24q/sm^3).

Expressions for size and rate of speed of the growth size of nanoparticles on time are:

\[
r(t) = r_{0} \left( \frac{2x}{3\sigma} + \frac{\sqrt{2x\sigma + \sigma^2}}{\pi} \right)^{1/3}
\]

\[
v(t) = \frac{1}{3} K \left( \frac{1}{3x^2 + \sqrt{\frac{2}{x\sigma + \sigma^2}}} \right)^{2/3} \left( \frac{3}{2} + \frac{\sqrt{\frac{2}{\pi}} \cdot \frac{x}{\sigma} + 2}{\frac{3}{\sigma}} \right) + 0.059 \left( \frac{2}{\sqrt{\frac{\pi}{4}}} \cdot \frac{x}{\sigma} + 2 \right)
\]

In the figures 5, 6 are presented size and speed of the growth size of nanoparticles on time. As see size of nanoparticles is increased with increasing time and at the end reach transient diameter. Initial time, speed of the growth size is big and it is decreased by time. This may be explained that concentration of jointing molecule around nanoparticles (number of jointing molecules) is decreased at increasing time.
The dependence of speed of the growth size of nanoparticles on size may be explained as nanoparticles size depended on physical-chemical properties of medium (viscosity, temperature and etc.). This dependent must be taking into account in the determination of coefficients $K$ and $D$.

Analysis of result showed that, at formation nanoparticles size is change by law $t^{1/3}$, although mean diameter of nanoparticles - by $t$. This may be explained as nanoparticles mean diameter is determinate by averaging of nanoparticles set.

5. Conclusion

In the fist stage of nanoparticle formation, distribution nanoparticles on size are described by Gauss function. Parameters of this function depended on time. Growth and collapse of nanoparticles depended on nanoparticle size. Size and speed of the growth size of nanoparticles depended on time. Size of nanoparticles is increased with increasing time and at the end reach transient diameter. Initial time, speed of the growth size is big and it is decreased by time.

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