Synthesis of a stable magnetite (magnetic fluid) colloid solution

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Abstract. The article is dedicated to the development and investigation of conditions for obtaining the aggregate stable colloid solutions of magnetite – magnetic fluids. The developed method differs from the known ones and involves new ways of producing and stabilizing magnetic nanoparticles with a narrow particle size distribution.

1. Introduction
Recent decades were marked by a rapid expansion in nanoscience. New magazines, monographs, professional institutes, departments, special laboratories, and even conferences have begun to implement nanoscience in their daily operations [1].

Numerous studies concerning the unique physical properties of nanoparticles have been conducted [2-4]. Many of these studies have focused on the magnetic properties of nanoparticles. These studies have revealed the differences between volumetric (three-dimensional) and nano materials [5-24]. For example, cubic spinel Fe₃O₄ is ferromagnetic at temperatures below 858 K.

Magnetic nanoparticles are prepared via two main approaches by:
(1) Grinding macroscopic materials and
(2) Generating new phases by imposing directional changes on the compositions of original chemical solutions (chemical synthesis) [1, 25].

In chemical synthesis (condensation), particles with specific sizes are obtained by limiting new phase size growth through various methods.

Magnetic fluids are widely used in the extraction of gold from placer (deposit) dressing products [26], medicine, biology, and technology [1].

2. Methodology
Two problems must be solved when synthesizing magnetic fluid. First, single-domain magnetic particles (15.4 nm for Fe, 21 nm for Co, and 40 nm for Ni) must be obtained since an increase in particle size can result in decreased sedimentation stability and magnetic property deterioration, particularly in low magnetic fields. In addition, the structure of the adsorbed stabilizer on the surface of the particles must provide for the stable aggregation of the colloid solution in the carrier liquid.

The most common and efficient method used to extract the nanoparticles of magnetic is chemical condensation via the Elmore reaction [26, 27]:
Another well-known reaction used to produce nanosized magnetite in analytical chemistry can be written as:

FeSO₄ + 2FeCl₃ + 8NH₄OH → Fe₃O₄ + 6NH₄Cl + (NH₄)₂SO₄ + 4H₂O  \hspace{1cm} (2)

In the reactions shown in (1) and (2), aqueous solutions containing ferrous salts and ferric ions are mixed at a temperature of 25-40 °C under constant stirring to limit particle growth. Then, an aqueous basic solution is added in sesquialteral (one-and-a-half), or stoichiometric, excess. The formation and growth of new phase nuclei (nucleation) occur simultaneously via homogeneous condensation. In order to obtain a stable ferromagnetic colloid solution (magnetic fluid), the energy expended through the particle interactions must be either eliminated or significantly reduced in order to prevent the formation of microaggregates. Therefore, the surfaces of magnetic nanoparticles should be protected with a chemically adsorbed stabilizer (e.g., oleic acid) at a temperature of 60-90 °C and converted into a carrier liquid (water or hydrocarbon) [25, 26].

The parameters that determine the dispersion properties of magnetic nanoparticles can also be altered. According to Uriev et al. [26, 27], the parameters of the condensation mechanisms of new phase formation include the nucleation rate (u₁)

\[ u₁ = k \frac{c_n - L}{L} \]  \hspace{1cm} (3)

and growth rate (u₂)

\[ u₂ = \frac{DS}{\delta} (c_n - L) \]  \hspace{1cm} (4)

where k denotes the proportionality coefficient; \( c_n \) denotes the concentration of the supersaturated solution; L denotes the solubility of the substance; (\( c_n - L \)) denotes the condensation pressure, which determines the rate at which the solid is released from the solution; D denotes the diffusion coefficient; S denotes the surface of the particle; and \( \delta \) denotes the thickness of the solution layer, through which diffusion occurs (the concentration increases from \( c_n \) to L).

A high rate of nucleation \( u₁ \) and relatively low rate of particle condensation \( u₂ \) lead to increased nanoparticle formation rather than coarse sediment formation. This was achieved by Uriev et al. [26-28] through the rapid injection of the concentrated solution of one component into the diluted solution of another component with vigorous stirring.

The kinetic model of particle aggregation-fragmentation (disaggregation) in the hydrodynamic shear field of coagulation dispersion was used to develop and study a method of obtaining monodispersed particles [29-32]. In the equilibrium state, when the annexation rate and aggregation detachment rate are equal, the dispersion process can be divided into two phases consisting of large aggregates and small particles (primary particles and small aggregates). Polydisperse system formation is primarily attributed to the differences in the Brownian and gradient growth mechanisms of small and large particles. The small- and large-fraction particles in a model are characterized by continuum mass spectra \( f(\mu) \) and \( F(m) \) (where \( \mu, m \) denotes the mass of the relevant particle fractions). Each of the functions \( f \) and \( F \) is denoted by the number of particles in the fraction. In the condensation method of obtaining nanoparticles, the reaction process slows after ~30% of the particles reach the required size. The formation of very small particles occurs slowly via nucleation. These small particles combine into large, unstable aggregates through coagulation with subsequent peptization. The particles that form the aggregates gradually increase in size, eventually forming stable nanoparticles. These stages can be described by the following kinetic equations:
\[
\frac{\partial f(\mu)}{\partial t} = \mu^{1/2} \int_{\mu}^{\infty} \beta(\mu', \mu) f(\mu') d\mu' - \\
- \int_{0}^{\infty} \beta(\mu, \mu') f(\mu) d\mu - \int_{0}^{\infty} \gamma(m, \mu) F(m) f(\mu) d\mu + \\
+ \int_{\mu}^{\infty} \gamma(m - \mu, \mu) F(m) d\mu \tag{5}
\]

\[
\frac{\partial F(m)}{\partial t} = \mu^{1/2} \int_{0}^{\infty} \beta(m - \mu, \mu) F(m - \mu) f(\mu) d\mu - \\
- \int_{0}^{\infty} \beta(m, \mu) F(m) f(\mu) d\mu + \int_{0}^{\infty} \gamma(m, \mu) F(m + \mu) d\mu - \\
- \int_{\mu}^{\infty} \gamma(m - \mu, \mu) F(m) d\mu \tag{6}
\]

where \( \beta(x, y) \) denotes the coagulation nucleus, or the specific rates of particle association \( x \) and \( y \) in the unit aggregate \( x+y \), and \( \gamma(x, y) \) denotes the collapse nucleus, or the specific unit rate of aggregate collapse \( x+y \) into particles \( x \) and \( y \). The functional forms of the coagulation and disintegration nuclei can be recorded based on the aggregate growth mechanism using an approach developed in [32]. Models can be used to investigate the kinetics of the concentration of sol particles in terms of size. This process begins with condensation particle growth and a reduction in the number of small particles, resulting in asymmetry. However, as shown in Figure 1, the degree of asymmetry is reduced once monodispersed sol particles are produced [26].

![Figure 1. Kinetics of the concentration of large particles per weight.](image)

In a previous study, Erin [8] proposed that magnetite particles should be condensed onto primers through heterogeneous condensation. Using this methodology, Zigmondi developed a method of hydrosol production with a narrow distribution of magnetite particles in terms of size.
First, the primer sol was obtained by pouring concentrated salt solutions of Fe2+ and Fe3+ with 10% more than the equivalent amount of excess of Fe2+ into boiling ammonia NH4OH. The dispersion phase concentration of the resulting sol was approximately 10-3 g/dm³.

As shown in Figure 1, the aggregation process began with particle growth via condensation, resulting in a decreased number of small particles and asymmetry. However, the degree of asymmetry gradually decreased over time, at which point particle aggregation played a secondary role to intensive nanoparticle crystallization and fragmentation due to the effects of hydrodynamic stress.

3. Experimental study and analysis
In this study, a method of obtaining magnetite nanoparticles with a narrow particle size distribution through heterogeneous condensation is developed based on the studies of Erin et al. [8, 26, 27, 32]. In the proposed method, condensation is performed on clusters, and <1 nm seeds are received by and adsorbed into the solution.

The seed clusters were prepared by pouring a concentrated salt solution containing Fe2+ and Fe3+ at a 10% Fe2+ salt excess into boiling ammonia NH4OH. The dispersion phase concentration of the resulting colloid solution was 10-3 g/dm³.

Due to their small size, the particles in seed clusters do not react significantly to magnetic field imposition. As a result, seed cluster particles should be enlarged in order to promote participation in thermal motion (chaotic Brownian oscillation) and the acquisition of explicit magnetic properties. For this reason, basic metallic solutions were poured into the ammonia colloid solution containing seed clusters. After mixing these solutions, new clusters (new phase nuclea) ceased to form and the available clusters increased in size. Monodispensible magnetic nanoparticles with a magnetic phase volume concentration of 1.8-7.8% were obtained through this process.

According to these results, the vibration of the dispersion system hindered the formation of large particles. The excitation energy (low frequency mechanical and ultrasonic frequencies) must exceed the interaction energy in order to achieve aggregation stability.

The obtained particles were washed with water in order to remove electrolytes, which are the co-products of chemical reactions.

The “double additive” method developed by Uriev et al. [26, 32, 34, 35] was used to obtain the stable magnetite colloid solution. This method involves the execution of the following technological operations.

The magnetic fluid was obtained via the method described by Berkovskii et al. [25, 26], but with double (vs. optimum) excess stabilizer, which consists of a mixture of oleic acid and kerosene. Next, the certain volume (υ1) was prepared by adding the excess stabilizer of the magnetic fluid to the magnetite colloid solution υ2. The resulting solution was heated to 90°C. Then, the heterogeneous condensation method was applied to the seed clusters. The obtained magnetic fluid was separated from the water with a Buechner funnel and then “pressed out” onto the magnetic separator.

The developed method resulted in two types of particle interactions. An adsorbed layer of stabilizer was noted on the surfaces of the nanoparticles in the magnetic fluid. The multilayer adsorption of the stabilizer was expected due to the adsorption mechanisms of the surface-active agents (SAA) on the salt-forming surfaces. Oleic acid and its sodium salt (sodium oleate), which are strong SAAs, formed the first adsorbed layer in the form of chemically fixed electrovalent molecules. In the next layer, which consisted of inversely oriented SAA molecules, the hydrocarbys of the adsorbate and adsorbent molecules were connected through hydrophobic interactions, in which the polar groups of the adsorbent molecules were oriented toward the liquid phase. The structure of the adsorbed layer was maintained by the free SAA molecules, which were diffusion-bonded with the chemically and physically adsorbed molecules on the particle surfaces. The number of these particles n1 was proportional to the volume of the magnetic fluid υ1. In addition, the number of other particles n2 was proportional to the volume υ2 of the colloid magnetite solution. The number of particles that entered the surface of the system n1 as well as the number of particles free from the surface of the system n2 were characterized by τ = υ1/υ2.
The number of particles $N$ was directly measured with a flow-line ultramicroscope VDK-4.

In the proposed method, $\tau_1$ represented the contact time of the oleic acid and nanodispersed magnetite, while $\tau_2$ represented the contact time of the magnetic fluid and nanodispersed magnetite. Adsorption equilibrium was rapidly achieved in the system after applying the stabilizer to the particle surfaces. When $\tau_1 = 10-15$ min., the reactions between the oleic acid and magnetite nanoparticles resulted in a reduction in the number of particles $N$ at a relatively slow rate. After further growth from $\tau_1$ to 70 min. (in the individual tests, the value of $\tau_1$ exceeded 24 hours) the effects of the stabilizer were almost unobservable. The number of particles $N$ decreased continuously as the contact time $\tau_2$ increased. Therefore, the kinetic factor significantly influenced the adsorption of the oleic acid by the magnetite nanoparticles. The particle concentration $N$ was estimated via direct measurements with a flow-line ultramicroscope VDK-4 (Table 1).

**Table 1.** Relationship between the particle concentration of the colloid solution $N$ and $\tau_1$ and $\tau_2$ at $\theta = \omega_1/\omega_2 = 1$.

| Process parameter | Time ($\tau_1$ or $\tau_2$), min |
|-------------------|----------------------------------|
|                   | 5      | 10      | 15      | 20      | 30      | 50      | 70      |
| $N \cdot 10^{-7}$ at $\tau_1$ ($\tau_2 = 30$ min) | 14,0   | 1,9     | 1,7     | 1,6     | 1,5     | 1,4     | 1,4     |
| $N \cdot 10^{-7}$ at $\tau_2$ ($\tau_1 = 30$ min) | 13,7   | 1,7     | 1,6     | 1,5     | 1,4     | 1,2     | 1,1     |

According to the results shown in Figure 2, the minimum nanoparticle concentration of the magnetite colloid solution $N$ was achieved at $\theta = \omega_1/\omega_2 \approx 1$ – the same number of $n_1$ and $n_2$ particles.

The probability that two $E$ particles will bond can be determined using the coagulation probability $\alpha$ (according to the theory of hydrophobic colloid stability DLFO [26, 27]) and flocculation probability $\varphi$ (the probability of aggregate formation on the surface of a particle upon contact with the stabilizer). If $\Sigma$ is a part of the surface with the stabilizer, the probability of contact between the surface areas of two particles without the stabilizer is $(1-\Sigma)$. Therefore, the coagulation and flocculation probabilities can be written as $\alpha(1-\Sigma)$ and $\varphi\Sigma^2$, respectively. The probability that a particle will bond via two mechanisms simultaneously can be expressed as:

$$E = 1 - (1 - \alpha) \cdot (1 - \Sigma)^2 - (1 - \varphi) \cdot \Sigma^2$$

This probability measurement can be used to determine the availability of the minimum value function $N = f(\theta = \omega_1/\omega_2)$ shown in Figure 2. As shown in Figure 3, the minimum value on the curve $N = f(\omega_1/\omega_2)$ did not influence the relationship between the magnetic fluid density ($\rho$, g/cm$^3$) and the ratio $\gamma = n_1/n_2$, which also passed through the minimum value at $\gamma = n_1/n_2 \approx 1$. Dependence was achieved at nanodispersed magnetite and oleic acid concentrations of $5.4 \cdot 10^2$ g/l and $10^3$ g-mol/l, respectively.
The effects of the stabilizer and dispersion phase concentrations on the stability of the aggregated nanoparticles in the magnetic fluid are shown in Figure 4. Dependence was achieved at nanodispersed magnetite concentrations of $4,7 \cdot 10^{-2}$ g/l (curve 1) and $4,4 \cdot 10^{-4}$ g/l (curve 2) when $\theta = v_1/v_2 = 1$. The interparticle repulsive force was lowest when $\theta = v_1/v_2 = 1$, which is equal to the same number of both particle types. This system state was characterized by decreased aggregate stability resulting from the aggregation of particles in the dispersion phase, the formation of residue, and a reduction in the magnetic fluid density. Any change in the ratio $\theta = v_1/v_2 = 1$ increased the aggregate stability of the magnetic fluid. The peptizing effects of solutions of low stabilizer concentrations can be described by the Rehbinder effect [26, 27]. In the Rehbinder effect, the elastic repulsion and mechanical strength of adsorbed SAA layers interfere with the aggregation of particles. High concentrations of oleic acid in the dispersion phase of the system resulted in the stabilization of the colloid solution. Therefore, the amount of excess oleic acid as well as the features of micellar structures should be considered since micelle can form structural and mechanical barriers in SAA solutions. These effects resulted in an increase in the minimum value on curve $\rho = f (\lg C)$ in Figure 4. According to the results of this study, the ratio $\theta = v_1/v_2$ should be adjusted in order to achieve an oleic acid concentration of $4 \cdot 10^{-2}$ mol/l when developing a stable magnetite colloid solution.
4. Conclusions
According to the results of this study, the mass crystallization of magnetite colloids can be achieved with a combination of the heterogeneous chemical condensation method developed by Zigmondi and the Weimam Rule. In addition, the method proposed by G.J. Fleer and J. Lyklema, in which portions of a colloid solution are mixed with and without stabilizer, can be used to achieve stabilization in colloid magnetite solutions.

Acknowledgement
This article was prepared with the support of the agreement on granting of subsidies № 14.577.21.0142 (RFMEFI57714X0142).

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