Fractal Structures on Fe$_3$O$_4$ Ferrofluid: A Small-Angle Neutron Scattering Study

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Abstract. A small-angle neutron scattering (SANS) which is a powerful technique to reveal the large scale structures was applied to investigate the fractal structures of water-based Fe$_3$O$_4$ ferrofluid, magnetic fluid. The natural magnetite Fe$_3$O$_4$ from iron sand of several rivers in East Java Province of Indonesia was extracted and purified using magnetic separator. Four different ferrofluid concentrations, i.e. 0.5, 1.0, 2.0 and 3.0 Molar (M) were synthesized through a coprecipitation method and then dispersed in tetramethyl ammonium hydroxide (TMAH) as surfactant. The fractal aggregates in ferrofluid samples were observed from their SANS scattering distributions confirming the correlations to their concentrations. The mass fractal dimension changed from about 3 to 2 as ferrofluid concentration increased showing a deviation slope at intermediate scattering vector $q$ range. The size of primary magnetic particle as a building block was determined by fitting the scattering profiles with a log-normal sphere model calculation. The mean average size of those magnetic particles is about 60 – 100 Å in diameter with a particle size distribution $\sigma = 0.5$.

1. Introduction

Magnetic fluid (ferrofluid) which is a liquid dispersion of magnetic nanoparticles has a potential number of applications in different fields as magnetism, optics, rheology, biophysics, and medicine or biomedical$^1$. A magnetic particle has a characteristic size of about 100 Å in diameter with a single magnetic domain (superparamagnetism) coated or stabilized by surfactant molecules to prevent them from aggregation. However, due to the molecular forces such as van der Waals attraction which is similar to a classical mechanism of colloidal coagulation, magnetic particles also have possibility to be aggregated. The present of aggregates and their internal structure greatly influence the properties of ferrofluid$^2$. Fractal aggregates from magnetic nanoparticles have been indicated theoretically$^3$ and experimentally$^4$ on a specific physicochemical condition of a solution.

Small-angle scattering (SAS), including neutron (SANS) and X-ray (SAXS) is a powerful technique for investigating the inhomogenities in materials on the scale range of 10 – 5000 Å. This technique directly provides valuable structure information of the particles, aggregation phenomena,
fractal structure and dimension as well. While by neutron, polarized or unpolarized neutrons, the magnetic structures can be possibly examined.

Fractal concept was found and then validated to be important in many structure studies of disordered materials since many processes as well as the structures can be described and understood in terms of non-integral dimensions. The theoretical and experimental small-angle scattering techniques on fractal structures have been developed and well established. A characteristic feature of the small-angle scattering from fractal scatterers and many other disorder solids is often obeys a “power-law” scattering in the magnitude of the scattering vector \( q \) given as

\[
\frac{d\Sigma}{d\Omega}(q) = I(q) \propto q^{-D}
\]

where \( D \) related to the structure of the scatterer or fractal dimension is a positive constant. Eq. (1) applies only in the regime of \( \xi \gg q^{-1} \gg a \), where \( a \) is a typical chemical or bond distance related to local structure and \( \xi \) is the correlation length or average diameter of a scatterer.

In order to find out more detail on aggregation phenomena and fractal structures in magnetic nanoparticles, a series of magnetic Fe\(_3\)O\(_4\) coated and stabilized by tetramethyl ammonium hydroxide (TMAH) was prepared as a function of concentration and then characterized by means of SANS. This work is also to distinguish the performance of the 36 meter SANS BATAN spectrometer (SMARTer) for investigating the aggregate structures of magnetic nanoparticle materials for the first time.

2. Experimental method

2.1. Materials and synthesis

The natural magnetite Fe\(_3\)O\(_4\) was extracted directly from iron-sands taken from several rivers in East Java, Indonesia, using a magnetic separator. The synthesis was started from a co-precipitation of 20 g of the natural magnetite at \( \sim 70 \) °C in 38 ml of 12 Molar (M) chloride acid solution and then stirred rigorously using magnetic stirrer for 20 minutes. The solution was then added by 24 ml of 6.5 M NH\(_4\)OH solution and stirred for about 1 hour. After continuous stirring, a dark-brown homogeneous solution obtained. This solution was filtered and then washed several time using distilled water until a clear filtrate solution attained. Finally, for each 5 g of the magnetic particles Fe\(_3\)O\(_4\) residue in the filter paper was then dispersed and stabilized in water containing tetra-methyl ammonium hydroxide (TMAH) of surfactant. The final concentrations of ferrofluid were 0.5, 1, 2 and 3 M with respectively the magnetite Fe\(_3\)O\(_4\) % volume concentrations were 0.28, 0.55, 1.11 and 1.67.

2.2. Small-angle neutron scattering (SANS)

The small-angle neutron scattering measurements using the 36 meter SANS BATAN spectrometer were carried out at the neutron scattering laboratory (NSL) in Serpong, Indonesia. All samples were exposed using a neutron wavelength \( \lambda \) of 3.90 Å with the sample-to-detector position of 1.5, 4 and 13 meters. These experimental settings cover the scattering vector of 0.004 < \( q \) < 0.3 Å\(^{-1}\) with \( q = (4\pi/\lambda) \sin \theta \), where \( \theta \) is the angle between the incident and scattered beams.

Scattering intensities of each solution sample were subtracted using a standard SANS data reduction program, GRASP by their solvent backgrounds (pure H\(_2\)O) and the dark electronic current. The ambient temperature was maintained during the measurements. The corrected scattering intensity data was normalized and then fitted with a combined log-normal spherical and clustered object model calculation using a data analysis program, SASfit.

2.3. Data analysis

The scattering intensity in SANS is calculated by

\[
I(q) = P(q) S(q) + Bkg
\]
where $P(q)$ is the scattering from randomly distributed spherical particles having a radius $r_0$ and its distribution, volume fraction $\phi$ and scattering length density difference (contrast) $\Delta \rho$:

$$P(q) = \phi V^2 \Delta \rho^2 F(qr_0^2) f(r)$$  \hspace{1cm} (3)$$

The volume of particle $V_p = (4/3) \pi r_0^3$ and spherical form factor is given by

$$F(qr_0) = \frac{3[\sin(qr_0) - qr_0 \cos(qr_0)]}{(qr_0)^3}$$ \hspace{1cm} (4)$$

For clustered object model, the spherical particle as a building block aggregate formed a fractal-like cluster with a correlation length $\xi$ corresponding to their overall size and self-similarity dimension $D$, known as a fractal dimension. Thus, for the interference from building blocks of fractal-like clusters, the structure factor $S(q)$ can be calculated by

$$S(q) = 1 + \frac{\sin((D-1) \tan^{-1}(q\xi)) \Gamma((D-1))}{(qr_0)^D \left[1 + \frac{1}{(q^2 \xi^2)^{(D-1)/2}}\right]}$$ \hspace{1cm} (5)$$

where $\Gamma(x)$ is a gamma function. This expression reduces to $S(q) \sim q^{-D}$ when $\xi >> q^{-1} >> a$ as given in Eq. 1, while the unity term in $S(q)$ becomes dominant at large $q$. Thus the scattered intensity $I(q)$ is dominated only by the form factor $P(q)$, Eq. 2. Hence, by applying a log-normal sphere model calculation which is a good approximation for the aggregates and clustered object models, the term of $f(r)$ in Eq. (3) is given as:

$$f(r) = \frac{N}{c_{LN} r^p} \exp\left(\frac{1}{2\sigma^2} (\ln r - \ln r_{med})^2\right)$$ \hspace{1cm} (6)$$

where

$$c_{LN} = \sqrt{2\pi r_{med}} \exp\left((1-p)^2 \frac{\sigma^2}{2}\right)$$ \hspace{1cm} (7)$$

The initial or primary magnetic nanoparticles size of about 100 Å in diameter can be determined by applying Eq. 6 into Eq. 3 for a spherical object at high $q$ region.

### 3. Result and discussion

It is necessary to subtract the measured intensity or raw data with respect to the scattering contribution of the backgrounds, i.e. solvent and aperture. By subtracting the measured data with the solvent, i.e. water which contains also the scattering intensity of the cuvette and the aperture scattering. At first, the log-normal sphere and aggregate fractal model calculations have been applied separately to fit the corrected scattering data of ferrofluid, Figure 1. A log-normal sphere model calculation is in agreement with the experimental data at high to intermediate $q$ region as $S(q) \approx 1$, Figure 1a. While at intermediate to low $q$ region, an aggregate fractal model calculation is fit with the data as $I(q) \approx S(q)$ and the primary particle was assumed in a spherical shape and monodisperse, Figure 1b. These preliminary fittings have been worked out in order to obtain the fitting parameters at two regimes. A combined two model calculation was then numerously calculated to find the best fitting on the corrected experimental data, Figure 2.
Figure 1. SANS profiles of ferrofluid sample fitted with two model calculations (a) log-normal sphere at high to intermediate $q$ region and (b) aggregate fractals at intermediate to low $q$ region. The circle symbol is the experimental data and the solid line is the theoretical model calculation.

Figure 2 shows the double logarithmic between scattering intensity $I(q)$ versus $q$ from ferrofluid Fe$_3$O$_4$ sample as a function of concentration fitted with the combined two theoretical model calculation. The experimental data showed as the concentration of ferrofluid increased, two regimes, Porod (high to intermediate $q$ range) and power-law scattering (intermediate to low $q$ range) become emerging. It can be understood as the magnetic concentration increased the scattering profile and intensity are also affected by the structure factor. Scattering profile at the lowest concentration of 0.5 M is purely indicating that non-correlated particle $I(q) \approx P(q)$ term is dominant in this sample. A large aggregate cluster formed and is dominantly composed of surfactant molecules and small fraction of the magnetic particles which shows a weak scattering intensity at intermediate to low $q$ range. Here, an individual small magnetic particle is not able to be determined.

Figure 2. SANS profiles of Fe$_3$O$_4$ ferrofluid samples in TMAH fitted with a combined two model calculation, log-normal sphere and aggregate fractals. The symbols are experimental data and the solid line is theoretical model calculation.
As magnetic concentration is increased the primary magnetic particles of the building blocks which can be distinguished from their aggregates in the two regimes, Porod and power-law (mass fractal region) are certainly appearing. The crossover of these two regimes which defined the estimated size of the building block of the large aggregate cluster is fairly fixed at $q = 0.025 \, \text{Å}^{-1}$ or about $\sim 500 \, \text{Å}$ in diameter. Meanwhile, from the fitting results, a log-normal sphere model calculation, the size of the magnetic Fe$_3$O$_4$ particles in TMAH at a given particle size distribution $\sigma$ of 0.5 are 95.6, 62.6 and 64.4 Å in diameter for the concentration of 1, 2 and 3 M, respectively. Those values verified that the magnetic Fe$_3$O$_4$ particle as an initial magnetic nanoparticle entirely has a particle size of about 100 Å in diameter which is a characteristic size of nanoparticle. From the size of aggregate and primary particle data can be calculated the aggregation number for the particle in cluster from the relation $N_{agg} = (\xi / r_0)^D$, from which we estimate around 30 – 70 small primary magnetic particles aggregated naturally as a building block of the large aggregate cluster due to the condensation reaction. This magnetic particle aggregation is confirmed by enhancing the scattering profile intensity.

On the other hand, the size of the primary magnetic particle is definitely affected by its concentration in the solution. The inter-particle correlation interference becomes dominating as magnetic concentration is increased which indicates the ordering, short and long-range orders of the magnetic particles in the system contributed to the scattering profiles. The repulsion between magnetic particles can be reduced by dilution and then has a possibility to interpenetrate or form a short range order. Therefore, the particles can be appeared as a single large particle or aggregate which composed of several small coated magnetic particles. As the concentration increased, it can be assumed that the possibility of magnetic particles collision is high. Those magnetic particles tend to be aggregated and then coated by the surfactant. It was found that as the magnetic concentration is low, a short range order is exist and showing the high the scattering intensity.

Due to the molecular force of each magnetic particle as a building block, those particles possibly aggregate to form a large aggregate cluster. Then, particle binding may be affected by van der Waals attraction between magnetic cores. The aggregation of magnetic Fe$_3$O$_4$ nanoparticles in TMAH which appeared from their SANS scattering profiles at intermediate to low $q$ region is also confirmed from a transmission electron microscopy (TEM) investigation, Fig. 3. However, the initial magnetic nanoparticle as the building blocks of fractal-like clusters and their fractal dimension is not probable to be verified by a microscopy technique. Here from SANS data, the slope at the magnitude of the scattering vector $q < 0.03 \, \text{Å}^{-1}$ showing a power law scattering which corresponds to the scattering intensity.

![Figure 3. Transmission Electron Microscopy (TEM) image of dried magnetic Fe$_3$O$_4$ nanoparticles aggregation in TMAH.](image)
distribution from fractal aggregates. The aggregate fractal dimension $D$ appeared between 3 and 2, Figure 2 showing that a small particle of building block is likely growing in 2-dimensional space direction to form a disc-like macrostructure.

The fractal dimension is strongly dependent on the mechanism of aggregates formation. The aggregates fractal dimension which determined in this work indicated that a reaction-limited mechanism occurred in magnetic nanoparticles system. In this mechanism, more compact structures formed as a slower restructuring process of the clusters is occurred. This result is dissimilar with the carbon black aggregates in solution. A diffusion-limited cluster aggregation mechanism may also occur in the carbon black aggregates where a particle by a slow Brownian process sticks to the first particle it encounters in a cluster and the cluster growth normally. Then, the extended aggregates of carbon black formed with the fractal dimension less than 2.

4. Conclusion

It was confirmed that a large aggregate cluster has already formed at the lowest magnetic concentration and the mass fractal structure dimension was evidently affected by the magnetic concentrations. The building block was formed by about 30 – 70 small magnetic particles with the size of 60 – 100 Å in diameter and particle size distribution $\sigma = 0.5$. The SANS BATAN spectrometer together with the experimental method including data reduction and analysis have demonstrated its performance in a low $q$ region for revealing the fractal structure aggregates of Fe$_3$O$_4$ ferrofluid.

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