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Size and Correlation Analysis of Fe_3O_4 Nanoparticles in Magnetic Fluids by Small-Angle Neutron Scattering

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Abstract. Size and correlation analyses of Fe_3O_4 nanoparticles have been carried out by the measurement of small angle neutron scattering. Particle size of magnetite is analyzed by employing Guinier region approximation in order to obtain gyration radius, which will be used to further determine the average radius of magnetite particles resulting in the value between 17.8 nm and 53.6 nm. Further approximation using a polycore-shell ratio model shows the average particle size of 25 nm with polydispersity of 0.4. The effect of magnetic fluids concentration on the thickness of surfactant layer on the particles surface has not shown a significant change with the value between 6 Å and 8 Å relating to the molar concentration between 0.5 M and 3 M, signifying no correlation among the particles in magnetic fluids.

Keywords: Fe_3O_4 nanoparticle, small angle neutron scattering, magnetic fluids.
PACS: 61.12.Ex, 61.46.Df

INTRODUCTION

Monodisperse magnetic nanoparticles in a self-assembled structure is of technological importance for possible data storage media and is a model system for the study of magnetic interaction in a ferromagnet[1]. The knowledge of magnetic fluids microstructure is very important to understand and control the mechanisms of their stabilization[2]. The neutron scattering methods have been largely used in the last two decades for determination of structural properties of magnetic liquids at microscopic level. Besides, this method can also be developed for examinations of particle size, phenomena of aggregation, magnetic fluid dynamics, particle interaction with surface active agent and magnetic behavior as well[3]. For studies on magnetic phenomena occurring over these length scales of magnetism, small angle neutron scattering (SANS) is exactly appropriate. SANS involves a monochromatic beam of neutrons scattered by the sample and measures the scattered neutrons intensity as a function of the scattering angle. The wave vector transfer extracted from SANS experiment is expressed by

$$Q = \frac{4\pi}{\lambda}\sin 2\theta \qquad (1)$$

where 2θ is the scattering angle and λ is the neutron wave length [4]. SANS is a technique that allows us for characterizing structures or objects on the nanometer scale and exploits the big momentum transfer and wavelength reaching out of 3 – 6 Å, which is applicable to observe particle structure in low ordering scattering system being close to the district distance of measurement between 20 – 1250 Å[5].

In this research, we report an analysis concerning the particle size in a low order scattering system in the form of magnetic fluids containing Fe_3O_4 particles using SANS technique. Particle size has been analyzed by Guinier region approximation. Besides, this research also studies the effect of magnetic particle content in magnetic fluids on the layer thickness of surface active agent and their particles correlations.

EXPERIMENT

The Fe_3O_4 magnetic nanoparticles have successfully been synthesized in an aqueous solution by means of the co-precipitation process. We have used iron-sands taken form some rivers in East Java (Sungai Brantas, Kali Madiun and Sungai Regoyo) from which the natural magnetite (Fe_3O_4) can be extracted using a magnetic separator. First, 20 g of natural magnetite was dissolved into 38 mL of 12.06

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M HCl at 70 °C under vigorous stirring for 20 minutes. To this solution, 24 mL of 6.5 M NH_4OH was added and the mixture was continuously heated at 70 °C for 20 minutes to induce precipitating process. The precipitate was then washed using de-mineralized water in step by step to gain magnetite nanoparticles using filter papers. The magnetic fluids were finally prepared by adding tetra-methyl ammonium hydroxide to the wet magnetite nanoparticles with varying ratio between surfactant and nanoparticles.

Characterizations of magnetite nanoparticle were conducted by employing X-ray diffractometer (XRD), magnetic force microscope (MFM) and SANS. The structural properties of the as-prepared nanoparticle were analyzed by X-ray powder diffraction with a JEOL JDX 3530 Diffractometer system. The average crystal size was estimated using Rietica internal program. The size distribution of particle has been measured from the enlarged MFM images. Experiments using non-polarized SANS were carried out at Neutron Scattering Laboratory, BATAN, Kawasan Puspiptek Serpong, Indonesia.

The objective of SANS experiment is to determine the differential cross section, which contains all the information concerning with shape, size and interaction of the scattering bodies in the sample [6]. The mathematical expression related to the SANS patterns scattered by the magnetic fluids in conjunction with differential cross section is given by

$$\frac{d\Sigma}{d\Omega}(Q) = n_p\left(V_p^{\,2}\right)(\Delta\rho)^2\left(P(Q)^2\right)S(Q) \tag{2}$$

where n_p is the number concentration of scattering bodies, V_p is the volume of one scattering body, $\Delta\rho$ is the difference in neutron scattering length density called the contrast for convenience, $P(Q)$ is a function known as the form or shape factor, $S(Q)$ is the interparticle structure factor, and Q is the modulus of the scattering vector[6].

In the dilute particulate system, particles are uniformly dispersed in a matrix. When the particles content is sufficiently small (dilute), the positions of individual particles are apart quite far away from each other to form a uncorrelated system. If the shape of the particles is known, or assumed from the basis of independent information, the intensity of scattering from individual particle can be calculated and compared with the observation. If the particles are of irregular or unknown shape, the data may be analyzed according to the Guinier law to determine the radius of gyration characterizing the size of the particles[7].

The differential scattering cross section for the dilute system is given assuming that the interparticle correlation is small enough and can therefore be neglected [8]. Using extrapolation for Q = 0, since $S(Q)$=1, the cross section is given by

$$\frac{d\Sigma}{d\Omega}(0) = n\left(V_p^{\,2}\right)(\Delta\rho^2) \tag{3}$$

Guinier [7] has shown that for small values of QR_g, where R_g is the linier dimension of the particle, $P(Q)$ is related to a simple geometrical parameter which is so-called the radius of gyration R_g. Guinier showed further that

$$P(Q) = \exp\left(-\frac{Q^2R_g^2}{3}\right) \tag{4}$$

scattering function given by equation (4) is called the Guinier law.

$$I(Q) = n\left(V_p^{\,2}\right)(\Delta\rho^2)\exp\left(-\frac{Q^2R_g^2}{3}\right) \tag{5}$$

R_g for a particle is defined by

$$R_g = \left[\frac{\int r^2\rho(r)dr}{\int \rho(r)dr}\right]^{\frac{1}{2}} \tag{6}$$

which is valid typically for $QR_g < 1$. A plot of scattered intensity in the logarithmic scale versus Q^2 results in a straight line for the low Q, and its slope gives the value of R_g.

$$\ln I(Q) = -\frac{1}{3}R_g^{\,2}Q^2 \tag{7}$$

The particle size, no matter whether its shape is geometrically well defined or irregular, can be conveniently characterized by its radius of gyration R_g. The concept of R_g is applicable to particles of any shape, for the purpose of determining the radius of particle [7].

RESULTS AND DISCUSSION

The average crystal size of the Fe_3O_4 analyzed by the powder XRD was around 7 nm, while the particle diameter shown by the MFM image, Fig. 1 varied from 10 to 50 nm. This indicates that Fe_3O_4 particle is secondary particle, meaning that each particle contains several grains. Further, the measured scattering data were converted to the total cross section by subtracting the scattering from an empty cell and ambient background, and by normalizing with the sample transmission and thickness. Fig. 2 shows the one-dimensional average of corrected scattering pattern

from magnetic fluids sample at 0.5M solution concentration and 0.28% of magnetite concentration.

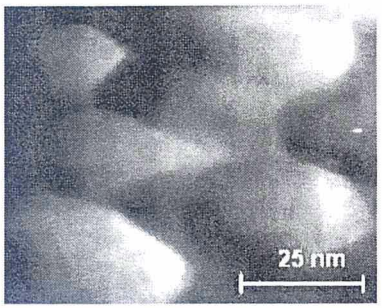

FIGURE 1. MFM images from magnetite particle with average diameter 25 nm

Size and correlation of magnetite particles were analyzed based on the experimental result using two methods. The first method is a fitting program using Guinier region approximation at interval Q-range between 0.8 nm^{-1} and 1.2 nm^{-1} to determine the average particle size. The gradient of ln (I) to Q^2 plot is applicable to determine radius gyration (R_g) which will be used then to determine the radius of magnetite particle. Gradient at Guinier region is proportional to $-{}^1/_3\ R_g^2$. In Fig. 3 there are three characteristics of particle size for the magnetic fluids with the concentration of 0.5 M and magnetite concentration of 0.28% (Fig. 3). They correspond to the length intervals of 17.8 nm, 29.4 nm, and 53.6 nm. We suppose that the reason may probably be connected with the polydispersity of magnetite particle size in magnetic fluids.

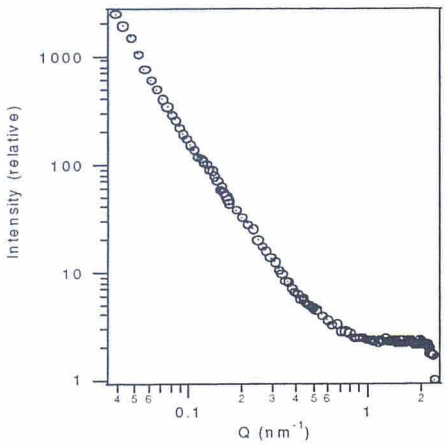

FIGURE 2. Scattering pattern from magnetic fluids with the concentration of 0.5 M and magnetite concentration of 0.28 %.

It is interesting to go further using the approximation of polycore-shell ratio model to determine the polydispersity of magnetite particles. It has been analyzed in this regards by assuming that the particle is spherical and the fluids contain of magnetite as core, surface active agent as shell and the water as solvent. This curve calculated according to the expected model of polydispered spheres with scattering length density of magnetite gives result ρ_c = 6.921x 10^{-5} $Å^{-2}$. The polydispersity of 0.4 shows that the most particles have average radius of 25 nm, Fig. 4).

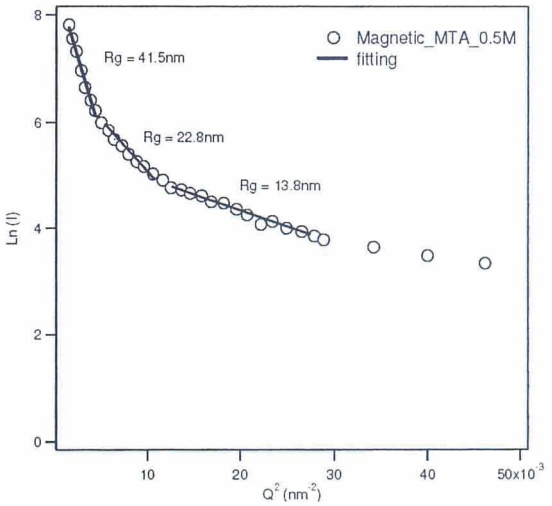

FIGURE 3. Characterize the radius of gyration of the magnetite particle

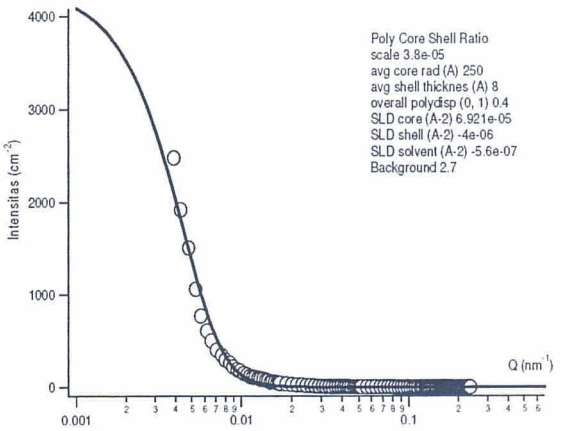

FIGURE 4. Polycore-shell ratio model to determine polydispersity of magnetite particle

The thickness of surfactant shell is the key parameter, which determines the stability of the fluids [11]. It has been shown that in the case of magnetite/tetramethyl ammonium hydroxide/water, the thickness of the surfactant layer will change, when the magnetite concentration is varied. The effect of magnetic fluids concentration on the thickness of

surfactant layer on the particles surface has not significantly been observed. A change with the value between 6 Å and 8 Å corresponds to the molar concentration between 0.5 M and 3 M, signifying no correlation among the particles in magnetic fluids. In the case of the magnetite concentration of 0.28 %, the large penetration between sub-layers of the double surfactant was detected.

TABLE 1. The result of pattern analysis of SANS to determine the thickness of surfactant layer

Concentration of magnetic fluids (M)	volume of magnetite particle Fe_3O_4 (%)	Q (nm^{-1})	Intensity (cm^{-2})	The thickness of surfactant layer (Å)
0.5	0.28	0.112	118.65	8
1	0.55	0.112	193.73	7
2	1.11	0.112	344.18	6
3	1.67	0.112	344.18	6

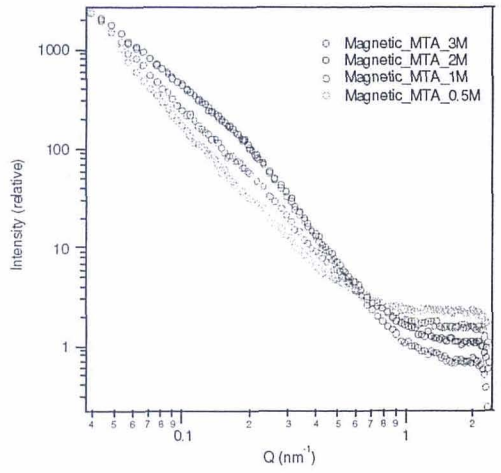

FIGURE 5. Scattering pattern of intensity $I(Q)$ versus Q at different magnetic fluids concentration

The average radius of particle has not been changed significantly with increasing the magnetic concentration. The particle radius ranges at interval between 17.8 nm and 53.6 nm using polycore-shell ratio model with average radius of 25 nm. It shows that there are no correlations of magnetite particle in the concentration range of 0.5 M and 3 M, Fig. 5. A significant decrease in the background of scattering pattern was observed from the sample with increasing magnetite concentration.

CONCLUSIONS

Size and correlation in magnetic fluids structure of magnetite/tetramethyl ammonium hydroxide/water were determined by means of non-polarized SANS. Three characteristics of the average radius of magnetite with the magnetite concentration in the range of 0.28-1.67 %-Volume were obtained and determined using Guinier region approximation and compared with polycore-shell ratio model to result in the thickness of surfactant layer, corresponding to the radius intervals of 17.8 nm, 29.4 nm, and 53.6 nm. We conclude that the reason may be connected with the polydispersity of magnetite particle in the magnetic fluids. The polydispersity of 0.4 shows that the most particles have average radius of 25 nm using polycore-shell ratio model. The effect of magnetic fluids concentration on the thickness of surfactant layer on the particles surface has not been shown significantly, signifying no correlation among the particles in the magnetic fluids.

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