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Paper

Preparation and Characterization of Silicone and Fluorine-Oil-Based Ferrofluids

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ABSTRACT: Magnetite nanoparticles were synthesized by adding an ammonium hydroxide to a mixed solution of iron (II) and (III) chlorides. A silicon surfactant of α,ω-(3-aminopropyl)polydimethylsiloxane was adsorbed on the particles as dispersant and a polydimethylsiloxane polymer was used to prepare ferrofluids of silicone oil base. Fluorinated surfactants of anionic ammoniated perfluoroalkyl sulfonamide and nonionic fluoroaliphatic polymeric esters were applied to the particles and a perfluoropolyether was used to prepare ferrofluids of fluorine oil base. The experimental conditions were used for preparing the ferrofluids with concentrations of 200, 300 and 400 mg/mL, and density, magnetization and viscosity of the products were characterized. The density values increased in proportion to the concentration, indicating 1.11-1.27 g/mL for silicone-oil-based fluids and 1.95-2.10 g/mL for fluorine-oil-based fluids in the range of 200-400 mg/mL. The saturation magnetization of the silicone-oil-based and fluorine-oil-based fluids indicated 14.7, 24.4, and 30.7 mT and 15.8, 23.3, and 33.7 mT for 200, 300, and 400 mg/mL, respectively, depending on the content of magnetic particles in the fluid. The viscosity of the silicone-oil-based ferrofluids was highly stable compared to that of the fluorine-oil-based with increasing temperatures. The ferrofluids are usually applied to seals and speakers with the silicone base and to seals with the fluorine base.

Key Words: Nanoparticles, Surfactant, Concentration, Dispersion, Magnetization, Viscosity

1. INTRODUCTION

Nanometer-sized inorganic particles can be dispersed into hydrophilic or lipophilic liquid base by covering them with the suitable surfactants. Magnetic ferrite nanoparticles with inverted spinel structure have attracted much attention owing to their potential application as ferrofluids [1]. These nanoparticles can be prepared by mechanical milling or chemical synthesis, in which more uniform and smaller particles are produced by chemical methods. Particulate magnetite have been usually obtained by coprecipitating iron ions with the addition of ammonium hydroxide to a solution containing both Fe^{2+} and Fe^{3+} [2,3]. In general, an unsaturated fatty acid is first adsorbed with two molecular layers onto the particle surface, in which the nonpolar group is positioned towards the outside of the inlayer and the inside of the outlayer. The outlayer is removed through an acid treatment to pH 5.0. Therefore, an anionic group of the first surfactant is conjugated to the cation of the iron oxide on the inside, with hydrophilic and/or lipophilic functional groups of the second surfactant compatible with the liquid base pointing towards the outside [4]. Since the magnetic nanoparticles are characteristic of superparamagnetism [5,6], their fluid flow can be reversibly controlled and localized at a specific site in dependence on the external magnetic field strength [7]. Moreover, the temperature properties of the ferrofluids are significantly important for use in vacuum seals, damping elements, etc. owing to decrease of their viscosity.

In this work, the magnetite nanoparticles were produced by coprecipitation with a solution of iron chlorides and ammonium hydroxide. As silicone and fluorine oil bases for dispersion of the nanoparticles, polydimethylsiloxane (PDMS: $(CH_3)_3SiO[SiO(CH_3)_2]_nSi(CH_3)_3$) and perfluoropolyether (PFPE: CF_3-[(O-$CFCF_3$-CF_2)$_m$-(O-CF_2)$_n$]O-CF_3)

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were used, respectively. The silicone oil has been adopted for a hydrophobic medium of magnetorheological fluids [8]. A silicon surfactant of α,ω-(3-aminopropyl)polydimethylsiloxane ($NH_2(CH_2)_3Si(CH_3)_2O[Si(CH_3)_2O]_nSi(CH_3)_2(CH_2)_3NH_2$) was applied to the nanoparticles for the silicone-oil-based ferrofluids, and fluorinated surfactants of anionic ammoniated perfluoroalkyl sulfonamide and nonionic fluoroaliphatic polymeric esters were used for a bilayer formation in the fluorine-oil-based ferrofluids. The density, dispersion and magnetization of the ferrofluids were studied with concentrations in the range of 200 to 500 mg/mL (particles weight to fluid volume), and their viscosity was investgated with different concentrations at various temperatures.

2. EXPERIMENTAL PROCEDURE

$FeCl_2{\cdot}4H_2O$ (M_w 198.81, >99%) and $FeCl_3{\cdot}6H_2O$ (M_w 270.29, >99%) were dissolved in 100 mL of distilled water, to give an Fe^{2+}/Fe^{3+} stoichiometric ratio = 0.5. The fine particles of iron oxide were synthesized by stirring this chloride solutions (300 rpm for 10 min at room temperature in a 500 mL 3-neck flask) and adding NH_4OH (28-30 wt% NH_3) in a 1.5 times excess over the stoichiometric reaction amount. The precipitate from the reaction was washed several times with distilled water using ultrasonication and magnetic decantation to remove the by-product of the ammonium chloride salt. The homogeneous black particles were obtained by drying the precipitate gel for a long time at a low temperature of 40°C. The proper surfactants were introduced to form a stable dispersion in the liquid base. An adequate amount of α,ω-(3-aminopropyl)polydimethylsiloxane (JNC Silaplane FM-3321: M_n 5000, d 0.97, 120 cSt) was adsorbed onto the particles by stirring for 1 h at 80°C in 80 mL of silicone oil (Dow Corning XIAMETER® PMX-200: d 0.96, 50 cSt) to prepare the silicone-oil-based ferrofluids, and ammoniated perfluoroalkyl sulfonamide (3M FC-5130: 1.1 g/mL, 10 cP) and fluoroaliphatic polymeric esters (3M FC-4434: 1.1 g/mL, ≤30 cP) were adsorbed by stirring for 1 h each at 80°C in 80 mL of fluorine oil (Solvay Plastics Fomblin® M Lubricant: 1.83 g/cm³, 150 cSt) to prepare the fluorine-oil-based ferrofluids. The ferrofluids were prepared with the concentrations of 200, 300, and 400 mg/mL. Fig. 1(a) and (b) show a typical process for preparing ferrofluids with the PDMS and PFPE bases, respectively.

The magnetic properties of the particles were measured with a vibrating sample magnetometer (VSM) using a field range of ±10 kOe. The saturation magnetization of ferrofluids was obtained from [9]

$$M_s = \sigma_s \cdot \rho_p \cdot (\rho - \rho_L)/(\rho_p - \rho_L) \quad (1)$$

where σ_s is the saturation value of bare particles and ρ, ρ_p and ρ_L are the density of as-prepared ferrofluid, dispersed particles and liquid base, respectively. The density value 4.8 g/cm³ was

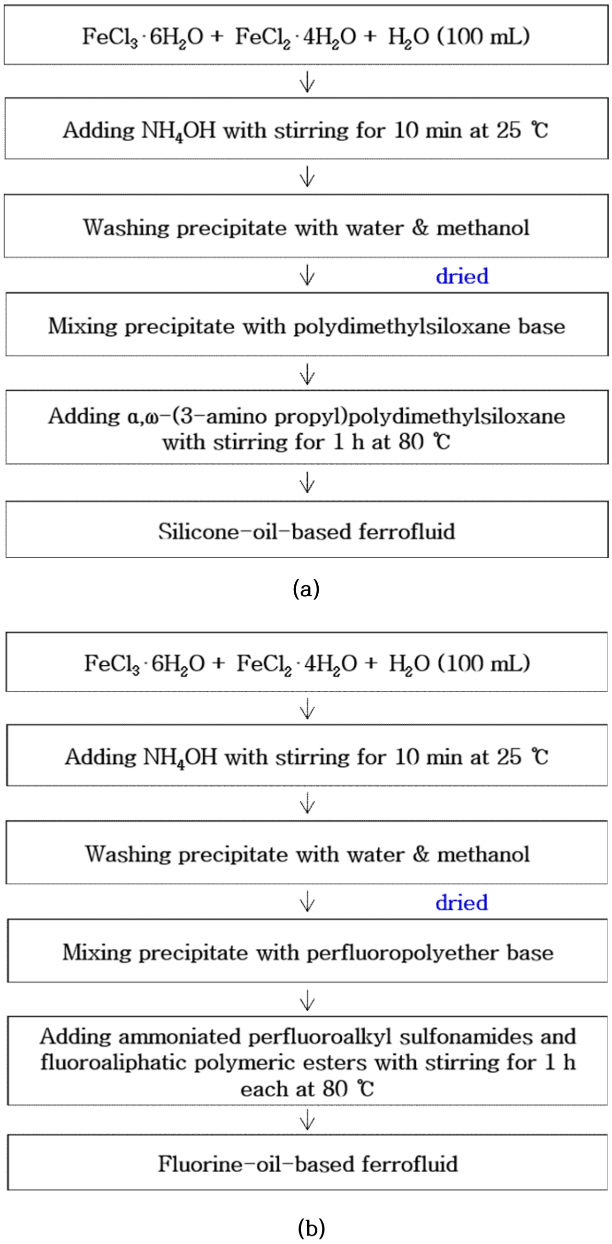

Fig. 1. A process for preparing ferrofluids of (a) silicone oil and (b) fluorine oil bases

applied to the Fe_3O_4 nanoparticles. The viscosity of the fluids was obtained using a Brookfield viscometer (LVDV-II + PRO) equipped with a small sample adapter (SSA 18/13R).

3. RESULTS AND DISCUSSION

3.1 Preparation of Ferrofluids

In the precipitation reaction of $FeCl_2 + 2FeCl_3 + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O$, 8 g of magnetic particles was produced from $FeCl_2{\cdot}4H_2O$ 6.88 g (0.0346 mol) and $FeCl_3{\cdot}6H_2O$ 18.72 g (0.0692 mol), which led to formation of magnetite phase with particle size of about 12 nm [3,10,11]. A 100 mg/

Table 1. Experimental conditions used for preparing ferrofluids of silicone oil base with various concentrations at a fixed volume of 80 mL

Fluid conc. (mg/mL)	$FeCl_3\cdot 6H_2O$ (g)	$FeCl_2\cdot 4H_2O$ (g)	NH_4OH (mL)	Fe_3O_4 yield† g (mL)	Silicon surfactant‡ (mL)	Silicone oil (mL)	Volume fraction (%)		
							Particle	Surfactant	Base
100	18.72	6.88	27.2	8 (1.6)	1.4	77	2	1.8	96.2
200	37.44	13.76	54.4	16 (3.2)	2.8	74	4	3.5	92.5
300	58.16	20.64	81.6	24 (4.8)	4.2	71	6	5.3	88.7
400	74.88	27.52	108.8	32 (6.4)	5.6	68	8	7.0	85.0
500	93.60	34.40	136.0	40 (8.0)	7.0	65	10	8.8	81.2

† The Fe_3O_4 volume was obtained using a density value of 5.0 g/mL.
‡ Silicon surfactant: α,ω-(3-aminopropyl)polydimethylsiloxane

Table 2. Experimental conditions used for preparing ferrofluids of fluorine oil base with various concentrations at a fixed volume of 80 mL

Fluid conc. (mg/mL)	$FeCl_3\cdot 6H_2O$ (g)	$FeCl_2\cdot 4H_2O$ (g)	NH_4OH (mL)	Fe_3O_4 yield† g (mL)	Fluorosurfactant‡		Fluorine oil (mL)	Volume fraction (%)		
					Anion	Nonion		Particle	Surfactant	Base
100	18.72	6.88	27.2	8 (1.6)	1	2	75.4	2	3.8	94.2
200	37.44	13.76	54.4	16(3.2)	2	4	70.8	4	7.5	88.5
300	58.16	20.64	81.6	24 (4.8)	3	6	66.2	6	11.3	82.7
400	74.88	27.52	108.8	32 (6.4)	4	8	61.6	8	15.0	77.0
500	93.60	34.40	136.0	40 (8.0)	5	10	57.0	10	18.8	71.2

† The Fe_3O_4 volume was obtained using a density value of 5.0 g/mL.
‡ Fluorosurfactants: anionic ammoniated perfluoroalkyl sulfonamide, nonionic fluoroaliphatic polymeric esters

mL fluid concentration was prepared to give 80 mL of the ferrofluid with that, and the ferrofluids of higher concentration were obtained using corresponding amounts of the particles in the fixed fluid volume. A single surfactant of α,ω-(3-aminopropyl)polydimethylsiloxane was applied to the magnetic nanoparticles to prepare the silicone-oil-based ferrofluids, whose functional groups were compatible with both particle surface and polydimethylsiloxane base. The anionic ammoniated perfluoroalkyl sulfonamide and nonionic fluoroaliphatic polymeric esters were applied to form a bilayer of surfactants for a stable dispersion of the magnetic particles in the PFPE base. Table 1 and 2 summarize experimental conditions used for preparing 80 mL of the silicone-oil and fluorine-oil-based ferrofluids at various concentrations, respectively. The amount of surfactants needed to form the monolayer on the magnetite particles is optimized with an area site occupied by each surfactant molecule on the particle surface [12]. The nonionic surfactant was added twice as much as the anionic surfactant, ensuring complete coverage of the particles.

3.2 Density of Fluids

The density of a completely dispersed ferrofluid was obtained by measuring the volume and weight of as-prepared ferrofluids. The density values were 1.11, 1.21, and 1.27 g/mL for the silicone-oil-based ferrofluids and 1.95, 2.01, and 2.08 g/mL for the fluorine-oil-based ferrofluids with concentrations of 200, 300, and 400 mg/mL, respectively, directly reflecting the density of each base oil. The dispersion of the ferrofluids was only a half compared with 70-80% of hydrocarbon-based

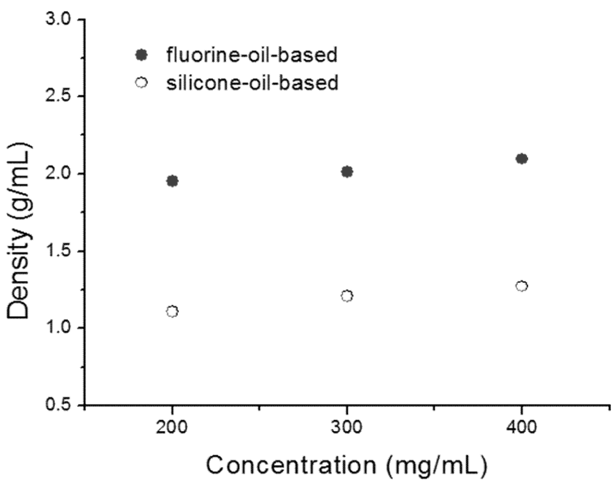

Fig. 2. Density values of silicone-oil and fluorine-oil-based ferrofluids as a function of concentration

ferrofluids [12,13], in which the prepared fluids were layer-separated within a day. Therefore, the agglomerated fluids were used after strongly shaking the bottles containing them for redispersion. Fig. 2 shows dependence of the density on concentration for the oil-based fluids.

3.3 Magnetic Properties

The magnetization measurement of the magnetite nanoparticles indicated the saturation value σ_s of 62.4 emu/g with superparamagnetism. Since the magnetization of ferrofluids is measured per unit volume, their saturation value can be

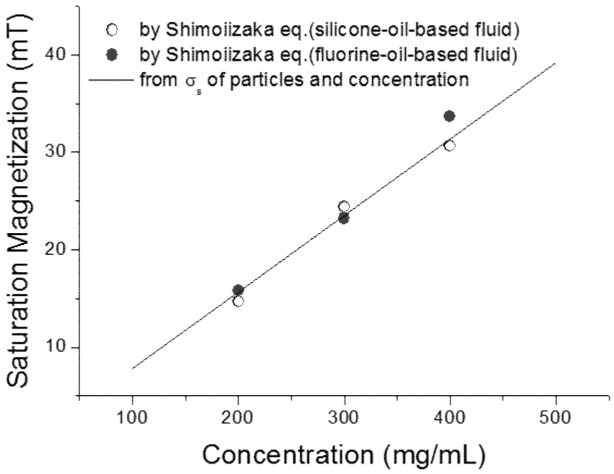

Fig. 3. Comparison of saturation magnetization values of silicone-oil and fluorine-oil-based ferrofluids approximated by Shimoiizaka equation with straight line obtained from saturation values of bare particles

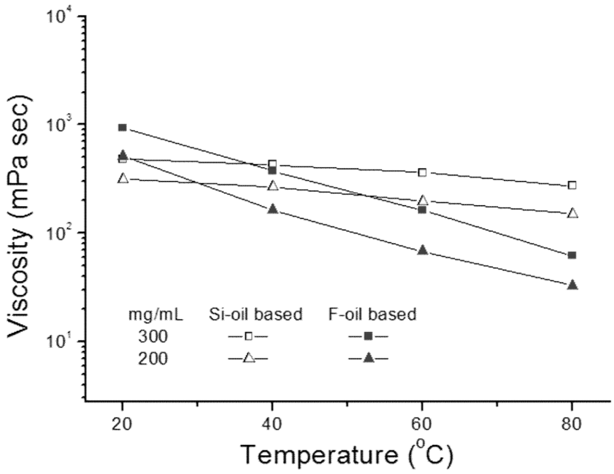

Fig. 4. Viscosity vs. temperature curves of silicone-oil and fluorine-oil-based ferrofluids obtained at different concentrations using 3.0 rpm of Brookfield S18 spindle

obtained by multiplying the saturation magnetization for bare particles by a concentration. In case of polyalphaolefin-based ferrofluids [12], the difference between the values approximated by eq. (1) and obtained from the saturation mgnetization of bare particles was all within 10% (error limit for measurement) in the range of 200-500 mg/mL. Therefore, the saturation magnetization observed in this experiment also would be practically the same with the calculated saturation values. The saturation magnetization values in eq. (1) were 14.70, 24.41, and 30.68 mT for the silicone-oil-based ferrofluids and 15.78, 23.25, and 33.71 mT for the fluorine-oil-based ferrofluids at concentrations of 200, 300, and 400 mg/mL, respectively, which corresponded to the values calculated with saturation magnetization of bare particles and fluid concentration. Fig. 3 shows the saturation magnetization values of ferrofluids approximated by eq. (1) along with the saturation values of bare particles at each concentration.

3.4 Viscosity of Fluids

The viscosity observed for the ferrofluids should be considered as a relative value under a certain condition because the viscometer indicated different viscosity values with the same specimens in dependence on spindle speed. The viscosity of the ferrofluids was measured with a spindle speed of 3.0 rpm (measurable up to 1000 cP) to hold the torque values within the confidence limits. Fig. 4 shows variations of the viscosity values with temperature at concentrations of 200 and 300 mg/mL ferrofluids. The viscosity of the ferrofluids decreased exponentially with increasing temperatures, with similar tendency to the curves for each oil base. The decrease in the viscosity with the temperature increase from 20°C to 80°C was on an average 48% (200 mg/mL: 314 to 151 cP, 300 mg/mL: 481 to 273 cP) for the silicone-oil-based ferrofluids and 94% (200 mg/mL: 516 to 33 cP, 300 mg/mL: 936 to 62 cP) for the fluorine-oil-based ferrofluids. Although the viscosity of the silicone-oil-based ferrofluids was lower than that of the fluorine-oil-based ferrofluids at the room temperatue, depending on the properties of each base oil, the former values decreased at a half level of the latter with increasing temperatures.

3.5 Sealing Ability

The field test was carried out using leak detector (ULVAC HELIOT 700) at a domestic motor manufacturer. The silicone-oil-based ferrofluid of 300 mg/mL was selected as a test sample, which was compared with a poly-α-olefin-based ferrofluid of the same concentration. The leak-detecting apparatus for magnetic fluids is shown in Fig. 5. A leakage at the testport decreased base pressures of the vacuum chamber. The test result revealed that the ultimate pressures were in the

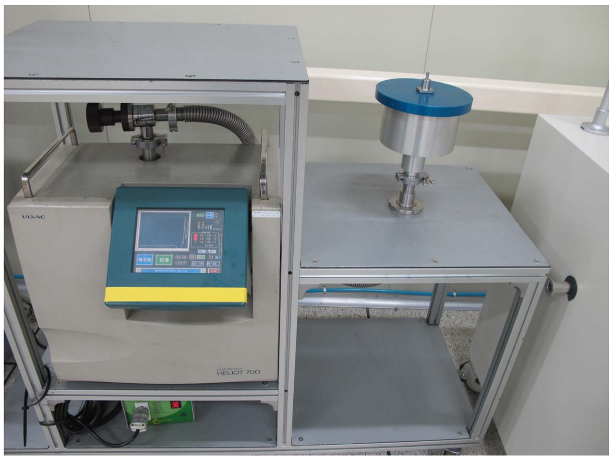

Fig. 5. Leak detector used for testing seal performance. The ferrofluid seal was positioned at the upper part of chamber

medium vacuum region, indicating 20 and 0.23 Pa for the silicone-oil-based ferrofluid and the poly-α-olefin-based ferrofluid, respectively. The higher vacuum degree in case of the latter than the former would be due to stabler dispersibility of the magnetic nanoparticles in the hydrocarbonaceous base, because the dispersion of the oil-based fluids was remarkably lower than that of the hydrocarbon-based fluids.

4. CONCLUSIONS

Magnetite nanoparticles were obtained by chemical precipitation using an iron chloride solution and ammonium hydroxide. The particles were covered with a silicon surfactant of α,ω-(3-aminopropyl)polydimethylsiloxane to disperse into polydimethylsiloxane base and with a combined fluorosurfactant of anionic ammoniated perfluoroalkyl sulfonamide and nonionic fluoroaliphatic polymeric esters to disperse into perfluoropolyether. Experimental parameters were determined for the silicone-oil-based and fluorine-oil-based ferrofluids of 200, 300, and 400 mg/mL, and the properties of density, magnetization and viscosity were studied with the prepared ferrofluids. The fluid density increased from 1.11 g/mL to 1.27 g/mL for the silicone oil base and from 1.95 g/mL to 2.10 g/mL for the fluorine oil base in proportion to the concentration. Values of the saturation magnetization of the ferrofluids were 14.7 to 30.7 mT for the silicone oil base and 15.8 to 33.7 mT for the fluorine oil base with increasing concentrations in the range of 200 to 400 mg/mL, depending on the content of magnetic particles in the fluid. In the viscosity-temperature property, the silicone-oil-based fluid was effective for practical use compared with the fluorine-oil-based fluid.

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REFERENCES

1. Betancourt-Galindo, R., Ayala-Valenzuela, O., Garcia-Cerda, L.A., Rodriguez Fernandez, O., Matutes-Aquino, J., Ramos, G., and Yee-Madeira, H., "Synthesis and Magneto-structural Study of $Co_xFe_{3-x}O_4$ Nanoparticles," *Journal of Magnetism and Magnetic Materials*, Vol. 294, 2005, pp. e33-e36.
2. Drummond, A.L., Feitoza, N.C., Duarte, G.C., Sales, M.J.A., Silva, L.P., Chaker, J.A., Bakuzis, A.F., and Sousa, M.H., "Reducing Size-Dispersion in One-Pot Aqueous Synthesis of Maghemite Nanoparticles," *Journal of Nanoscience and Nanotechnology*, Vol. 12, No. 10, 2012, pp. 8061-8066.
3. Kim, J.-H., Kim, S.-M., and Kim, Y.-I., "Properties of Magnetic Nanoparticles Prepared by Co-Precipitation," *Journal of Nanoscience and Nanotechnology*, Vol. 14, No. 11, 2014, pp. 8739-8744.
4. Acar Havva Ya ci, Garaas Rachel S., Syud Faisal, Bonitatebus Peter, and Kulkarni Amit M., "Superparamagnetic Nanoparticles Stabilized by Polymerized PEGylated Coatings," *Journal of Magnetism and Magnetic Materials*, Vol. 293, No. 1, 2005, pp. 1-7.
5. Silva Juliana B., Brito Walter De, andMohallem Nelcy D.S., "Influence of Heat Treatment on Cobalt Ferrite Ceramic Powders," *Materials Science and Engineering: B*, Vol. 112, No. 2-3, 2004, pp. 182-187.
6. Wang Dan, Ma Qian, and Yang Ping, "Synthesis of Fe_3O_4 Nanoparticles with Tunable and Uniform Size through Simple Thermal Decomposition," *Journal of Nanoscience and Nanotechnology*, Vol. 12, No. 8, 2012, pp. 6432-6438.
7. Senyei Andrew, Widder Kenneth, and Czerlinski George, "Magnetic Guidance of Drug-carrying Microspheres," *Journal of Applied Physics*, Vol. 49, No. 6, 1978, pp. 3578-3583.
8. Kim, J.H., Kim, C.G., Lee, S.G., Hong, T.M., and Choi, J.H., "Viscosity of Magnetorheological Fluids Using Iron-Silicon Nanoparticles," *Journal of Nanoscience and Nanotechnology*, Vol. 13, No. 9, 2013, pp. 6055-6059.
9. Shimoiizaka, J., Kakatsuka, K., Fujita, T., and Kounosu, A., *Fine Particles Processing*, American Institute of Mining, Metallurgical and Petroleum Engineers, Inc., New York, 1980, pp. 1310-1324.
10. Kim, J.H., Lee, C.H., and Lee, S.K., "Superparamagnetic Gd- and Mn-substituted Magnetite Fluids Applied as MRI Contrast Agents," *Bulletin of the Korean Chemical Society*, Vol. 30, No. 6, 2009, pp. 1305-1308.
11. Kim, J.-H., Kim, S.-M., Kim, K.-H., and Kim, C.-O., "Applicability of Radioactive $^{99m}Tc\text{-}O_4^-$ Magnetic Fluid to Nuclear Medicine," *Journal of Physics: Conference Series*, Vol. 266, No. 1, 2011, pp. 012073.
12. Kim, J.-H., and Park, K.-B., "Properties of Polyalphaolefin-Based Ferrofluids," *Journal of Magnetics*, Vol. 20, No. 4, 2015, pp. 371-376.
13. Kim, J.-H., and Park, K.-B., "Properties of Ferofluids Prepared with an Isoparaffin Base," *Journal of Nanoscience and Nanotechnology*, Vol. 16, No. 6, 2016, pp. 6440-6444.