

Properties of Polyalphaolefin-Based Ferrofluids

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(Received 18 July 2015, Received in final form 21 September 2015, Accepted 21 September 2015)

Magnetite nanoparticles were synthesized by adding excess ammonium hydroxide to a solution of iron (II) and (III) chlorides. The surfactants of oleic acid and Span 80 were applied in sequence to the magnetic particles as a combined stabilizer, and poly- α -olefin (PAO) 30 or 60 was used as the liquid base with a low or high viscosity, respectively. The ferrofluids were prepared with the concentrations of 200, 300, 400, and 500 mg/mL, and characterized by density, dispersion, magnetization, and viscosity. The density of the fluids increased proportionally to the concentration from 0.98 to 1.27 g/mL and 1.01 to 1.30 g/mL with PAO 30 base and PAO 60 base, and the dispersion stability was 77-95 and 81-74% for the PAO-30 and PAO-60-based fluids, respectively. The observed saturation magnetization values of the PAO-30 and PAO-60-based ferrofluids were 16 to 42 mT and 17 to 41 mT with the concentration increase in the range 200-500 mg/mL, respectively, depending upon the content of magnetic particles in the fluid. The viscosity variation of the PAO-30 and PAO-60-based ferrofluids in the temperature range 20-80°C was the least with the concentrations of 400 and 300 mg/mL, respectively.

Keywords : nanoparticles, fluid concentration, dispersion, saturation magnetization, viscosity

1. Introduction

Nanometer-sized inorganic particles can be dispersed into hydrophilic or lipophilic liquid base by covering them with the suitable surfactants. The fluidized magnetic nanoparticles have been applied under various fields owing to their interesting magnetic properties [1]. The nanoparticles are usually prepared by mechanical milling or chemical precipitation, in which the particles synthesized by the latter method are characterized by a narrower size distribution. Particulate magnetite has been usually synthesized by adding ammonium hydroxide to a solution containing both Fe²⁺ and Fe³⁺ [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 outer layer. The outer layer is removed by the acid treatment in the pH range 5.0-5.5. Therefore, an anionic group of the first surfactant is conjugated to the cation of the iron oxide on the inside, with the functional groups of the second surfactant com-

patible with the liquid base pointing towards the outside [4]. Because the magnetic nanoparticles have superparamagnetism characteristic [5, 6], their fluid flow can be reversibly controlled and localized at a specific site in dependence on the external magnetic field strength [7]. The high temperature viscosity of the ferrofluids is significantly important for vacuum seals, because the temperature of the motor reaches ~57°C under normal operating conditions.

In this study, magnetite nanoparticles were produced by the chemical coprecipitation using a solution of iron (II) and (III) chlorides and ammonium hydroxide. The surfactants of unsaturated oleic acid and nonionic Span 80 were used for a bilayer formation to prepare the ferrofluids, and poly- α -olefin was selected as the hydrophobic liquid base, because its synthetic lubricants possess good thermal stability and low pour point. The density, dispersion, and magnetization of the ferrofluids were studied in the concentration range 200-500 mg/mL, and their viscosity was investigated at different concentrations at various temperatures.

2. Experimental

FeCl₂·4H₂O (M_w 198.81, > 99%) and FeCl₃·6H₂O (M_w

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270.29, > 99%) were dissolved in 100 mL of distilled water to prepare a solution with a $\text{Fe}^{2+}/\text{Fe}^{3+}$ stoichiometric ratio of 0.5. Magnetic particles were synthesized by stirring this chloride solution for 10 min at room temperature in a 500 mL three-neck flask and adding NH_4OH (28-30 wt% NH_3) in a 1.5 times excess over the stoichiometric reaction amount [8], forming a magnetite phase with the particle size of 12 nm [3]. The resulting precipitate was washed several times with distilled water using ultrasonication and magnetic decantation to remove the ammonium chloride salt by-product, and the resulting black gel was then subjected to prolonged drying at a low temperature of 40°C to prevent the particles from being surface-oxidized.

As oleic acid was applied to the particles as the first stabilizer, the nonionic surfactants of Span 20 (sorbitan monolaurate, HLB value 8.6) and Span 80 (sorbitan monooleate, HLB value 4.3) were comparably combined with oleic acid as the second stabilizer. PAO-30-based fluids were prepared with different combinations of the stabilizers at various quantities to observe the dispersibility using a Turbiscan ageing station (Formulation, France), in which the combination of oleic acid and Span 80 was more effective than that of oleic acid and Span 20, indicating lower stability indices for ageing time.

An adequate amount of oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, M_w 282.46, d 0.89) was first adsorbed onto the nanoparticles by stirring for 30 min at 60°C in 80 mL 2-butanone (MEK, $\text{C}_2\text{H}_5\text{COCH}_3$), and subsequently

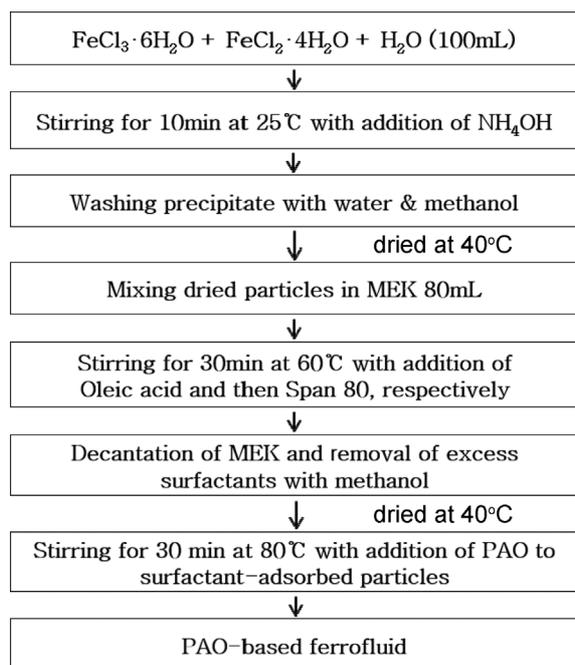


Fig. 1. A typical process for preparing PAO-based ferrofluids.

Span 80 ($\text{C}_{24}\text{H}_{44}\text{O}_6$, M_w 428.60, d 0.986) was applied under the same conditions for the formation of a bilayer. The MEK solution was decanted from the suspension, and the excess surfactants were washed several times with methanol, and the treated nanoparticles were dried at 40°C. The components of MEK and methanol remaining on the dried particles were completely volatilized during the dispersion at 80°C in the PAO base. Fig. 1 shows a typical process for preparing the hydrophobic ferrofluids using PAO 30 of low viscosity (30.5 cSt/40°C) and PAO 60 of high viscosity (61 cSt/40°C). The ferrofluids were prepared at the concentrations of 200, 300, 400, and 500 mg/mL (particles weight to fluid volume).

The magnetic properties of the magnetic particles and ferrofluids were measured using a vibrating sample magnetometer (VSM) in the field range of ± 10 kOe. The viscosity of the fluids was recorded using a Brookfield viscometer (LV DV-II+PRO) equipped with a small sample adapter (SSA 18/13R). The dispersion stability of particles in the fluid was evaluated from the density values of the as-prepared fluid, fully stabilized fluid, and liquid base.

3. Results and Discussion

3.1. Preparation of ferrofluids

A mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (6.88 g, 0.0346 mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (18.72 g, 0.0692 mol) was precipitated by adding ammonium hydroxide following the reaction $\text{FeCl}_2 + 2\text{FeCl}_3 + 8\text{NH}_4\text{OH} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{NH}_4\text{Cl} + 4\text{H}_2\text{O}$, affording 8.0 g magnetite particles, from which a 100 mg/mL fluid concentration was prepared to give 80 mL of the ferrofluid. The fluids of higher concentration were obtained using increasing amounts of the particles in the fixed fluid volume.

The optimum amount of oleic acid needed to form the monolayer on the magnetite particles was evaluated with an area site occupied by each oleic acid molecule on the Fe_3O_4 surface. The number of Fe_3O_4 particles per gram (N_p) and the total area A available for coverage were calculated by $(1/\rho_{\text{Fe}_3\text{O}_4})/(4\pi r^3/3)$ and $4\pi r^2 N_p$, respectively; the amount of oleic acid adsorbed per gram of Fe_3O_4 particles is represented by the following equation [9]:

$$g_{\text{oleic-acid}}/g_{\text{Fe}_3\text{O}_4} = A/\tau \cdot M_w/N_A, \quad (1)$$

where r is the particle radius, $\rho_{\text{Fe}_3\text{O}_4}$ the specific gravity of magnetite particles, τ the adsorption area occupied by each oleate ion, M_w the molecular weight of oleic acid, and N_A the Avogadro's number. The diameter of Fe_3O_4 particles observed by TEM was found to be 12 nm [3]; a density value of 4.8 from Fe_3O_4 Aldrich powder (< 50

Table 1. Experimental conditions used for preparing PAO-based ferrofluids with various concentrations at a fixed volume of 80 mL.

Fluid conc. mg/mL	FeCl ₃ ·6H ₂ O g	FeCl ₂ ·4H ₂ O g	NH ₄ OH mL	Fe ₃ O ₄ yield [†] g (mL)	Oleic acid mL		Span 80 mL		PAO mL	Volume fraction %		
					added	adsorbed	added	adsorbed		particle	surfactant	liquid base
100	18.72	6.88	27.2	8(1.6)	4	2.1	6	2.9	73	2	6	92
200	37.44	13.76	54.4	16(3.2)	8	4.3	12	5.8	67	4	13	83
300	58.16	20.64	81.6	24(4.8)	12	6.4	18	8.8	60	6	19	75
400	74.88	27.52	108.8	32(6.4)	16	8.6	24	11.7	53	8	25	67
500	93.60	34.40	136.0	40(8.0)	20	10.7	30	14.6	47	10	32	58

[†]The Fe₃O₄ volume was obtained using a density value of 5.0 g/mL

nm: d 4.8–5.1) gives $N_p \approx 2.303 \times 10^{17}$ particles/g and $A \approx 1.042 \times 10^{20}$ nm²/g. Considering that τ is 0.205 nm² [9], the total weight of monolayered oleic acid is 0.238 g (8.426×10^{-4} mol) per gram of Fe₃O₄ particles from Eq. (1). Based on a Fe₃O₄ weight of 2.0 g, the volume of oleic acid corresponds to 0.53 mL, and Span 80 of the same mole as oleic acid is 0.73 mL. Oleic acid (1.0 mL) and Span 80 (1.5 mL) twice as much as the calculated amount were used for the adsorption process of Fe₃O₄ (2.0 g) to sufficiently cover the particles with a bilayer, after which the surplus surfactants were completely removed to have no effect on the properties of PAO liquid. Table 1 summarizes the experimental conditions used for preparing 80 mL of the PAO-based ferrofluids at various concentrations in the range 100–500 mg/mL.

3.2. Bilayer formation of particles

Water-based ferrofluids have usually been prepared by forming a bilayer on the particles, sometimes with oleic acid as the first surfactant and dodecyl benzene sulfonate as the second [8, 10]. From a structural viewpoint, an imperfect FeO(OH) layer exists on the surface of synthesized magnetite nanoparticles, which can form OFe⁺ by reacting with acid. The first shell layer results from the

formation of a chemical bond between the metal cation of core particles and the carboxyl anion of oleate. However, the oleate-adsorbed particles have a low long-term stability of the alkyl chains, even though they can be dispersed in hydrocarbon liquids. The shell surfactant, therefore, should possess both an additional steric repulsion between the particles and an affinity towards the liquid base. Using nonionic Span 80 as the second layer, the inside of the layer is attracted by dispersion (van der Waals) forces towards the nonpolar group of the first layer, whereas the outside region is matched to the poly- α -olefin liquid. As a result, the stability of fluid was achieved by the formation of bilayer shells on the core magnetite particles.

3.3. Fluid density and dispersion

The density of a completely dispersed ferrofluid was obtained by measuring the volume and weight of the as-prepared ferrofluids. The densities of the PAO-30 and PAO-60-based fluids were 0.98, 1.07, 1.18, and 1.27 g/mL and 1.01, 1.11, 1.20, and 1.30 g/mL for the fluids with the concentrations of 200, 300, 400, and 500 mg/mL, respectively. In order to observe the dispersion stability of ferrofluids, the density of one-week-old fluids was measured at the upper part of a fully stabilized fluid.

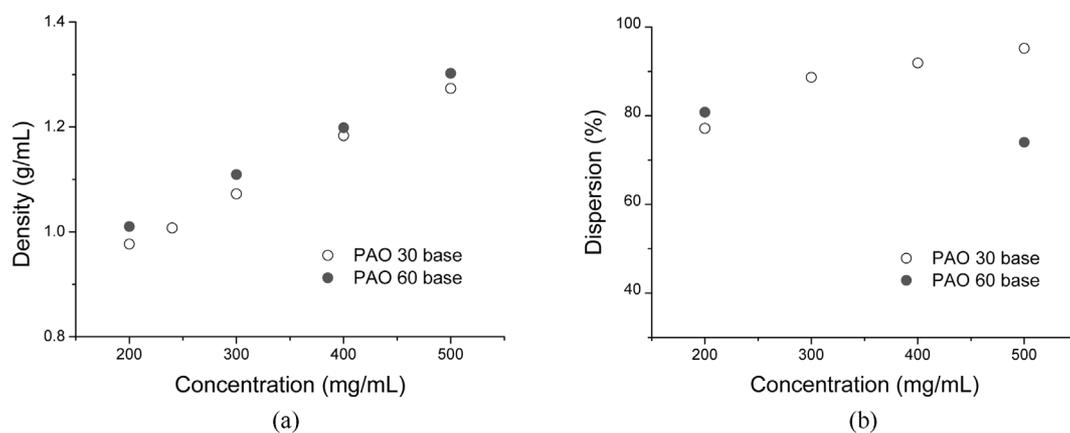


Fig. 2. (a) Density and (b) dispersion of PAO-based ferrofluids as a function of concentration.

The dispersion stability was evaluated by calculating the dispersion with the density of different species as given by Eq. (2) [11].

$$Dispersion = (\rho_2 - \rho_L) / (\rho_1 - \rho_L), \quad (2)$$

where ρ_1 , ρ_2 , and ρ_L are the density values of the as-prepared fluid, one-week-old fluid, and liquid base, respectively. The dispersion percentages of the fluids obtained quantitatively from the relevant densities were in the range 77-95% at the concentrations of 200 to 500 mg/mL with the PAO 30 base, indicating 81 and 74% at 200 and 500 mg/mL, respectively, with the PAO 60 base. Figs. 2(a) and (b) show the density and dispersion of the PAO-based ferrofluids at various concentrations, respectively. Slightly high-density values of the PAO-60-based fluids compared to the PAO-30-based fluids result from the property of each liquid base (PAO 30: d 0.822, PAO 60: d 0.840). A remarkable difference in the dispersion between two types of ferrofluids at the high concentration reflects difficulty in treating the fluids for the density measurement because of the increase in the viscosity.

3.4. Magnetic properties

The saturation magnetization of the synthesized magnetite decreased from 62.4 emu/g for the pristine particles to 54.6 emu/g and 46.4 emu/g for the oleate-monolayered particles and the oleate/Span-bilayered particles, respectively, because of the shell of the nonmagnetic organic component [12]. The magnetization curves of the nanoparticles were typically superparamagnetic. The saturation magnetization M_s of ferrofluids can be obtained by multiplying their concentration by the saturation value of the pristine particles, because its values were usually measured per unit volume and can also be approximated

by the following equation [11]:

$$M_s = \sigma_s \cdot \rho_p \cdot (\rho - \rho_L) / (\rho_p - \rho_L), \quad (3)$$

where σ_s is the saturation magnetization of the pristine particles, and ρ , ρ_p , and ρ_L are the density values of ferrofluid, particles, and liquid base, respectively.

At 200, 300, 400, and 500 mg/mL concentrations, the values of the saturation magnetization of the PAO-30-based fluids were 12.4, 19.2, 27.1, and 33.2 emu/cm³ respectively, corresponding to 15.5, 24.1, 34.0, and 41.7 mT; the saturation values of the PAO-60-based fluids were 13.3, 20.7, 27.7, and 32.9 emu/cm³ respectively, corresponding to 16.7, 26.0, 34.8, and 41.4 mT. Figs. 3(a) and (b) show the deviation of the saturation values calculated from the content of the pristine particles and approximated by Eq. (3) from the saturation magnetization observed directly with the PAO-30 and PAO-60-based ferrofluids, respectively. The difference in the observed and calculated values was within an error limit of 10% for the magnetization measurement. Such a close approach of the observed saturation values to the calculated data indicates that the magnetization of the ferrofluids depends principally on the content of the magnetic particles in the fluid, without any dependence on the properties of the organic liquid base.

3.5. Fluid viscosity

From the result that the viscosity values of Brookfield fluid 10 and 100 measured at different spindle speeds showed a difference within 5% from the standard, the room temperature viscosities of the PAO 30 and PAO 60 bases were estimated to be 49 and 102 mPa·s (cP), respectively. The viscosity of the PAO-based ferrofluids with different concentrations was measured at 20, 40, 60, and

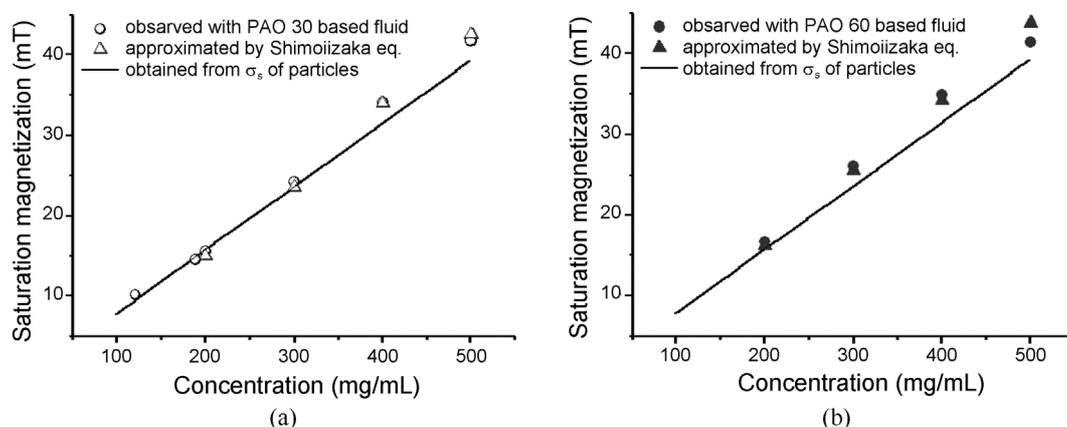


Fig. 3. Comparison between saturation magnetization observed directly and approximated by Shimoiizaka equation for (a) PAO-30-based and (b) PAO-60-based ferrofluids and data (straight line) obtained from saturation value σ_s of pristine particles at each concentration.

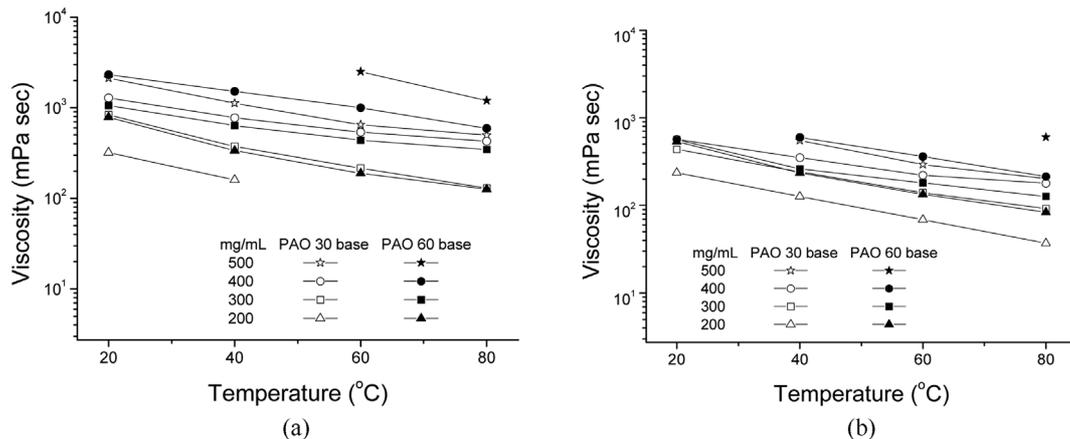


Fig. 4. Viscosity vs. temperature curves of PAO-30-based and PAO-60-based ferrofluids obtained at different concentrations using (a) 1.2 and (b) 5.0 rpm of Brookfield S18 spindle.

80°C without an applied magnetic field. 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 depending on the spindle speed. The viscosity of the ferrofluids was measured at the spindle speeds of 1.2 and 5.0 rpm (max. measurable level: 2500 and 600 cP, respectively). Their usefulness in the field of seal design was evaluated by the viscosity-temperature property.

Figures 4(a) and (b) show the variations in the viscosity with temperature at the concentrations in the range 200-500 mg/mL for PAO-based ferrofluids, using measurements of 1.2 and 5.0 rpm, respectively. The fluid viscosity decreased exponentially with increasing temperatures. The viscosity values of PAO-60-based fluids were considerably higher than those of PAO-30-based fluids under the same conditions, reflecting a viscosity difference between the two liquid bases. At 1.2 rpm, the viscosity of 500 mg/mL PAO-60-based fluid could be measured at 60°C, because the torque exceeded 100% below that temperature, and the viscosity of the 200 mg/mL PAO-30-based fluid could be determined only at 40°C and less, with a torque value over the minimum confidence limits of 10%. The decrease in the viscosity with increasing temperatures from 20 to 80°C was 66.7% (1282 to 427 cP), 76.7% (2125 to 495 cP), and 84.4% (832 to 130 cP) for the PAO-30-based fluids with the concentrations of 400, 500, and 300 mg/mL, respectively, and was 67.5% (1060 to 345 cP), 74.4% (2315 to 592 cP), and 84.0% (786 to 126 cP) for the PAO-60-based fluids at the concentrations of 300, 400, and 200 mg/mL, respectively. The viscosity curves at 5.0 rpm also showed a similar tendency with a 43% level of the values at 1.2 rpm,

starting from 570 cP at 20°C for both 400 mg/mL PAO-30-based fluid and 300 mg/mL PAO-60-based fluid.

4. Conclusions

Magnetite nanoparticles were prepared by the precipitation of bivalent and trivalent iron chlorides. A combined stabilizer involving the unsaturated oleic acid and non-ionic Span 80 was adsorbed onto the surface of the particles. The bilayer-coated particles were dispersed into PAO 30 and PAO 60 with low and high viscosity values, respectively. Experimental parameters were determined for the PAO-based ferrofluids of 200, 300, 400 and 500 mg/mL, and the density, dispersion, magnetization, and viscosity were studied in detail. The fluid density increased from 0.98 to 1.27 g/mL with the PAO 30 base and from 1.01 g/mL to 1.30 g/mL with the PAO 60 base in proportion to the concentration. The average dispersion stability was 88 and 77% for the PAO-30 and PAO-60-based fluids, respectively. The observed magnetization of the PAO-30 and PAO-60-based ferrofluids was saturated at the values of 16 to 42 mT and 17 to 41 mT in the range 200-500 mg/mL, respectively, depending mainly on the content of magnetic particles in the fluid. The viscosity-temperature property was excellent for 400 mg/mL PAO-30-based and 300 mg/mL PAO-60-based ferrofluids. Considering their magnetic properties, the concentrated ferrofluid would be more useful for practical purposes.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education,

Science and Technology (NRF-2012R1A1A2039083).

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