Journal of Colloid and Interface Science 506 (2017) 162–168

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Studies on the role of unsaturation in the fatty acid surfactant molecule on the thermal conductivity of magnetite nanofluids

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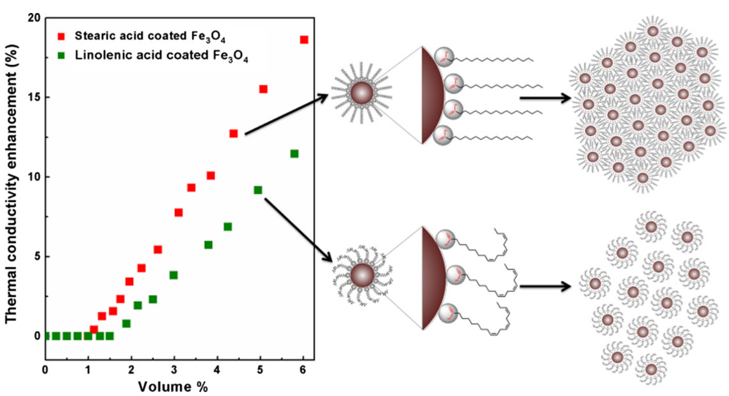
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 March 2017
Revised 9 July 2017
Accepted 13 July 2017
Available online 14 July 2017

Keywords:
Magnetic fluid
Nanofluid
Surfactant
Unsaturation
Conformation
Thermal conductivity
Viscosity

ABSTRACT

To study the role of unsaturation in the surfactant molecule on the thermal conductivity of magnetite nanofluids, four different fatty acid (stearic, oleic, linoleic, and linolenic acids with different degree of unsaturation) coated magnetite nanoparticles of comparable size are prepared and dispersed in toluene. It is found that the nanofluid with the saturated fatty acid coated nanoparticles show larger viscosity than the fluid with the unsaturated fatty acid coated particles at all concentrations. Thermal conductivity studies show enhancement only above a critical concentration for all fluids. The critical concentration for thermal conductivity enhancement varies with the surfactant, possibly due to the difference in the degree of aggregation of the nanoparticles in the fluid, because of the difference in the conformation of the surfactant molecules on the nanoparticle's surface. The experimental thermal conductivity follows the Maxwell model at higher concentrations. From the overall studies, it is observed that the thermal conductivity of the fluids with aggregated or assembled nanoparticles shows slightly larger enhancement than that of the fluids with isolated particles. However, in the presence of a magnetic field, the fluids with isolated nanoparticles showed relatively larger enhancement, possibly due to the easy response of the isolated magnetite nanoparticles to the applied field.

1. Introduction

Heat transport using magnetite (Fe_3O_4) nanofluids is one of the recent research areas due to their tunable thermal properties by

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http://dx.doi.org/10.1016/j.jcis.2017.07.038
0021-9797/

the application of an external magnetic field [1–14]. A large thermal conductivity enhancement is reported at very low magnetic fields for oleic acid coated magnetite nanoparticles dispersed in kerosene [1]. There are many reports in the literature on the thermal conductivity studies on magnetite based nanofluids [1–25] with different degree of enhancement in the thermal conductivity, possibly due to many factors related particle, fluid, interfacial, and nanoscale effects. The stability of the magnetic nanofluids is one of the major criteria for their use in the heat transfer applications. Compared to other fluids, the aggregation of the nanoparticles in a magnetic fluid is more prominent due to the magnetic interaction (dipole-dipole) between the particles apart from the van der Waals interactions [26]. Surfactant molecules play a crucial role in the stabilization of magnetic nanoparticles in a fluid against the aggregation or clustering [27]. Fatty acids are the most widely used surfactants for stabilizing magnetite nanoparticles in aqueous as well as in non-aqueous medium [28,29]. In a non-aqueous medium, a monolayer of the fatty acid stabilizes the magnetite nanoparticles from the magnetic as well as van der Waals interactions, through the long alkyl chain in the surfactant.

The aggregation/clustering of the magnetic nanoparticles in a fluid is known to influence the thermal conductivity of magnetic nanofluids [11,18]. The large aggregates in a fluid could lead to decreased thermal conductivity due to the less concentration of the particles in the suspension (due to sedimentation) and less mobility (reduced Brownian velocity) than that of the individual particles [17]. However, it has also been observed that fluids with slight aggregation/clustering of magnetic nanoparticles show larger thermal conductivity enhancement compared to that for highly aggregated and well-dispersed nanoparticles [10,11,18]. The magnetic nanoparticles in a fluid could form reversible aggregation in the presence of a magnetic field, and the thermophysical properties can be tuned by varying the magnetic field [11]. The directed assembly of magnetic dipoles of magnetite nanoparticles in the presence of a magnetic field has been found to be responsible for larger anisotropic thermal conductivity in magnetic nanofluids [6–9,13].

Unlike the directed assembly [30], self-assembly of magnetic nanoparticles in a fluid is also possible in the absence of a magnetic field, due to the internal forces between the nanoparticles [31,32]. The dipolar interaction between the thermally fluctuating magnetic moments cannot be neglected for larger particles, even with a surface coating. For smaller magnetic nanoparticles, the self assembly of the particles in a fluid is mainly due to the van der Waals interaction than the magnetic interaction (dipole-dipole), because of the larger thermal fluctuation of the magnetic moments [17,26]. In a highly concentrated fluid, the nanoparticles are close to each other, and the interparticle separation is less than twice the length of the surfactant molecule on the nanoparticle's surface, leading to interpenetration (interdigitation) of surfactant molecules attached to the neighboring particles [33]. In addition to the van der Waals attraction between the particles, the interpenetration of (interdigitation) surfactant molecules attached on the neighboring nanoparticles also causes the self-assembly [34,35].

Philip et al. observed high thermal conductivity enhancement for oleic acid coated magnetite nanofluid, in a low magnetic field, and this has been attributed to the formation of nanoparticle chains (aggregation) in the direction of the applied magnetic field and the heat energy transferred through these chain-like structures [1]. Altan et al. [12] evaluated the thermal conductivity of decanoic (capric) acid coated Fe_3O_4 nanoparticles dispersed in water and heptane. A linear enhancement with magnetic field is observed even at low concentrations and at low magnetic fields. From the studies, it is concluded that the observed enhancement is due to the thermomagnetic convection in the nanofluid in the presence of the magnetic field. In the former case, the magnetite nanoparticles are coated with an unsaturated fatty acid (18-carbon oleic acid with a kink at 9th carbon atom), and in the latter case, the magnetite nanoparticles are coated with a saturated fatty acid (capric acid with 10-carbon straight chain). The conflicting reports on the changes in the thermal conductivity of the fluids with magnetite nanoparticles stabilized using two different types of surfactants suggest that probably the nature of the surfactant at the interface could play a role in the thermophysical properties of the magnetic nanofluids.

The different conformations of the surfactant molecules on the surface of the nanoparticles are likely to affect the wetting of the nanoparticle's surface and dispersibility of the nanoparticles in a base fluid. Tadmor et al. [36] studied the interaction of the solvent, hexadecane, with stearic acid (saturated) and oleic acid (unsaturated) layers on mica surfaces. Hexadecane as the solvent is found to solvate the oleic acid layer more effectively than the stearic acid layer on the mica surface and the effective wetting of the oleic acid layer on the mica surface is ascribed to the kink conformation of the oleic acid molecules with less nematic interaction. Jiang and Wang [17] reported that the nature of the coating layer has an effect on self-assembly of nanoparticles in nanofluids and the self-assembled structures strongly influence the thermal conductivity of nanofluids. Sahoo et al. [37] observed different interactions between the surfactants for saturated and unsaturated fatty acid coated samples which directly affect the amount of the secondary surfactant over the primary surfactant on the nanoparticle's surface.

From the reported studies using different surfactants and solvents, it appears that the surface of the nanoparticles is one of the important factors to be considered for thermal conductivity studies other than the properties of the dispersant (nanoparticles) and the dispersing medium (base fluid). The interaction between the surfactant molecules and between the surfactant and the solvent can be different for different surfactants on the surface of the nanoparticles. The influence of the interface related factors such as the nature and conformation of surfactant on the thermal conductivity of nanofluids is still not understood properly. To understand the role of the conformation of the surfactant molecule and the resultant surfactant-solvent interaction on the thermal conductivity, four different fatty acid coated magnetite nanoparticles of comparable size and distribution are prepared using different fatty acid as surfactants with the same number of carbon atoms (18 carbons) and different degree of unsaturation in the carbon chain. The fatty acids; stearic, oleic, linoleic and linolenic acids, containing the number of unsaturation as 0, 1, 2, and 3, respectively, are used for surface coating of the magnetite nanoparticles. The fatty acid coated magnetite nanoparticles are dispersed in toluene at different volume concentrations and used for thermal conductivity studies.

2. Materials and methods

2.1. Synthesis

For the synthesis of different fatty acid coated magnetite nanoparticles, $FeCl_3{\cdot}6H_2O$ (97%), $FeCl_2{\cdot}4H_2O$ (99%), stearic acid (octadecanoic acid, 95%), oleic acid (cis-9-octadecenoic acid, 90%), linoleic acid (cis,cis-9,12-octadecadienoic acid, 74%), and linolenic acid (cis,cis,cis-9,12,15-octadecatrienoic acid, 70%) were purchased from Aldrich Chemicals. Aqueous ammonia (25%), toluene (99.5%), acetone (99.5%), hexane (95%), 2-propanol (99.5%), and hydrochloric acid (37%) were purchased from Merck Chemicals. All the chemicals were used as-received and double distilled water was used for the synthesis.