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The wettability of PTFE and glass surfaces by nanofluids

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ABSTRACT

Wetting of solid surfaces by surfactant solutions is well focused in the literature compared that of nanofluids. Similar to the surfactant solutions nanofluids are also able to reduce the surface tension as well as influence on contact angle at the solid, liquid and gas interface. The surface tension and wettability of two different nanofluids containing hydrophilic (TiO_2) and hydrophobic (S) particles have been experimentally studied here. The surface tension reduction of nanofluids strongly depends on material property, particle size and as well as concentration. These parameters also influence the change in contact angle on both hydrophilic (glass) and hydrophobic (PTFE) surfaces. Three important factors such as surface tension, surface hydrophobicity after deposition of particles on a solid surface, and the disjoining pressure influence the final contact angle of nanofluids on a solid surface. Sulfur nanofluids show maximum enhancement in contact angle (30.6°) on the glass surface; on the other hand TiO_2 nanofluids show maximum reductions in surface tension (25.4 mN/m) and contact angle on the PTFE surface (17.7°) with respect to pure water.

1. Introduction

Nanofluids are suspensions (colloidal state) of nanomaterials in a base liquid. Nanofluids have drawn attention of researchers initially because of their enhanced thermo-physical properties (thermal conductivity, thermal diffusivity). In addition to their thermal applications in industrial and nuclear reactor cooling, cooling in electronics, heavy engines transportation [1,2], the nanofluids have also potential applications in biomedical (magnetic or ferrofluids in drug delivery, MRI contrast), magneto-optical wavelength filter, antibacterial activity, optical modulators, nonlinear optical materials, ink jet printing, soil remediation, oily soil removal, lubrication and enhanced oil recovery, surface coating, wetting and surface cleaning, energy storage and so on [1–6]. During the past few years, the researchers' attention as well as the publications on nanofluids increasing exponentially because of these exciting applications. Similarly, the wetting of solid surfaces by liquids is also of immense interest towards a broad research community from the past few decades surely because of the practical, and scientific importance [7–9]. Wettability of the flat solid surfaces by pure liquids or surfactant solutions is a complex phenomenon; it depends on the movement of the triple line, where the three phases are in mutual contact; which in turn depends on physical properties of a solid (homogeneity, roughness, surface energy) as well as liquid (surface tension, polarity, viscosity). But the wettability of solid surfaces by nanofluids is a more complex process because of the presence of particles, where the well-established theories of wetting by pure liquids or solutions are insufficient to explain the observations [10,11]. In this case several additional factors such as particle size, concentration at the triple line, particles solid, particles fluid, particles particles interactions are also equally important in addition to the common factors for pure liquids or solutions. The detail explanations of individual factors are mentioned in result and discussion section. There are numerous studies available on the wetting behavior of surfactant solutions on solid surfaces [8,9,12,13], however, limited on nanofluids [14–16].

Liquid surface tension plays an important role in the wetting process, in general, lower surface tension liquid favors the wetting of low surface energy or hydrophobic surfaces. Similar to surfactants, addition of nanoparticles also can reduce surface tension as well as influenced the movement of the triple line because of strong attachment of the particles at fluid–fluid interface, whether the particles are hydrophobic or hydrophilic [17,18]. But these interfacial properties of nanoparticles suspension or nanofluids greatly depend on the material property, size, shape, and the concentration of the particles [16]. The literature available on wetting of nanofluids can be broadly classified into three categories: (i) bubble growth or dynamics on solid surface inside the liquid [19,20], (ii) removal of oil droplets from a solid surface [10], (iii)

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wetting of solid surface [15,16,21,22]. Vafaei and Wen [19,20,23] reported the extent of surface wettability of a solid–liquid–gas system which is dependent on the material property, size and concentration of the particles. More specifically, a unique pinning behavior of the triple line was observed when bubbles formed on a metal surface inside the gold nanofluids compared to that of pure water, whereas a spreading of triple line was observed for bubbles forming inside alumina nanofluids for a constant bubble volume [20]. The nanofluids containing alumina, zirconia, and silica have shown a significant enhancement in critical heat flux (CHF) because of improvement in the wettability of the fluid on the solid surface [24,25]. The pool boiling characteristic of nanofluids as a heat transfer fluid, highly dependent on both particle concentration and fluid/surface wetting characteristics [20]. The removal of oil drops from the solid surface by nanofluids is another important application. Where the nanoparticles are deposited near the triple line and generate an excess structural disjoining pressure which favors removal of oil droplets from the surface. Most of the studies in this field are theoretical based but some experimental papers are also available by different research groups [10,14,26]. Wasan and coworkers are the pioneer in this field [10,14,26–29], however gradually some other research groups have also started working in this area [14–16,30]. Finally, the studies on wettability of solid flat surfaces by nanofluids are also limited [15,16,21,31]. Vafaei et al. [15,16] studied the wetting of a solid surface by the nanofluids which containing Bi_2Te_3 particles on different hydrophilic surfaces (glass and silicon wafer) and their results show the contact angle depends on both particle size and concentration. They used 2.5–10.4 nm particles functionalized with thioglycolic acid and studied the contact angle and surface tension of the suspensions. According to their results, for a particular particle size, the contact angle initially increases with increasing particle concentration and attains a maximum for both surfaces. Further, at a constant particle concentration lower size particle is more efficient to increase the contact angle.

It can be seen from the literature that until now most of the studies on the wetting properties of nanofluids are theoretical based and only limited experimental studies are available [15,17]. The available experimental studies are mostly in the presence of capping agents or functionalized the particles with some molecules. Herein, we studied the effect of possible different parameters of nanofluids on the wetting properties of the solid surfaces and surface tension. A detailed knowledge about the mechanism of increase or decrease the wetting of hydrophobic or hydrophilic surfaces by these nanofluids could be useful in various applications such as paint, antimicrobial or antifungal agents, energy storage, heat transfer fluids, or any other thermal applications. Based on the applications nanofluids of different materials are used. Especially TiO_2 nanofluis are widely used with other nanofluids (Al_2O_3, Fe_2O_3, graphene or Fe) to enhanced the heat transfer and used as nanorefrigerant [32], used in enhanced oil recovery [33]. Similarly, sulfur (S) based nanofluid is used and antimicrobial or anti fungal agents, in a recent study it has been reported that S nanofluids can be as used a green pesticide for agricultural applications [34], where wetting is also an important issue. So, aiming to these applications this study reports the wetting behavior of nanofluids containing hydrophobic (S) and hydrophilic (TiO_2) particles in the absence of any capping agents on both hydrophobic (PTFE) and hydrophilic (Glass) surfaces. The particles were synthesized in situ in aqueous media without any dispersing agent. Effects of various parameters on wettability and surface tension, such as particle size, particle concentration, and material property were studied which may have lots of practical importance as well as academic interest. To the best of our knowledge similar studies have not been reported.

2. Experimental Section

2.1. Materials

The required chemicals used for this study were taken from the following companies: sodium thiosulphate ($Na_2S_2O_3{\cdot}5H_2O$) from Rankem (99.5% assay), nitric acid (HNO_3) from Merck (69% assay), and Tetrabutyl ortho titanate (TBOT) from Sigma Aldrich (97% assay). All the chemicals were used as those were received without any further purification. Ultrapure water of 18.2 MΩ cm resistivity 71.5 mN/m surface tension, and 6.4–6.5 pH was used for all the experiments. The constant temperature 28 ± 0.5 °C was maintained throughout the experiments.

2.2. Methods

2.2.1. Particles synthesis

Sulfur nanoparticles was synthesized from HNO_3 catalyzed reaction of sodium thiosulphate in aqueous media according to our previous study [35]. Both precursors sodium thiosulphate and HNO_3 were filtered through 0.2 μm nylon 6, 6 membrane filter paper (from Pall Corporation, USA).

The stock $Ti(OC_4H_9)_4$ solution was prepared in anhydrous ethanol. TiO_2 particles were synthesized by the acid catalyzed (HNO_3) sol–gel method. In this reaction first $Ti(OC_4H_9)_4$ was hydrolyzed to $Ti(OH)_4$ in the presence of acid, then $Ti(OH)_4$ was polymerized and condensed to TiO_2 according to the following reactions.

$$n\mathrm{Ti(OC_4H_9)_4} + 4n\mathrm{H_2O} \rightarrow [\mathrm{Ti(OH)_4}]_n + 4n\mathrm{C_4H_9OH} \quad (1)$$

$$[\mathrm{Ti(OH)_4}]_n \rightarrow nTiO_2 + 2nH_2O \quad (2)$$

In both cases, reactants were added under continuous mixing, and the solution was kept for 1 h to complete the reactions and particle sizes were measured immediately by dynamic light scattering (DLS) method after 10 min sonication in a bath sonicatior.

2.2.2. Particle and solid surface characterization

Particle size and zeta potential measurement were carried out by DLS using a Malvern Zeta Size analyzer, (Nano ZS) where size was measured with the help of cumulant fitting model and intensity based size distribution within the media; whereas, zeta potential was measured by using Smoluchowski model. The size, shape, and phase of the particles were characterized by the help of scanning electron microscope (JEOL, JSM-6480LV) and X-ray diffraction (XRD) (Philips, PW 1830 HT). Roughness of both solid surfaces (glass and PTFE) was characterized using atomic force microscopy (Veeco).

2.2.3. Surface tension and contact angle measurements

The particles were synthesized with the increasing reactants (thiosulphate and TBOT) concentrations and after the particle formation each suspension was diluted to the desired concentration with water. Then the suspension was sonicated for 10 min in a water bath sonicator and surface tension and contact angle were measured immediately by using surface tensiometer, (Data Physics, DCAT-11EC) and video based contact angle meter (Data Physics, OCA-20) respectively. The surface tension was measured by the Wilhelmy plate technique. The contact angle was measured by the sessile drop technique with 4 μl drop volume. Before each measurement both platinum plate and solid surfaces (glass and PTFE) were dipped in an ultrasonic cleaning bath for 15 min, then washed thoroughly using water and acetone and finally dried blowing hot air. To get better repeatability quality of solid surfaces were also cheeked in terms of contact angle by the pure water time to time and if required plates were changed after few measurements.