

Effect of various surfactants on the stability time of kerosene–boron nanofluids

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Nanofluid fuels, a new class of nanotechnology-based fluids, are liquid fuels with a stable suspension of nanometre-sized particles. The preparation of fuel mixtures and achieving to a stable and long-term suspension is the key step in nanofluid synthesis. The idea of this work is to suspend nano- and micron-sized boron particles in kerosene, exploring the differences between the complete sedimentation times of particles in fuel at various weight fractions of surfactants and investigating the viscosity of nanofluid at low weight concentration of nanoparticles. Various surfactants including oleic acid, propylene glycol, sorbitan oleate, Tween 85 and CTAB were used to prepare stable kerosene/boron slurries. Suspensions were prepared with varying surfactant loadings of 0.1–2.0% by weight, in steps, for the same particle loading of 0.5 wt%. The results showed that sorbitan oleate was the best surfactant and the optimum weight ratio of boron particle to sorbitan oleate for enhanced stability of nanofluid was determined to be 2. The complete sedimentation time of nanoparticles at the most stable nanofluid was ~57 h. At low temperature and high weight fraction of particles, nanofluids showed similar 67% enhancement in viscosity properties.

1. Introduction: Nanofluids are liquids with stable suspension of nano-sized particles which are typically made of carbon nanotubes, metals or oxides. Studies show that this innovative class of composite fluid exhibit much higher thermo-physical properties such as thermal conductivity and diffusivity as compared with the base fluid, and thus can be applied for more effective cooling or heating for various thermal and energy applications [1, 2]. Previous studies have shown nanofluid fuels at the presence of energetic nanomaterials have demonstrated suitable performance, e.g. shortened ignition delay, higher energy release, increased ignition probability, increased burning rate and enhanced catalytic effect [3–10].

The ignition probability of diesel fuel [8], n-dodecane [11] and ethanol [4] containing a small amount of Al nanoparticles was studied and showed that the ignition probability of nanofluid was higher than the pure fuel. Sabourin *et al.* [7] studied the combustion of nitromethane/colloidal particles of functionalised graphene sheets mixture and found that with an additive of even 1.0 wt% particles, the burning rate was significantly increased. Young *et al.* [12, 13] evaluated the potential of nano-sized boron particles as fuel additive for high-speed airbreathing driving force. Van Devener and Anderson [9] examined the catalytic combustion of JP-10, using soluble CeO₂ nanoparticles as the catalyst and reduced the ignition temperature of JP-10 significantly. Unoxidised (air-stable) boron nanoparticles that were coated with a combustion catalyst ceria [10, 14], used as fuel additives because of the energy density of the core particle and catalytic effect of the outside layer. Rotavera *et al.* [15, 16] found that by using CeO₂ nanoparticles in toluene, the soot deposition on the wall of shock tube under the conditions of high fuel concentration reduced. Sonawane *et al.* [17] showed significant effect of temperature on the thermal conductivity of the aviation turbine fuel–alumina nanofluids. They reported 55% increase in viscosity and 17.0% increase in thermal conductivity for 0.3% volumetric concentration of particle in nanofluid at 50°C. Li *et al.* [18] prepared kerosene–Cu nanofluids by surface modification of particles and showed the effect of surface modification on the viscosity and thermal conductivity of nanofluids. The publications of International Nanofluid Property Benchmark Exercise (Buongiorno *et al.* [19] and Venerus *et al.* [20]) have studied thermal conductivity and viscosity of the nanofluids. Buongiorno *et al.* [19] used a variety of experimental approaches, to calculate the thermal conductivity.

Results showed that thermal conductivity of the nanofluids increased with particle concentration.

The preparation of nanofluids does not simply mean to disperse particles in fuels. Special approaches are needed to achieve a stable, homogeneous and long-term suspension. Dispersion of inorganic nanoparticles in non-polar solvents is difficult. An alternative method to solve this problem is to use small molecules such as phosphate esters, amines, glycerides of fatty acids and carboxylic acids [21–26], which the polar group reacts with the nanoparticle surface, and the non-polar group acts as a surface modification and dispersion agent.

To obtain stable nanofluid fuels, many studies have shown that sonication and adding of surfactants can reduce the coagulation of nanoparticles in nanofluids [27]. When a liquid is exposed to ultrasound, the sound waves that diffuse into liquid result in periodic low-pressure and high-pressure cycles. Sonication uses mechanical stress to separate the particles from each other and reduces agglomeration. Adding a surfactant overcomes the van der Waals force among particles by changing their surface properties with a chemical agent [28]. Two types of stabilisation techniques are used for the preparation of stable nanofluid: steric and electrostatic stabilisations. In steric stabilisation, surfactants cover the surface of the nanoparticles and modify the hydrophobic surfaces of particles to hydrophilic and vice versa for non-aqueous liquids. In the case of electrostatic stabilisation, the pH of nanofluids is changed and departed from the iso-electric point of particles by addition of acid or base into the solution. This causes the nanofluid become more stable [29, 30].

The objective of this Letter is to investigate dispersion and suspension of nano- and micron-sized boron particles in kerosene at the presence of various surfactants. The effect of particle concentrations and temperature on the viscosity of nanofluid is also analysed experimentally. This Letter starts with synthesis of boron nanoparticles and stable suspensions, nanofluid formulation methods including particle dispersion and stabilisation, and finally, nanofluid characterisation.

2. Experimental

2.1. Materials: The boron microparticles used in this Letter (prepared in Malek-Ashtar University of Technology, Iran) had purity of 89 ± 1 wt% and a particle size distribution of 1–5 µm. Fig. 1 shows a scanning electron microscopy (SEM) image of

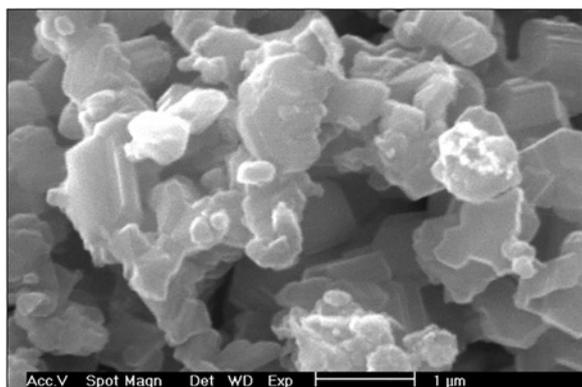


Fig. 1 SEM image of boron microparticles [31]

boron microparticles [31]. Several various surfactants such as oleic acid, propylene glycol (PG), sorbitan oleate and Tween 85 (as non-ionic surfactants) and CTAB (as an ionic surfactant) were used (all surfactants were from Merck Co. Germany). Kerosene (aviation turbine kerosene type), as a non-polar solvent, was selected as the base fuel.

Fig. 2 shows energy-dispersive X-ray spectroscopy (EDAX) analysis of boron microparticles. As shown in Fig. 2, the purity of boron microparticles is about 85%. The presence of carbon in the results is related to the system structure and Au vision is because of particles coating in EDAX apparatus. Only about 1.5 wt% of oxygen is detected in boron particles structure which may be related to the boron oxide or other impurities.

2.2. Synthesis of boron nanoparticles: Boron has a volumetric heat of combustion (~136 MJ/l) around twice that of Al (81 MJ/l) and three to four times that for hydrocarbon fuels. When boron particles are exposed to air, an oxide layer is formed which inhibits combustion and causes an increase in ignition delay time [14]. By using the ball milling method, the unoxidised boron nanoparticles were synthesised that could be dispersible in kerosene fuel. Boron microparticles were used as feedstock for milling. The milling was carried out in a ball mill (Planetary Ball Mill, NARYA-MPM 2 × 250 H, Amin Asia Co.) using two iron-milling jars. The ratio of ball to powder mass was kept high at 60:1 to reduce the particles size to sub-100 nm. In each run, 2.5 g of boron microparticles, 21.25 ml of n-hexane and 1.25 ml of oleic acid were milled in each jar. N-hexane was added to prevent the formation of caking and reduce the milling time. To generate protected boron nanoparticles, oleic acid was added to the boron/n-hexane mixture. During milling, the boron particles were kept in a nitrogen atmosphere. In order to remove

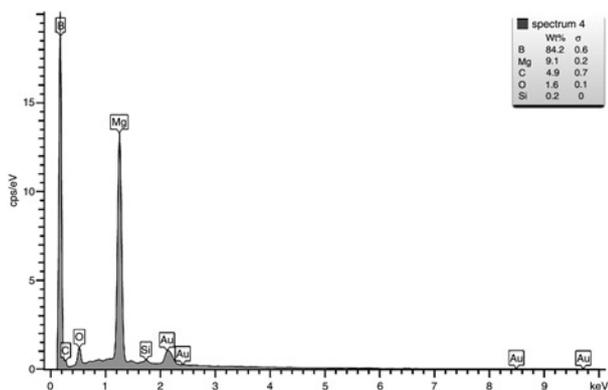


Fig. 2 EDAX analysis of boron microparticles [31]

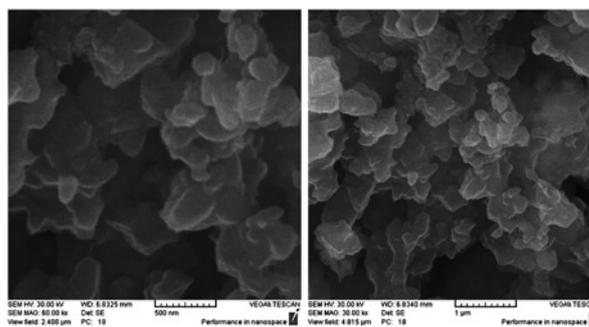


Fig. 3 SEM images of synthesised boron nanoparticles with ball mill

the excess amount of oleic acid, particles were dispersed in methanol and then centrifuged [14].

2.3. Synthesis of nanofluid fuel: Kerosene-based suspensions with boron microparticles and synthesised boron nanoparticles were prepared, separately. At first, surfactants were mixed with the liquid fuel and then particles were added. After that, suspensions were sonicated with a bath ultrasonic (Pro-Sonic, 350 W, 47 kHz, Sultan Chemists) to disperse particles uniformly and avoid agglomeration. Sonication was performed in an ice bath to maintain a constant temperature for nanofluid. The sonicator was turned on about 30 min [31] for each mixture.

3. Results and discussion

3.1. Characterisation of boron nanoparticles: To determine the characteristics of synthesised boron nanoparticles, SEM and EDAX analyses were used. Fig. 3 shows SEM images for boron nanoparticles (XL30, Philips). Due to aggregation during drying, it is difficult to determine a size distribution from the SEM images. By using Digimizer software (4.1.1), it was realised that the particles were in a range of 60–90 nm and there were no primary particles larger than 100 nm.

Fig. 4 shows EDAX (EM208, Philips) results for the synthesised boron nanoparticles. As is shown in Fig. 4, the carbon concentration in nanoparticles structure is more than micron particles (Fig. 2). In fact, the increase of carbon concentration confirms coating of nanoparticles with oleic acid. Also, Fig. 4 shows about 5.0 wt% Fe in the structure of boron nanoparticles which is related to the ball mill jars. The amount of impurities is small and is negligible.

3.2. Characterisation of kerosene nanofluid stability: Kerosene nanofluids were prepared by varying the concentration of surfactants between 0 and 2 wt%. The particle concentration was constant (0.5 wt%) in all samples. The stability of nanofluids was inspected by Turbiscan™ Classic (MA 2000, 27.5 × 13 × 23.5) and the complete sedimentation time of each sample was

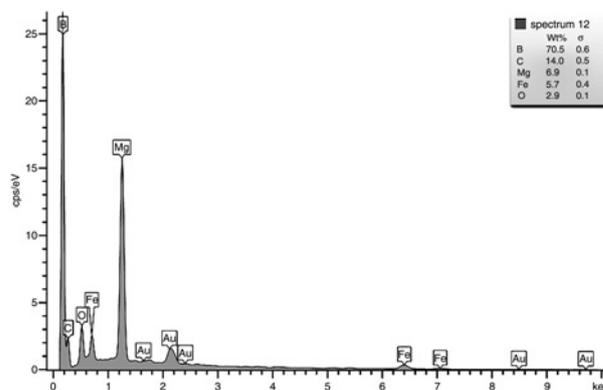


Fig. 4 EDAX analysis of nano-sized boron particles

Table 1 Appropriate concentrations of surfactants used for preparation of various suspensions

Suspensions	Kerosene, ml	Ultrasonication time, min	Surfactant, wt%	Complete sedimentation time (h) at 33°C				
				Oleic acid	PG	sorbitan oleate	Tween 85	CTAB
boron microparticle	10	30	0	2	2	2	2	2
	10	30	0.1	4	0.17	6	1	2.5
	10	30	0.3	5.75	0.08	6	0.75	2.5
	10	30	0.5	4.75	deposition	6	0.5	2.5
	10	30	1	4.5	deposition	6.5	0.25	2.5
	10	30	1.5	4.25	deposition	5.5	0.25	2.5
	10	30	2	2.25	deposition	3.5	0.25	1.5
boron nanoparticle	10	30	0	13	13	13	13	13
	10	30	0.1	23	20	22	3	4
	10	30	0.3	26	20	57	1.5	4
	10	30	0.5	27	20	52	1.5	4
	10	30	1	28	20	30	1.5	4
	10	30	1.5	10	20	9	1	4
	10	30	2	3	20	6	1	2.5

measured. The concentration of surfactants in all suspensions at all boron particle size (nano- and micron-size) and the time of complete sedimentation for all samples are tabulated in Table 1.

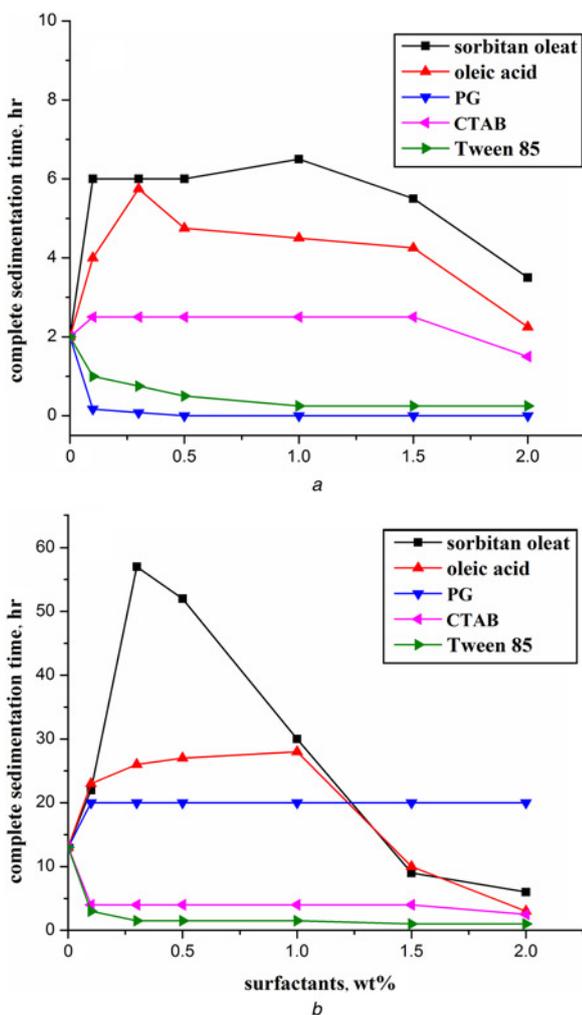


Fig. 5 Comparison of full sedimentation time at the presence of different surfactants
 a Boron microparticles
 b Boron nanoparticles

Data in Table 1 shows that among all surfactants, sorbitan oleate has the most stability time for nano- and micron-sized boron particles. Sorbitan oleate has more active sites rather than other surfactants to link with nanoparticles surface, so makes more metal complexes. Also, the length of linear alkyl chain of sorbitan oleate is higher than other surfactants, which can stand in the linear structure of kerosene and create repulsion forces between particles. Accordingly, this surfactant can reduce surface energy and surface tension of suspensions and thus increase the stability of particles [1]. However, the excessive amount of sorbitan oleate forms macromolecules that are free in the solution and called depletion stabilisation. Depletion stabilisation reduces stability of suspensions [32]. The stability comparisons of all surfactants for micron and boron nanoparticles have been shown in Figs. 5a and b, respectively.

By comparing the sedimentation time data of nano- and micron-sized boron particles (Table 1), it is observed that the stability times of nanoparticles in kerosene are higher than microparticles at the same weight percentage of each surfactant. The increase in stability time of nanoparticles is for two reasons. First, the particle size has decreased so by increasing the ratio of surface area to volume; the interaction between particle surface and fuel is strong enough to overcome the difference in density. Another reason is the oleic acid coating on the surface of nanoparticles. Oleic acid surrounds nanoparticles and creates steric stability by its long chains. Also according to Stokes law, by decreasing the size of particles, the sedimentation velocity and therefore the stability of particles increase significantly. The comparison of sedimentation time of nano- and micron-sized boron particles at the presence of different surfactants is shown in Fig. 6.

3.3. Dynamic viscosity of nanofluid fuel: The aim of this work is to determine the optimum amount of nanofluid fuel in order to use in ramjets. In ramjets, the viscosity of nanofluid is very effective on performance. For liquid fuels, plunger micropumps are widely used for generating single droplet; however, at high viscosity of nanofluids, the droplets generating system may be blocked. Also the pumping power increases with increasing the viscosity of nanofluid. Hence, the optimum nanofluid must be having the high energy content and low viscosity, simultaneously. Thus, the viscosity measurement of nanofluid samples at different temperature was determined and compared.

The dynamic viscosity of kerosene–boron nanofluid was measured using Brookfield DV-II digital viscometer at the spindle rotation of 100 rpm. Dynamic viscosity of nanofluids was measured at various weight concentrations of boron nanoparticles and

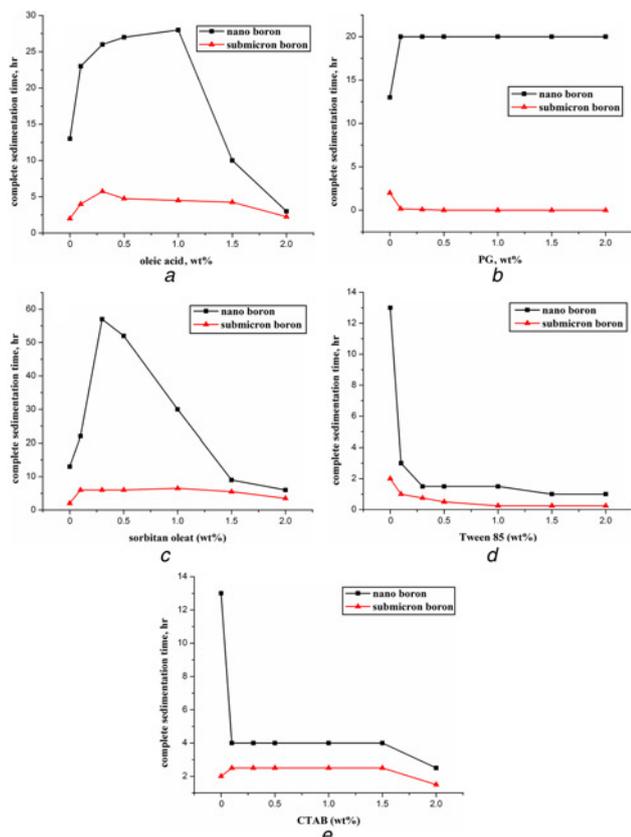


Fig. 6 Comparison of full sedimentation time of nano- and micron-sized boron particles at the presence of different surfactants
a Oleic acid
b PG
c Sorbitan oleate
d Tween 85
e CTAB

temperature ranges. Samples of pure kerosene and nanofluids of kerosene were prepared and their dynamic viscosity was measured at 5, 25 and 40°C. Fig. 7 shows an increase in dynamic viscosity in the presence of nanoparticles. As shown, by adding the boron particles to kerosene at a given temperature, the dynamic viscosity of the base fuel increases significantly.

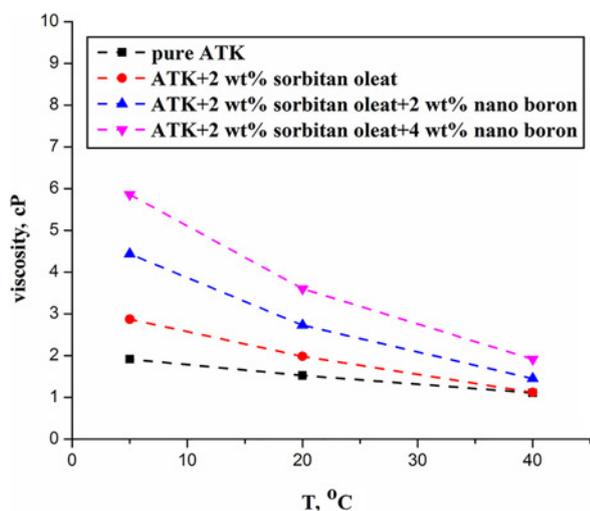


Fig. 7 Effect of temperature on viscosity of kerosene-boron nanofluid

Fig. 7 shows that the dynamic viscosity of nanofluid decreases as temperature increases. As shown, the viscosity decreases from 1.92, 2.87, 4.43 and 5.86 cP at 5°C to 1.1, 1.12, 1.45 and 1.92 cP at 40°C for pure kerosene and mixtures of kerosene/2 wt% sorbitan oleate, kerosene/2 wt% sorbitan oleate/2 wt% boron nanoparticles and kerosene/2 wt% sorbitan oleate/4 wt% boron nanoparticles, respectively. For pure kerosene as temperature increases, due to thermal expansion of the fluid, viscous shear stress reduces and results in lower viscosity at high temperature. In nanofluids, thermal expansion of kerosene at high temperatures results in higher Brownian motion of boron nanoparticles which leads to a higher percentage reduction in viscosity of fuel.

4. Conclusion: To prepare a colloidal stable, nano- and micron-sized boron suspensions in non-polar kerosene fuel, the hydrophilic surface of boron particles have to be changed to have hydrophobic characteristics by using surfactants. Except the surface characteristics of surfactants-modified boron particles, the compatible solubility parameters between surfactant and fuel are also needed. This helps to enhance the extension of the hydrophobic end of surfactant in kerosene and thus the repulsive forces between particles increases. This Letter aims at characterisation and assessing the potential use of different surfactants (ionic and non-ionic) on stability time of kerosene-boron suspensions. The results showed that the sorbitan oleate-modified boron nanoparticles dispersed in kerosene had the best dispersion characteristics rather than other surfactants chosen in this Letter. An optimum quantity of particle to sorbitan oleate weight ratio of 2 was determined after a series of trials for enhanced stability and the complete sedimentation time of nanoparticles at the most stable nanofluid was measured ~57 h. Detailed measurements were carried out to determine the effect of particle weight concentration and temperature on the dynamic viscosity of kerosene-boron nanofluid. The viscosity increased 67% over a particle loading range of 0–4 wt% at 5°C. The results also showed that the viscosity value of nanofluids decreased about 67% by increasing temperature from 5 to 40°C at 4 wt% of boron nanoparticles.

5 References

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