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Experimental Study: Impact of Surfactant on the Stability of Alumina Nanofluids

Hemantkumar H. Kadam[1], Ashok T. Pise[2], Ayush V. Sali[3], Vaibhav G. Talandage[4]
[1]Research Scholar, Department of Mechanical Engineering, Shivaji University, Kolhapur, India 415124
[2]Professor, Department of Mechanical Engineering, Shivaji University, Kolhapur, India 415124
[3] Research Student, Department of Mechanical Engineering, Savitribai Phule, Pune University, India 411044
[4]Research Scholar, Department of Mechanical Engineering, Shivaji University, Kolhapur, India 415124

Abstract- To address the instability of nanoparticles (NPs) in base fluids (BF) due to agglomeration and sedimentation, nanofluids (NFs) were developed to enhance heat transfer and thermal system efficiency. Surfactants are commonly added to improve NP stability by inducing steric or electrostatic repulsion to counteract Van der Waals forces. In this study, NFs were prepared by ultrasonically dispersing Al_2O_3 (0.02–0.5 wt.%) in distilled water, stabilized with Rhamnolipids (RHL, 200–600 ppm) bio-surfactant and synthetic surfactants (SDS, SLS, and PVP, 2000–4500 ppm). Stability was assessed using UV-spectroscopy, dynamic light scattering, zeta potential, and viscosity measurements. Results indicated that stability improved with surfactant concentration, peaking at 3750 ppm (SDS), 4250 ppm (SLS), and 550 ppm (RHL). However, stability declined beyond 0.1 wt.% NP concentration. While RHL showed slightly lower stability than SDS and SLS, it is an eco-friendly alternative. PVP was ineffective and not recommended for further research. These surfactants are promising for heat transfer applications with alumina NFs.

Keywords- Nanofluid, Nanoparticle, Stability, Surfactant, Zeta-Potential, Dynamic light scattering, UV-Spectroscopy

1. INTRODUCTION

Nanofluids (NFs), is the concept proposed by Choi in 1993 prepared by suspending nano-meter sized particles into the heat transferring base fluids (BFs). NFs have received considerable attention to date due their advanced thermal properties including greater heat transfer efficiency and increased thermal conductivity which are very important for cooling electronics devices or solar collectors as well as industrial heat exchangers. One of these nanoparticles (NPs) is aluminium oxide (Al_2O_3), which due to its thermal properties, chemical stability, widespread availability, well dispersed and long lasting characteristics in water, makes it one of the most frequently used in heat exchangers and heat transfer application [1]. Other researchers likewise reported similar favorable outcomes, leading NFs to be dramatically applied for effective heat transfer augmentation and becoming an active research field up until now [2]. There have been many possible uses for NFs but their large scale application out of the laboratory is still uncommon and there has been hardly any uniformity in the technology for NFs. The cost of NPs is one such reason with prices generally in the range of several hundreds to thousands US dollars per kilo [3]. Also, the lack of certainty on the actual enhancement particles can provide may be another major hindrance as apparent thermal properties and heat transfer gains differ considerably even within the same class of NP [4]. Another major challenge is stability, the stability of NFs is a key challenge as particles have strong tendency to agglomerate and settle down over time because of high surface energy causing significant deterioration in performance, such as increase the viscosity and reduce the thermal conductivity, dispersion properties, and stability of the NF. [5][6]. The hydrodynamic size and shape of NPs have several physical constraints [7]. Consequently, it is important to ensure the stability of NFs to uphold the enhancement of their thermophysical characteristics over a diverse range of use.

Ultrasonication has the potential to alter the surface properties of NPs, is a technique that has been widely adopted for the purpose of disintegrate larger particles into tiny pieces or better uniform sized pieces inside the BF and dispersing NP agglomerates into a BF to achieving a steady suspension [8]. NFs can be sonicated by exposing the suspension to sound energy that disperses the NPs [9][10]. Sonicator can be classified into two primary categories based on the type of ultrasonic probe: bath type and probe type. When it comes to sonication techniques, there are profound variation in terms of effectiveness, sonication features, and performance.

Nomenclature and abbreviation

Al_2O_3	Aluminium Oxide	PVP	Polyvinylpyrrolidone
BF	Base fluid	RHL	Rhamnolipid
CMC	Critical Micelle concentration	RPM	Revolutions per minutes
CTAB	Cetyltrimethylammonium bromide	SDS	Sodium dodecyl sulfate
DW	Distilled water	SLS	Sodium lauryl sulfate
NFs	Nanofluids	wt %	weight concentration
NPs	Nanoparticles	N	Spindle speed, RPM
PPM	Parts per million		

Cavitation is the primary force behind the ultrasonication beneficial effects which include, homogenization, dispersion, deagglomeration and sonochemical effects. In ultrasonic bath instruments, cavitation occurs randomly within fluids which mean that conventional baths provide low intensity and irregular ultrasonic treatment. However, ultrasonic probe instrumentation generate a sharp cavitation region just under the probe tip, and thus resulting in enhanced and targeted ultrasonication impact. Furthermore, it is a fully controllable, repeatable, and provides a uniform intensity process. Out of the two methods, probe sonication is efficient and potent for NP dispersion when compared to ultrasonic baths [11][12][13]. In the present ultrasonic bath setup, the ultrasonication is relatively mild, with power density of about 20–40 W/L, and with very poor uniformity. However, according to the ultrasonic probe device, additional 20000 W/L power can be generated into the given fluid. This also means that the ultrasonic probe device is 1000x more powerful than the ultrasonic bath device [14]. The effect of NFs on different nanomaterials using ultrasonication is not an uncommon subject and several scholars have touched on this issue. Particle size distribution of $CaCO_3$ (20–50 nm) in a water based NF was checked by Zhu et al. [15] under different ultrasonication times. Their study found that, from 1 to 40 minutes, the size distribution became narrower as the ultrasonication was increased. Notably, extending the time to 20 min in ultrasonication decreased the average particle size to 36 nm, indicating the effective breakage of NP clusters into individual NPs. Tajik et al. [16] Investigated is the type of ultrasonic waves, either continuous or discontinuous ultrasonication, which had an effect on the particle size distribution of TiO_2 and Al_2O_3 nanoparticles dispersed in water. For discontinuous ultrasonic vibration pulses they chose 50% for the ultrasonic vibration pulse and 100% for continuous ultrasonic vibration. It was observed that the continuous ultrasonication was superior in dissociating the clusters into smaller particles and hence they yielded a narrow particle size distribution compared to that for the discontinuous approach. The authors said that, in the study, they found that the application of continuous ultrasonication is preferable for the preparation of NPs in water. Many researchers have also studied the effect of ultrasonic frequency on the dispersion of particles in a liquid medium especially on the colloidal suspension of Al2O3 in water Mahbubul et al. [17]. Samples were prepared through ultrasonication for 1–5 h at 25% and 50% amplitude. Analysis of microstructure provided information on the best dispersion; at 50% amplitude took only 3 hours while 25% amplitude took 5 hours to achieve the same. The study also analyzed the average cluster size when different ultrasonication conditions were being used, and it was shown that rising in the ultrasonication time decreases the cluster size. Also it noticed that 50% amplitude generated smaller clusters than 25%. However, increase of time of ultrasonication did not decrease the size of the cluster formation. Interestingly, the zeta potential (ZP) value also supports the statement that both samples have good physical stability.

As can be seen, ultrasonication provides good results in the fragmentation of NP clusters and enhancement of dispersion in suspensions though often it is not enough to guarantee the long-term stabilization of the process. The integration of surfactants alongside ultrasonication has several advantages which make the NP suspension more effective and stable. Sonication disperses the NP agglomerates for a short time, but when the sonication process is ceased, the NPs can re-agglomerate because of strong attractive forces with a high surface energy, which promotes to the particles for agglomeration over time which make NF unstable. This results from surfactants to adsorb onto the surface of the NPs thus forming a barrier that prevents these particles from re aggregating [18][19]. This improves for a long-term dispersion of the factor and stability. Surfactants are help to reduce the surface tension that exist between the NPs and the BF. This also ensures that after ultrasonication the NPs do not settle or aggregate due to the balance achieved in dispersion throughout the fluid [20][21]. This increases the NPs compatibility with the BF since the surface properties of the former are modified by surfactants to enhance their wettability [22]. This leads to enhanced dispersion of the NPs during and after ultrasonication is obtained. Surfactants can offer repulsive forces between the NPs; this imparts a surface charge on the particle which stops them from coming into contact and forming large clusters.

Several methods have been outlined to determine the stability of NFs and while each seems to provide information on the stability in a different way, they all give information on NP dispersion and their behavior. One of them is the method of determining the ZP or, in other words, the effective electric charge of the surface of NPs, which is dispersed in the BF. Apart from ZP analyzer, other instruments are employed to determine stability, cluster size and distribution in working fluids. Most of the used technique of the literature is X-ray powder diffraction (XRD) which identifies the crystal structure in nanomaterials [23]. UV-spectrometer is used to find the absorbance frequency of dispersed NPs [1], Dynamic light scattering (DLS) is another common method used to determine size and agglomeration of NPs in the nano-suspensions [24]. Fourier transform infrared (FTIR) spectroscopy is also used in surface chemistries [25]. Morphological data about the Nano particles are described by the field emission scanning electron microscopy (FESEM) [17], transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [26]. These methods are used to measure NP structure and agglomeration size which give valuable information about the stability of NFs.

The main focus of this study is centered on the stability of aluminum oxide (Al_2O_3) NPs when using Rhamnolipids as a bio-surfactant, assuming potential advantages over synthetic surfactants, that is, conventional sodium dodecyl sulfate (SDS), sodium lauryl sulfate (SLS) and polyvinylpyrrolidone (PVP) polymer. Through a combination of ZP measurements, DLS, UV-visible spectrometry, viscosity evaluation, and sedimentation, the stabilizing efficacy of the bio-surfactant compared to synthetic surfactants is assessed and compared. The environmentally friendly nature of the bio-surfactant and its ability to enhance NP dispersion and stability in the colloidal system are also highlighted. Such results may further inspire an interest in viewing bio-surfactants as eco-friendly alternatives worthy of being implemented in applications that ensure not good but better performance with the support of practice toward sustainability in different industrial applications.

2. EXPERIMENTATION

A. Materials

The NFs were prepared by dispersing Al_2O_3 (30-50 nm diameter from Platonic Nanotech, Jharkhand, India) NPs (>= 99% purity) with conc. ranging from 0.02 wt.% to 0.5 wt.% in DW, which is used as BF. Because DW is pure and guarantees that no unwanted ions, minerals, or contaminants affect the stability and characteristics of the NF, it is frequently employed in the manufacture of NFs. These contaminants may react with the NPs or have an impact on the dispersion, which could cause sedimentation or agglomeration. Using DW in this research offers a more consistent and controlled environment for examining the properties and behavior of the NF. Al_2O_3 NPs were selected due to their wide availability and their status as one of the most commonly used and well-studied materials for NF preparation. Additionally, Al_2O_3 NPs offer high TC, chemical stability, cost-effectiveness, non-toxicity, and excellent dispersibility [27]–[29]. To examine the effect of the anionic bio-surfactant Rhamnolipids (sourced from Altinbio Scientific Pvt. Ltd., Mumbai, India) on the stability of NPs in BF, it was incorporated into NFs at conc. ranging from 200 ppm to 600 ppm. For comparative analysis, similar anionic synthetic surfactants, SDS, SLS (identified as SDS with 5-10% impurities) and non-ionic polymer PVP is used as surfactant (acquired from D. Haridas and Company Advance Labs Scientific Pvt. Ltd., Pune, India), were utilized at varying conc. between 2000 ppm and 4000 ppm. The concentrations of all surfactants begin to rise above their critical micelle concentration (CMC) values: 2000 ppm for SDS and SLS, and 200 ppm for RHL. These mixtures were thoroughly homogenized to ensure uniform dispersion of NPs and surfactants within the BF. The hydrophilic heads of anion-containing surfactants solely have a negative charged group on them. These are some of the surfactants that are most frequently utilized in different applications and research fields [30], [31]. SDS surfactants are employed in this study because, as noted by researchers, SDS and PVP is a commonly used surfactant in NFs, offering several advantages such as improved stability, enhanced TC, reduced sedimentation, and overall better performance of these fluids. However, there is limited research available on the use of SLS and the bio-surfactant Rhamnolipids in NFs. Since Rhamnolipids are entirely biodegradable and exist naturally, they are environmentally friendly surfactant than manufactured ones. They pose fewer threats to the environment and human health when used than many synthetic surfactants due to their lower toxicity.

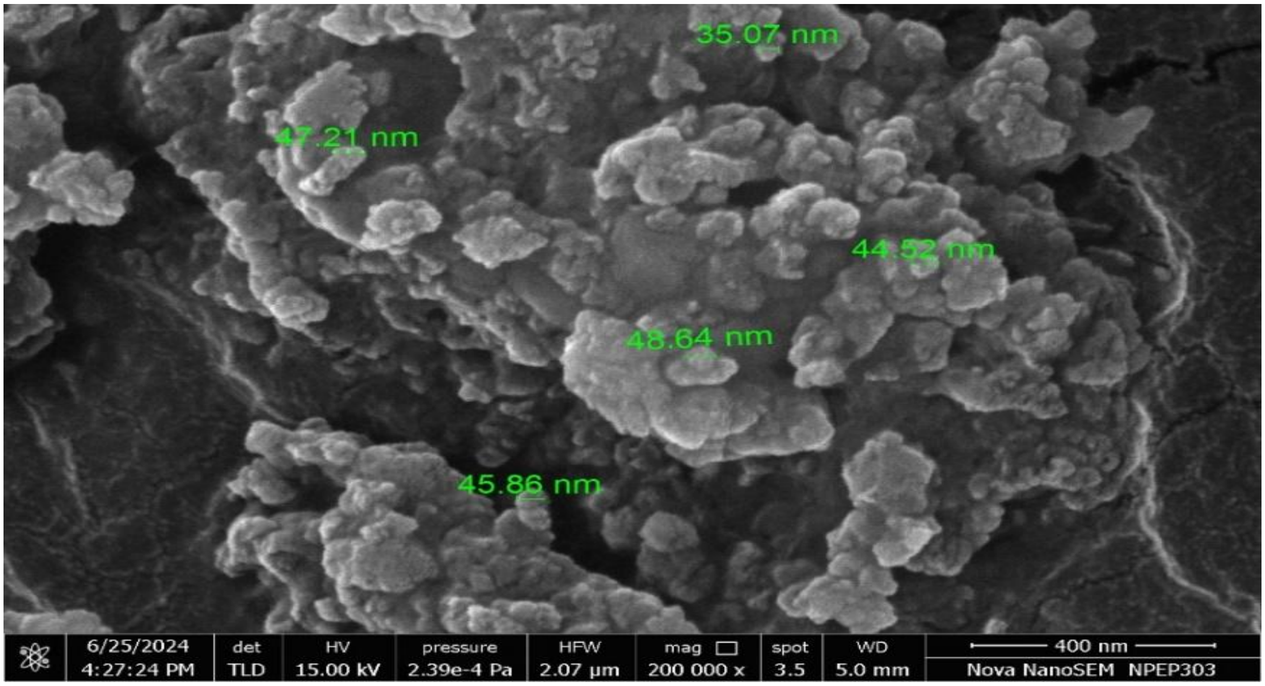


Fig. 1 FESEM results of Al_2O_3 nano-powder

B. Nano Powder Characterization

The thermophysical properties of NFs are well influenced by the particle morphology [32][33]. The Al_2O_3 Nano-powder was closely examined using a field emission scanning electron microscope (FE-SEM), (Refer Fig.1) revealing that the nanomaterial consists of spherical particles with distinct morphological characteristics. The SEM imaging was conducted at the Central Instrumental Facility, Savitribai Phule Pune University. For this analysis, the Al_2O_3 NPs were dispersed onto a conductive substrate, specifically a carbon-coated copper grid, before being placed in the SEM chamber and scanned with a focused electron beam. The observations indicate spherical particle shapes with an average size of less than 50 nm.

C. NF Preparation

In order to make the NFs, the two step method is applied. Firstly, equation 1 is used to find the mass of the surfactant required for the specified surfactant conc. and weight is measured by using an electronic weighing equipment with high accuracy upto 0.001 gms (Contech Instruments Ltd., Mumbai, India) at Pimpri Chinchwad College of Engineering, Pune.

$$ppm = \frac{\text{mass of surfactant}}{\text{mass of solvent}} * 10^6 \qquad (1)$$

The deionized DW used as the BF in this experimental work was obtained from a double unit supplied by Equitron Company. Next, using a magnetic stirrer with a hot plate made by Remi Sales and Engineering Ltd., the surfactant is mixed with the DW and swirled for 30 min at 700 rpm to achieve a fully dissolved and homogeneous mixture of surfactant in the BFs. The bio-surfactant Rhamnolipids had a conc. range of 200 ppm to 600 ppm in this experiment, while the conc. of SDS, SLS surfactants and PVP polymer varied from 2000 ppm to 4000 ppm, 4500 ppm and 3500 ppm respectively. Every sample was made using 100 milliliters of DW. Later, the small amount of Al_2O_3 NPs required for particular conc. 0.02 wt.%, 0.05 wt.%, 0.1 wt.%, 0.3 wt.% and 0.5 wt.% in 100 ml DW is calculated by using equation 2.

$$\emptyset_{np}\% = \frac{m_{np}}{m_{np}+m_{bf}} \text{ x } 100 \quad [34] \qquad (2)$$

Where, Ø is the weight fraction of the NPs, m_{np} and m_{bf} are the masses of NPs and BFs respectively. Subsequently, the calculated amount of NPs, based on the required conc., is added to the surfactant solution and stirred using a magnetic stirrer for 60 minutes. After that mixture is sonicated for 1 h by using the bath tub ultrasonicator (Dakshine Ultrasonic, Mumbai, India) and for 1 h by using the probe Sonicator (Orchid Scientific & Innovative Pvt. Ltd., Nashik, Maharashtra) with 100 watt capacity and 30±3 Hz frequency at Modern College of Pharmacy, Moshi, Pune. Ultrasonication has been proven to be the most effective and efficient method for uniformly dispersing particles into the BF [1][32].

D. Stability Measurement

In this experimentation work stability of Al_2O_3 NPs in DW is observed by five different methods. The sedimentation observation method is a straightforward technique for evaluating the stability of NPs in a BF by monitoring how quickly particles settle over time. This method provides visual and quantitative insights into the suspension's stability, as stable dispersions exhibit minimal sedimentation over extended periods, while unstable dispersions settle rapidly due to particle agglomeration. It is simple, affordable, and relies on capturing pictures at regular intervals to observe how suspensions precipitate [35]. ZP is widely used as it measures the electrostatic potential of particles, with higher absolute values (above ±30 mV) indicating better stability against aggregation [24][29]. The size distribution of the nanoparticles in the nanofluids was determined using the Dynamic Light Scattering (DLS) technique which ultimately gives the idea about particle agglomeration as well as stability of synthesized fluid [36]. The DLS method working principle is based on Brownian motion theory [24]. Both Particle size and ZP of NF samples with different concentration of different surfactant is measured through the Horiba particle size analyser at Modern College of Pharmacy, Yamunanager, Pune. Another important metric for assessing the stability of NFs is absorbance, quantity of light absorb by solution. There is a positive correlation between the absorbance value and the concentration of solid particles in the liquid. A larger concentration of Al2O3 NFs is indicated by a higher absorbance value. Higher absorbance therefore suggested that the NFs had a high stability of dispersion. Conversely, low stability NFs have low absorbance [37]. The relative stability of nanofluids was evaluated using UV–visible spectral spectroscopy over a wavelength range of 190–600 nm. This method tracks the concentration of suspended nanoparticles over time to quantitatively assess colloidal stability, providing insights into sedimentation behavior. UV-spectrometer test is carried out at D.Y. Patil College of Pharmacy, Akurdi Railway Station, Pune. To perform the absorbance test at wavelengths between 190 and 600 nm, the solution was placed inside a UV-visible spectrophotometer. After 1, 10, and 20 days of standing, the absorbance of the Al2O3/DW NFs was tested using SDS samples in the same manner. 0.1 wt. % concentrated Al2O3/DW NFs with SLS and RHL surfactant samples undergo the same process for the same span of time. The measurement of the absorbance was conducted at wavelength 228 nm which is the maximum absorption wavelength found for alumina nanofluid experimentally. Before the ZP, particle size and UV-visible absorbance value was measured, the 0.1 wt. % concentrated Al2O3/DW NFs were introduced into the cuvette, and they were diluted ten times with deionized water for all concentrations of surfactants. And the cuvette are places into the respective measuring devices.

Fig. 2 a) Horiba particle size analyser b) UV-spectrometer c) Brookfield Viscometer

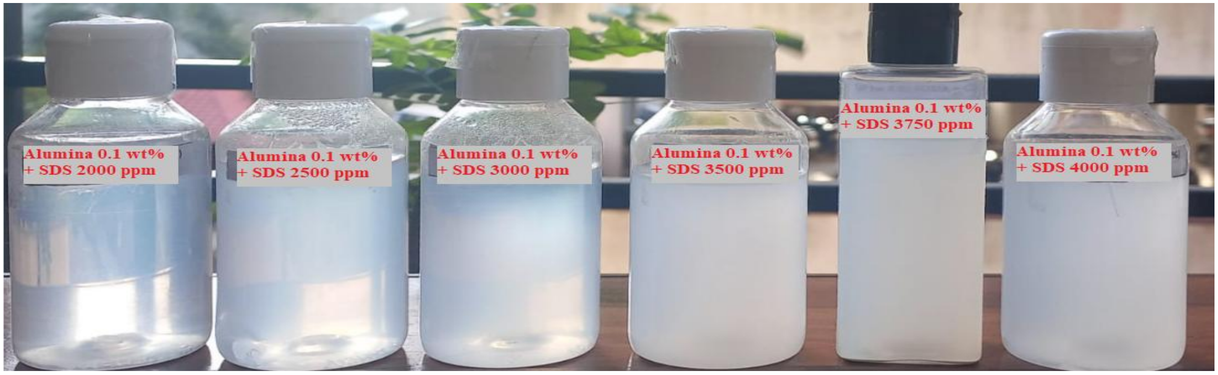
Finally, after preparing NFs with varying surfactant concentrations, the viscosity of each sample was tested using a Brookfield Viscometer at room temperature (299 K) at the Modern College of Pharmacy, Moshi, Pune. Variations in viscosity due to surfactant addition provide insights into the shear-thinning or shear-thickening behavior of the samples, which helps in assessing the stability of the NFs. For these all stability analysis, to avoid the experimental results, each experiment was conducted three times in full, and the mean values are presented in the results Section. All the instrument used in this research are shown in Fig. 2.

3. RESULTS AND DISCUSSIONS

A. NF stability visualisation analysis

Fig. 3 presents comparative images captured for 0.1 wt.% Al_2O_3 NF with varying concentrations of SDS, PVP (2000–4000 ppm), SLS (2000–4500 ppm), and RHL (200–600 ppm) over a 15-day period, with photographs taken at 7-day intervals. These images, captured at 2 hours, 7 days, and 15 days post-preparation, provide insights into the stability of the Al_2O_3 NF. The Fig. 3 a clearly indicates that the NF of any concentration without surfactant are unstable and particles are agglomerated and settled down before completion of 7 days and shows the clear liquid. Same results are also shown (Fig. 3e) in case of addition of PVP surfactant means PVP polymer does not work effectively as a surfactant. On the other hand, addition of SDS, SLS and RHL surfactant across all concentration shows uniformly distribution of NPs into BF after 2 hrs. of preparation, indicating good dispersion of NPs and maintained stability without sedimentation. After 7 days of preparation some signs of sedimentation or slight transparency differences start to appear, especially in the samples with lower SDS concentrations 2000 ppm, 2500 ppm, lower SLS concentration 2000 ppm, 2500 ppm, 3000 ppm and lower RHL concentration 200 ppm, 300 ppm. This indicates a slight reduction in stability at lower surfactant concentrations, as the surfactants may not be sufficient to fully stabilize the NPs over time. After 15 Days the stability differences become more pronounced. At lower concentrations, there is noticeable sedimentation, leading to a clearer liquid at the top and sediment at the bottom, indicating lower stability. However, at higher concentrations, the samples remain more uniformly dispersed, suggesting that these concentrations are more effective in preventing agglomeration and maintaining NP stability over a longer period. Refer Fig, 3 b,c,d.

After 2 hrs. After 7 days



After 15 days

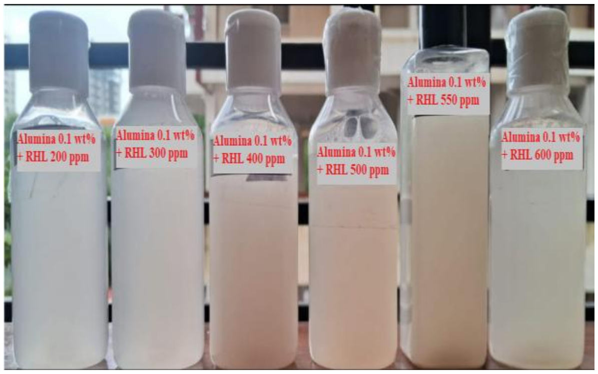
(a)

After 2 hrs.

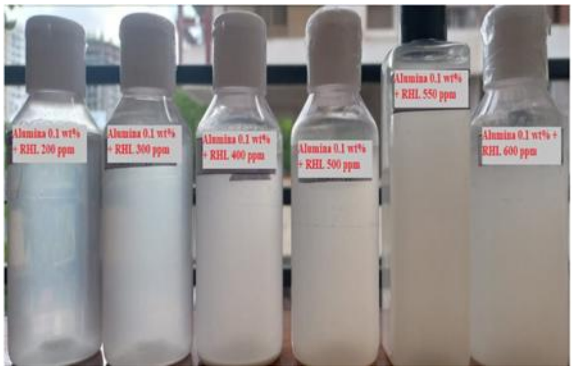
After 7 days

After 15 days

(b)



After 2 hrs.



After 7 days

After 15 days (c)

After 1 days

After 7 days

(d)

Fig. 3 Sedimentation photographs after preparation of Al_2O_3/H_2O NFs (0.1 wt.%) with different concentration of (a) SDS (b) SLS (c) RHL (d) PVP surfactant

B. Effect of surfactant on ZP

The stability of Al_2O_3/DW NFs was further examined through ZP measurements, as the electrokinetic properties of NPs and the BF significantly influence particle interactions within the suspension. High surface charge densities promote well-dispersed NFs by generating strong repulsive forces, making electrophoretic behavior analysis through ZP measurements essential to understanding NP behavior in the BF [38]. Higher ZP values indicate smaller NP clusters within the fluid, signifying improved NF stability.

ZP tests were conducted to assess the surface charge on the NPs. Fig. 4 and 5 illustrate the ZP values of Al_2O_3 (alumina) NPs in distilled water (DW) at a concentration of 0.1 wt.% stabilized with various surfactants—SDS, SLS, PVP, and RHL—across a range of concentrations, as well as without surfactants. Without surfactant, the ZP of alumina at concentrations between 0.02 and 0.5 wt.% ranges from 21.5 mV to 12.3 mV, suggesting that Al_2O_3 particles are positively charged due to the protonation of surface hydroxyl (–OH) groups. Typically, the ZP of Al_2O_3 in water varies with pH, surfactant type, and surfactant concentration: at pH values above 9, Al_2O_3 carries a negative charge; it is neutral between pH 8 and 9, and positively charged below pH 8. Here, due to the low pH, Al_2O_3 particles have a positive surface charge, which is modified upon the addition of negatively charged anionic surfactants. These surfactants dissociate into ionic groups that adsorb onto the NPs, progressively increasing the net negative surface charge and enhancing the repulsive forces.

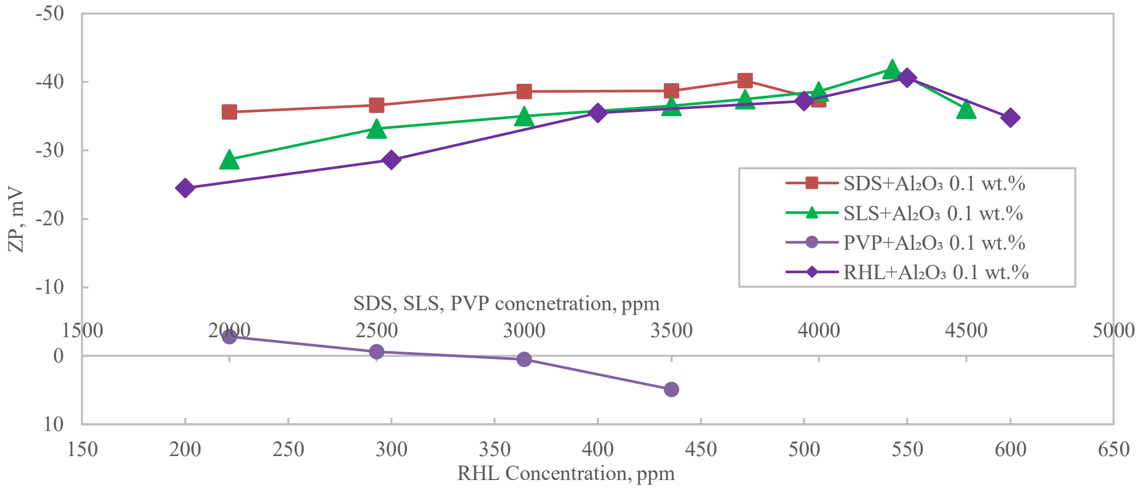


Fig. 4 Effect of different conc. of SDS, SLS, PVP and RHL on the ZP of Al_2O_3/DW (0.1 wt. %) NFs

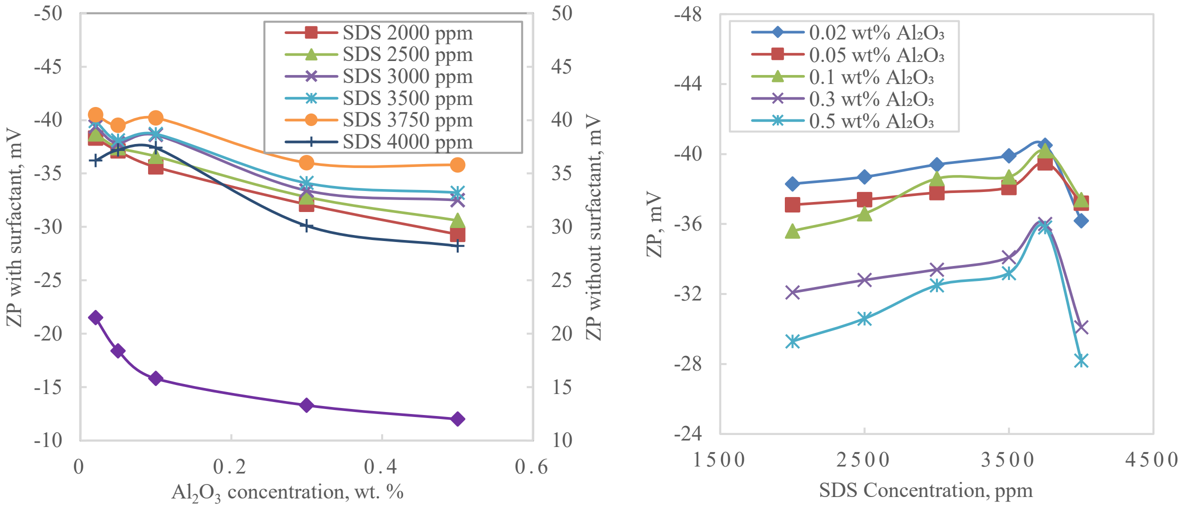


Fig. 5(a) Effect of SDS surfactant and Al_2O_3 NP concentration on the ZP of Al_2O_3/DW NFs

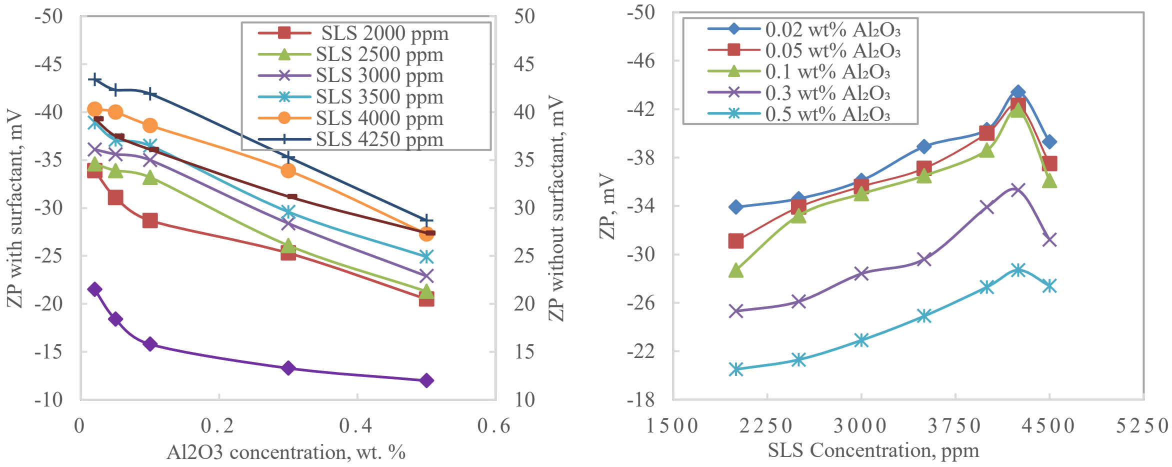


Fig. 5 (b) Effect of SLS surfactant and Al_2O_3 NP concentration on the ZP of Al_2O_3/DW NFs

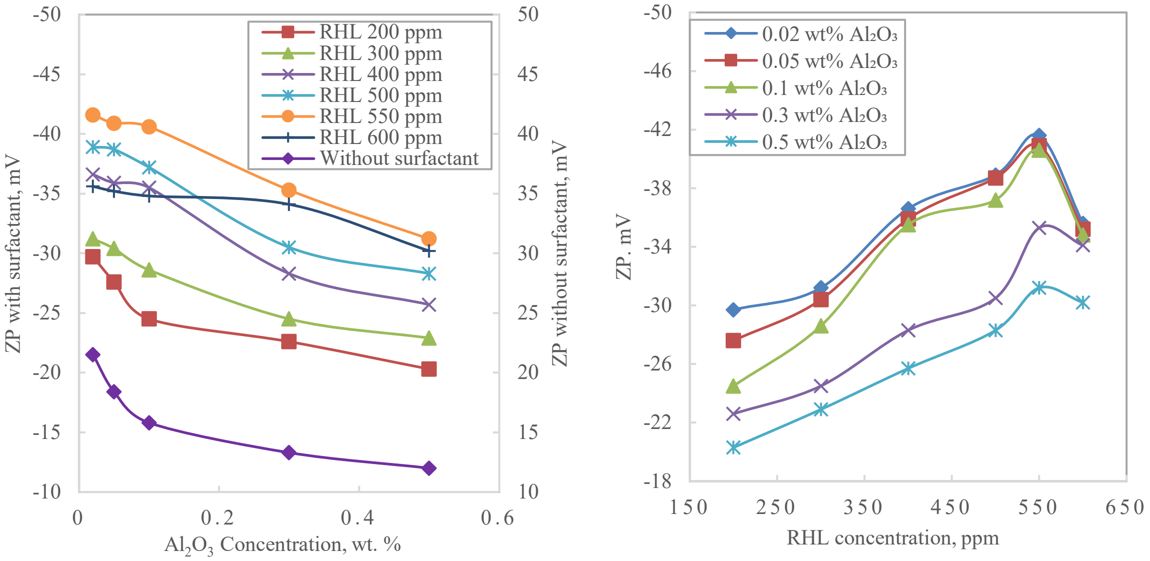


Fig. 5 (c) Effect of RHL surfactant and Al_2O_3 NP concentration on the ZP of Al_2O_3/DW NFs

Fig. 5 shows that ZP values remain consistently high, near -40 mV, when SDS is used as the surfactant across the tested concentration range. Similarly, SLS achieves stable ZP values, though slightly lower than SDS. With both surfactants, ZP increases, peaking at 3750 ppm for SDS and 4250 ppm for SLS, after which it begins to decline. This trend suggests that SDS and SLS provide strong electrostatic stabilization for alumina NPs, promoting stable dispersion through adequate repulsive forces. In contrast, at low concentrations of RHL (up to 300 ppm), the ZP of Al_2O_3 NPs is initially lower than that observed with SDS and SLS. However, as the RHL concentration rises, the ZP reaches values similar to those of the synthetic surfactants at around 550 ppm, after which it too starts to decrease. Unlike SDS, SLS, and RHL, PVP shows a continuous decrease in ZP with increasing concentration, with values approaching 0 mV, indicating minimal electrostatic stability. These findings provide insights for surfactant selection in stabilizing Al_2O_3 NP dispersions in NF applications: SDS and SLS show high stability, making them effective choices for stable dispersions, while RHL, though offering slightly lower stability, is environmentally friendly and warrants further investigation in stability and heat transfer applications. Due to its poor stabilization performance observed through sedimentation and ZP, PVP is not recommended for further studies.

Fig. 5 compares the ZP of Al_2O_3 NPs with and without the addition of SDS, SLS, and RHL surfactants across various concentrations of both surfactants and Al_2O_3. In all cases, NFs without surfactant exhibit significantly lower ZP, indicating reduced stability, with ZP decreasing as Al_2O_3 concentration increases. The addition of surfactants renders the ZP negative, with values becoming more negative as surfactant concentration increases, reaching -40.2 mV at 3750 ppm for SDS, -41.9 mV at 4250 ppm for SLS, and -40.6 mV at 550 ppm for RHL. These results demonstrate that the NFs achieve stability with all surfactants immediately after preparation.

C. Effect of surfactant on the particle size

Fig. 6 illustrates the effect of varying concentrations of SDS, SLS, and RHL surfactants, as well as the PVP polymer, on the particle size of NPs in Al2O3/DW NFs at a concentration of 0.1 wt. % after one day. The results indicate that particle size decreases consistently with increasing concentrations of SDS, SLS, and RHL surfactants, reaching minimum values of 113.9 nm, 119.9 nm, and 122.8 nm at concentrations of 3750 ppm, 4250 ppm, and 550 ppm, respectively. Beyond these concentrations, further addition of surfactants causes only a slight increase in particle size. In contrast, the use of PVP polymer as a surfactant leads to significant variations in particle size. At a lower concentration of 2000 ppm, PVP achieves a remarkably low particle size of 83.2 nm compared to other surfactants. However, this performance diminishes with increasing concentrations, as the particle size starts to rise, peaking at 271.4 nm at 3500 ppm. But in all the prepared solutions particle size of

NPs in NFs is comparatively higher than the prescribed size by vender 30-50 nm. This behavior can be attributed to three key phenomena. First, the energy imparted in the sonication process might be not sufficient to fully disintegrate the primary clusters of alumina, commensally left some large agglomerates intact even after sonication. Second, in an initial experimentation, imbalance in surface charge, along with Brownian motion, may have creates chances to bring them to colloids, leading to aggregate very rapidly. Third, during the dispersion process, multiple layers form due to hydration or solvation, with the ions in the fluid absorbing onto the surface of NP or Nano cluster, thereby increasing their hydrodynamic diameter.

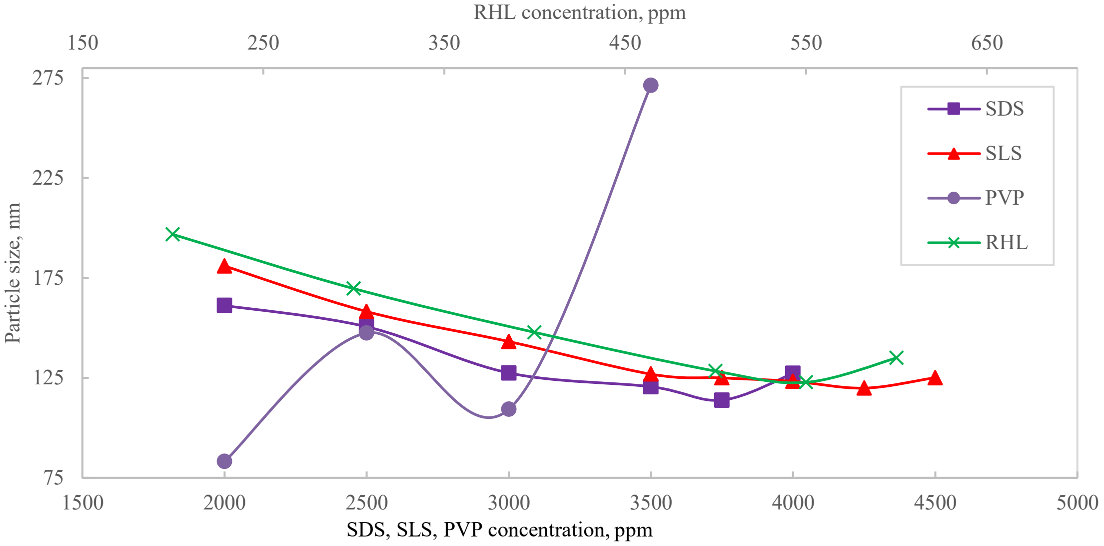


Fig. 6 Effect of SDS surfactant and Al_2O_3 NP concentration on the particle size of Al_2O_3/DW (0.1 wt. %) NFs

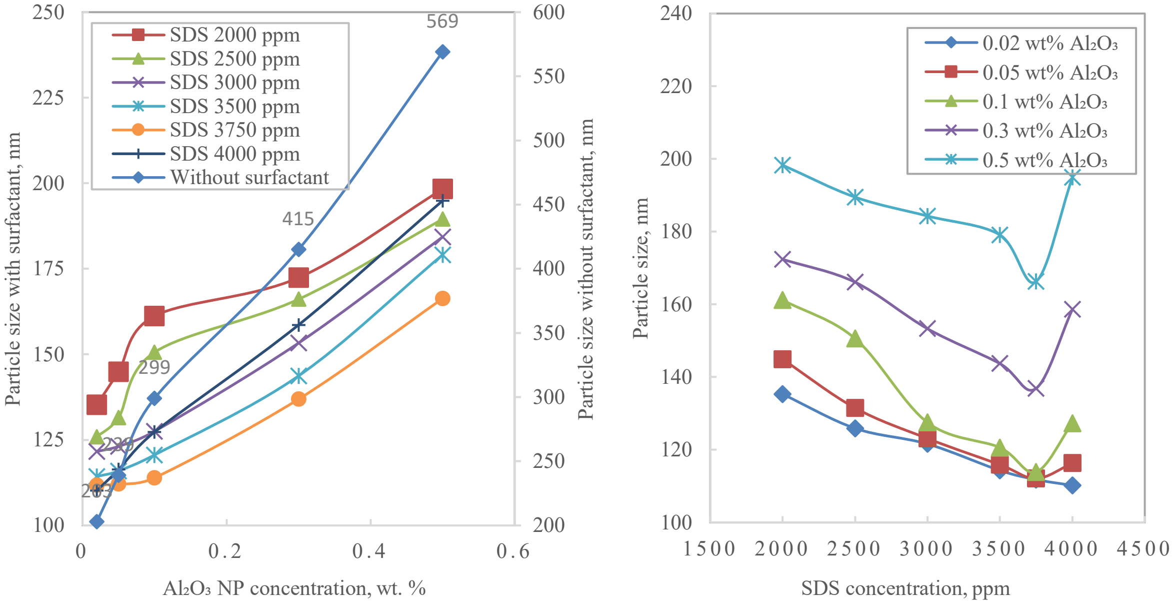


Fig. 7 (a) Effect of SDS surfactant and Al_2O_3 NP concentration on the particle size of NPs

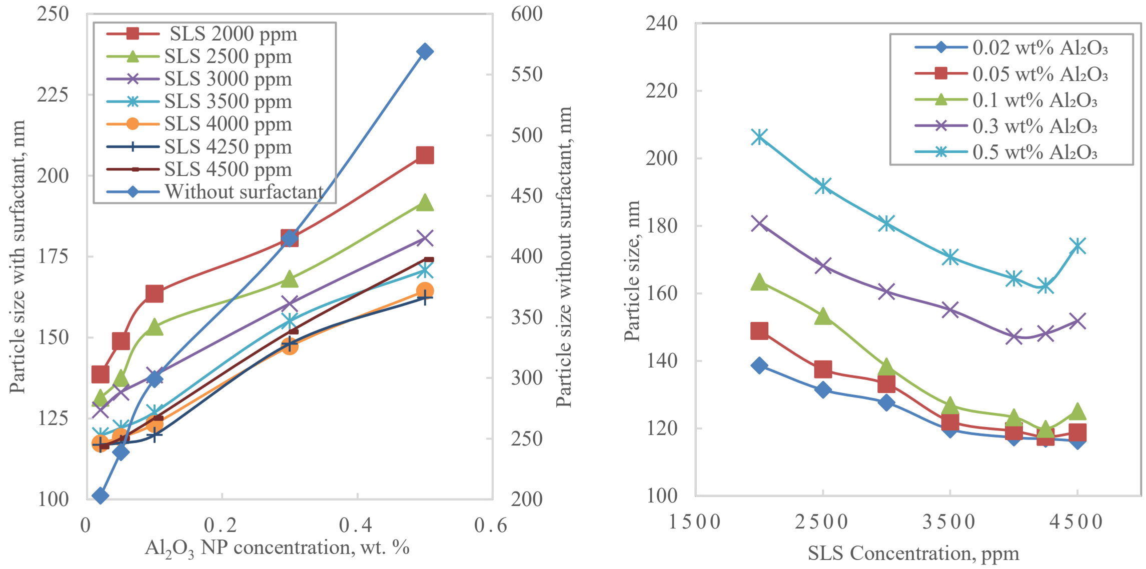


Fig. 7 (b) Effect of SLS surfactant and Al_2O_3 NP concentration on the particle size of NPs

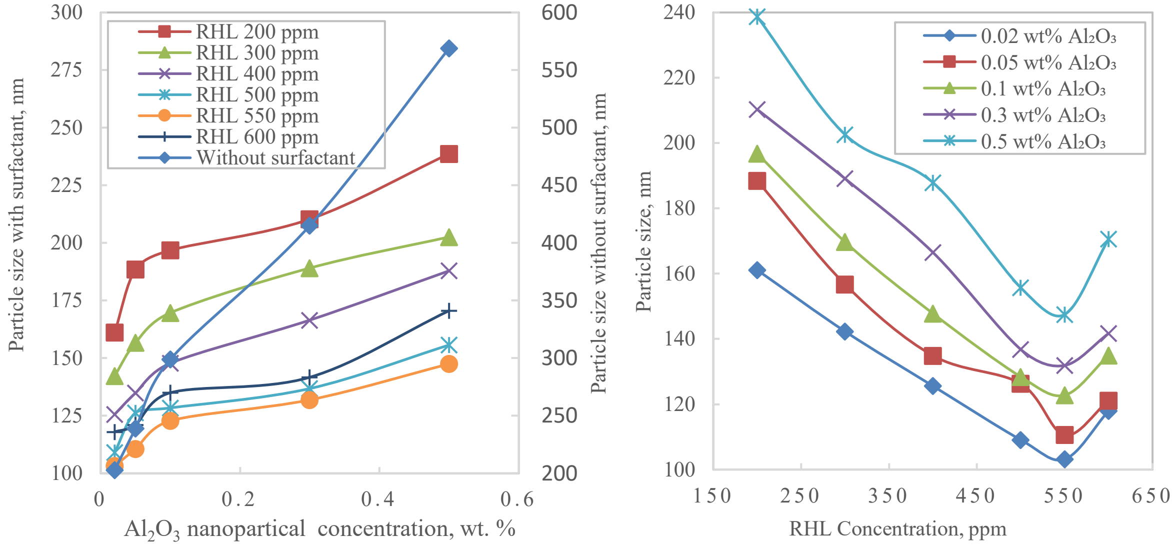


Fig. 7 (c) Effect of RHL surfactant and Al_2O_3 NP concentration on the particle size of NPs

Fig. 7 illustrates the influence of Al_2O_3 NP concentration (0.02–0.5 wt. %) on the particle size of NPs in Al_2O_3/DW NFs, both with and without surfactants. In the absence of surfactants, the particle size is consistently larger compared to NFs containing surfactants and increases significantly with higher NP concentrations. The recorded particle size ranges from a minimum of 203 nm to a maximum of 569 nm. The addition of surfactants (SDS, SLS, and RHL) markedly reduces the particle size across all concentrations. For SDS at 3750 ppm, the particle size ranges from 111.8 nm to 166.3 nm, while for SLS at 4250 ppm, it ranges from 116.9 nm to 162.3 nm. For RHL at 550 ppm, the particle size is further reduced, ranging from 103.2 nm to 147.5 nm. These minimum and maximum particle sizes correspond to NP concentrations of 0.02 wt. % and 0.5 wt. % respectively. The figure also highlights that at lower Al_2O_3 concentrations (0.02, 0.05, and 0.1 wt. %), the particle size remains relatively stable across all surfactant types and concentrations. However, beyond 0.1 wt. %, the particle size increases rapidly with rising NP concentrations. Additionally, the particle size decreases significantly with increasing surfactant concentrations up to 3500 ppm for SDS and SLS, and 500 ppm for RHL, with only minimal changes observed at higher surfactant concentrations.

D. Effect of surfactant on the absorbance

As shown in Fig. 8, after 1 day of sample preparation, at the critical micelle concentration (CMC) concentrations of each surfactant, the absorbance of the Al_2O_3/DW NF at 0.1 wt. % is lower. When surfactant concentrations increase beyond the CMC, absorbance begins to improve, reaching peak values at 3750 ppm for SDS, 4250 ppm for SLS, and 550 ppm for RHL, after which it starts to decline. These concentrations are thus considered the optimal levels for each respective surfactant. This indicates that at the CMC, only a small amount of NPs are effectively suspended in the BF, with many particles agglomerating and settling out. In contrast, at the optimal concentrations above the CMC, a larger number of NPs remain well-dispersed in the BF, while fewer particles aggregate and settle.

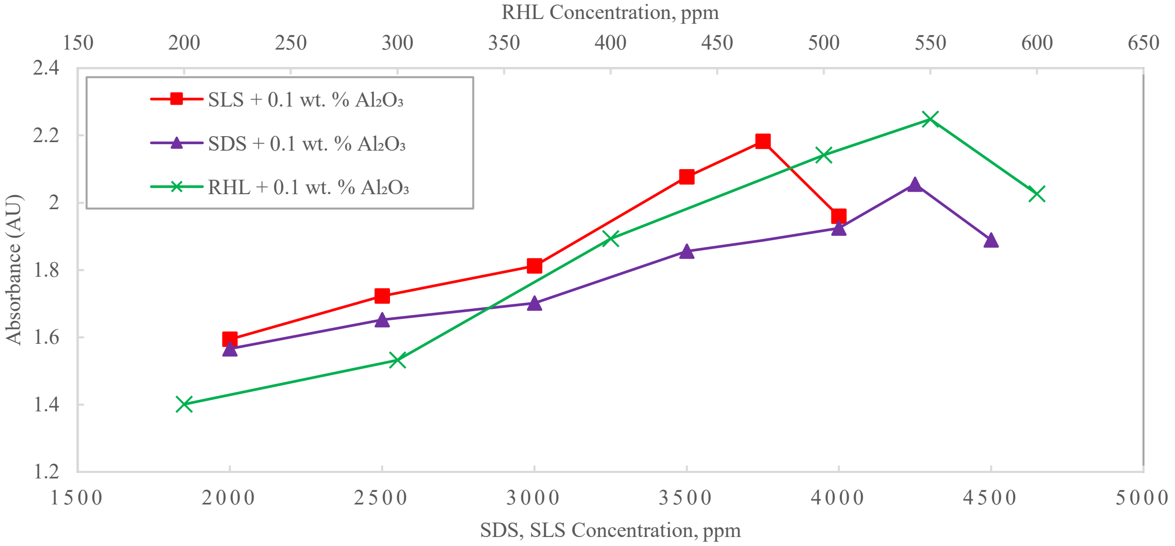
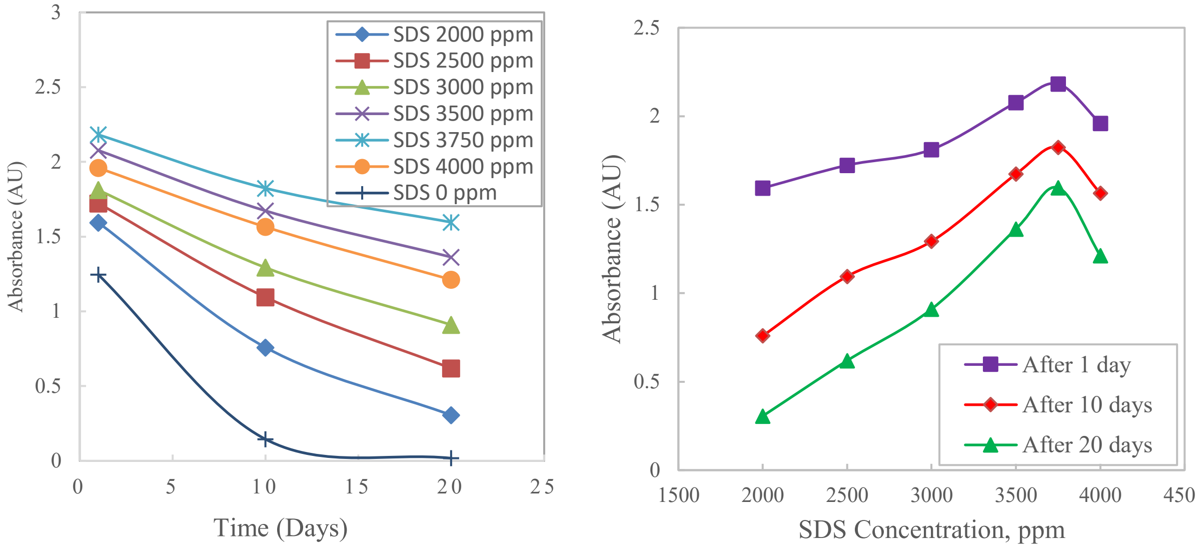


Fig. 8 Absorbance of 0.1 wt. % Al_2O_3/DW NF w.r.t. concentration of surfactants measure after 1 day of preparation

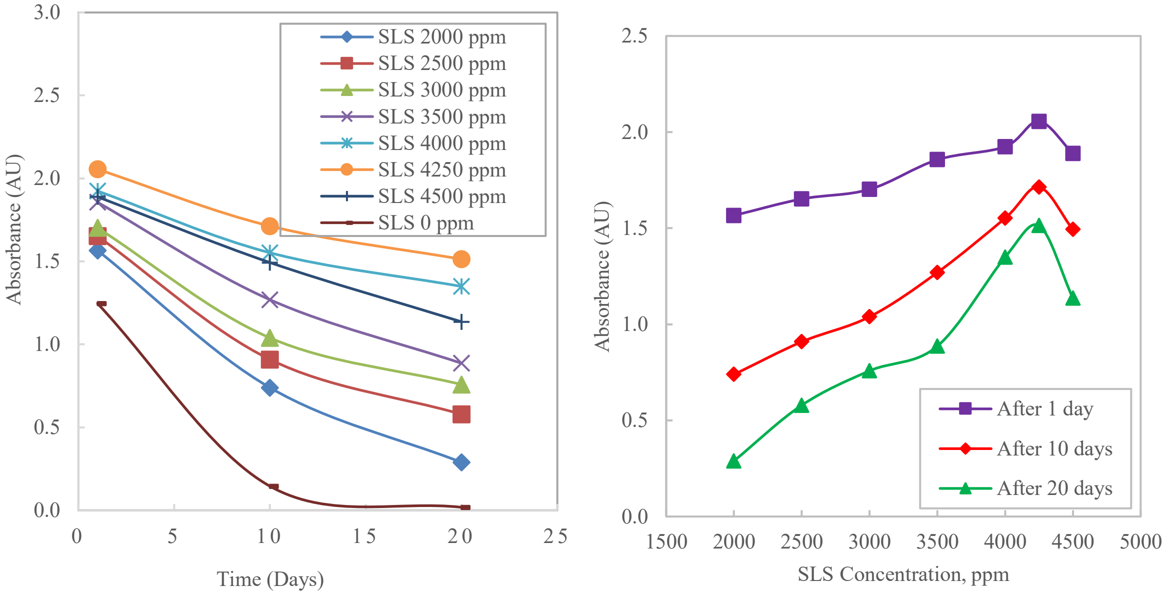
At the CMC, absorbance is low because this concentration allows for micelle formation in distilled water but is insufficient to fully coat all NPs or their surfaces. As a result, particles tend to agglomerate and settle quickly, reducing NP absorbance and decreasing stability. When surfactant concentration is increased from the CMC to an optimal level, surface coating improves, reducing particle agglomeration. At this optimal concentration, surfactant molecules are adequate to completely coat particle surfaces, stabilizing the maximum number of NPs. This enhanced stabilization promotes a more uniform dispersion of NPs in the BF, leading to increased absorbance due to the higher concentration of well-suspended particles. However, beyond these optimal concentrations, excess surfactant molecules can form large micelle aggregates or multilayer coatings on NPs. This oversaturation can destabilize the dispersion by promoting re-agglomeration or altering the fluid properties, resulting in a decrease in absorbance. It is also observed that absorbance of NF with SDS is slightly more and with SLS slightly less than the other two surfactants. But RHL shows the higher value of absorbance (2.248 AU) at its optimal concentration as compared to optimal concentration of SDS and SLS (2.182 AU and 2.055 AU respectively).

Fig. 9 illustrates the effect of surfactants (SDS, SLS and RHL) concentrations on the absorbance of 0.1 wt. % Al2O3/DH NFs after the time period of 1 day, 10 days and 20 days and also compare with the NFs without surfactants. It is observed that the overall trend is decrease in absorbance of NF over time across all concentration of all three surfactants as well as without surfactant, but it rate of decrease varies with concentration of surfactants. In the early days, a higher sedimentation rate was observed which is also found by Mehta et al. [36] for CTAB surfactant. Also, after preparation of NFs rate of agglomeration of particles is very high in case of NFs without surfactant and absorbance almost decreased near to zero AU before 10 days. At higher SDS concentrations (3750 ppm and 4000 ppm), SLS concentration (4250 ppm and 4500 ppm) and similarly RHL concentration (550 ppm and 600 ppm) maintain higher absorbance over the 20-day period, indicating improved stability due to sufficient NP coating. This suggests that these concentrations of surfactants effectively prevent particle agglomeration. At lower SDS, SLS concentrations (e.g., 2000 ppm and 2500 ppm) and RHL (200 ppm and 300 ppm) absorbance decreases significantly over time, showing a very rapid drop by day 10. This instability indicates that these concentrations are insufficient for stabilizing NPs, leading to rapid sedimentation. The optimal range of surfactants, where NPs remain well-dispersed with high absorbance levels over time. While the other reasons may be, surfactants initially aid in dispersing NPs and preventing clumping, the stabilization they provide, whether through electrostatic or steric mechanisms, is not always long-lasting.



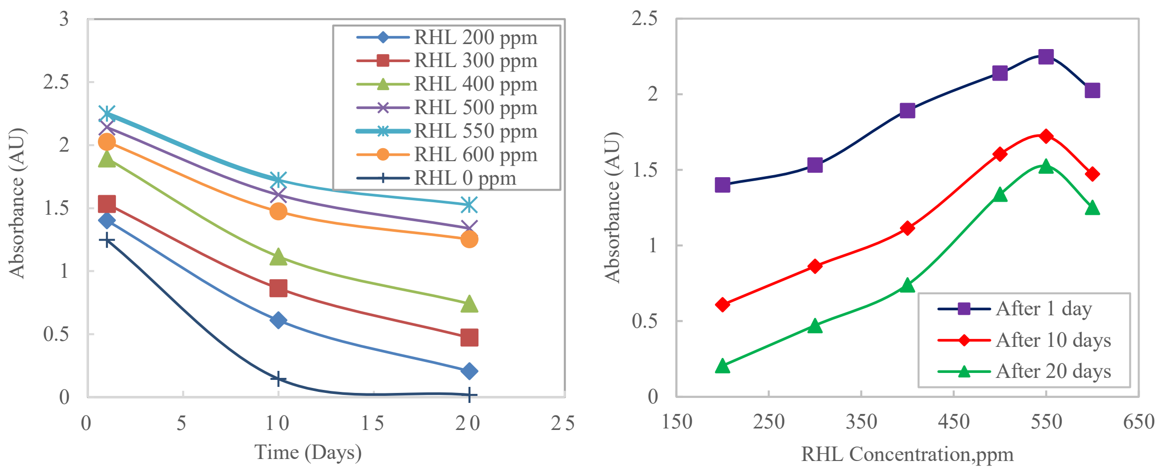
(i) (ii)

Fig. 9 (a) Absorbance of 0.1 wt. % Al_2O_3/DW NFs variation w.r.t. time for different concentration of SDS surfactant



(iii) (iv)

Fig. 9 (b) Absorbance of 0.1 wt. % Al_2O_3/DW NFs variation w.r.t. time for different concentration of SLS surfactant



(v) (vi)

Fig. 9 (c) Absorbance of 0.1 wt. % Al_2O_3/DW NFs variation w.r.t. time for different concentration of RHL surfactant

Over time, the Van der Waals forces between particles can overcome these stabilizing effects, leading to gradual agglomeration. Additionally, surfactant molecules adsorbed on NP surfaces may slowly desorb, especially under conditions like temperature changes, pH shifts, or extended storage periods. As surfactants detach from the particle surfaces, the NPs lose stability, which results in aggregation and settling. NPs are still influenced by gravity, particularly if they are denser than the BF, and this can cause them to slowly settle over time, especially as the surfactant layer weakens. This settling diminishes the homogeneity of the suspension and reduces its stability. Furthermore, NFs can be sensitive to environmental factors like temperature and light, which may alter the behavior of the surfactant or the properties of the fluid. For example, temperature fluctuations can change the fluid's viscosity, affecting particle movement and overall stability.

4. CONCLUSION

In this experimental study examine the stability of aluminium oxide NPs into the distilled water with varying concentrations (0.02 to 0.5 wt. %) using three synthetic surfactants SDS, SLS, PVP (in the range of concentration 2000 ppm to 4500 ppm) and RHL as a bio-surfactant (200 ppm to 600 ppm). The following conclusions are derived from the experimental results:

- The results shows that addition of surfactants plays important role in enhancing the stability of NFs by mitigating NP agglomeration and sedimentation electrostatic repulsion mechanisms, therefore this effort would give the current research a more trustworthy reference base, making it easier for other researchers to select appropriate surfactants for subsequent investigations.
- Among the surfactants studied, SDS and SLS exhibited superior stability enhancement due to their ability to provide high ZP values and uniform particle size distribution at optimal concentrations of 3750 ppm and 4250 ppm, respectively. Rhamnolipid, at an optimal concentration of 550 ppm, also significantly improved stability, achieving comparable performance to synthetic surfactants. Despite its slightly lower efficacy, Rhamnolipid offers the advantage of being biodegradable and environmentally friendly, making it a viable alternative to synthetic surfactants for sustainable applications.
- Furthermore, the findings of the viscosity and absorbance tests also demonstrate that the addition of surfactants at concentrations of 3700 ppm SDS, 4250 ppm SLS, and 550 ppm RHL has notable effects, while the results of additional surfactant mixing slightly deteriorate. Consequently, these are the optimal concentrations of the corresponding surfactants.
- Particle size analysis revealed that increasing NP concentrations led to rapid agglomeration without surfactants, while surfactant addition effectively

minimized particle size, particularly at lower NP concentrations (0.02–0.1 wt.%).

- On the contrary, PVP surfactants failed to maintain the stability of NPs over an extended period. Agglomeration of particles was observed within 7 days, with the NPs settling at the bottom. ZP measurements across all concentrations were found to be close to 0 mV, indicating poor stability. While particle size at lower concentrations was notably smaller, a rapid increase in particle diameter was observed with further additions. Consequently, PVP surfactants are not recommended for continued investigation.
- All things considered, this study emphasizes how important surfactant concentration and choice are in stabilizing NFs for improved heat transfer and other industrial uses. Greener NF technologies are being made possible by the promising potential of Rhamnolipids bio-surfactants in particular as ecologically friendly substitutes. Optimizing bio-surfactant formulations and investigating their long-term performance in real-world applications should be the main goals of future research.

REFERENCES

[1] S. Baek *et al.*, “Influence of amphoteric and anionic surfactants on stability, surface tension, and thermal conductivity of Al_2O_3/water nanofluids,” *Case Stud. Therm. Eng.*, vol. 25, no. November 2020, p. 100995, 2021, doi: 10.1016/j.csite.2021.100995.

[2] A. Kaggwa, M. Atkins, A. Tarighaleslami, M. Walmsley, and J. K. Carson, “Thermal Performance of Selected Nanofluids with Surfactants,” *Int. J. Thermophys.*, vol. 44, no. 11, pp. 1–15, 2023, doi: 10.1007/s10765-023-03271-6.

[3] O. Mahian, A. Kianifar, S. A. Kalogirou, I. Pop, and S. Wongwises, “A review of the applications of nanofluids in solar energy,” *Int. J. Heat Mass Transf.*, vol. 57, no. 2, pp. 582–594, 2013, doi: 10.1016/j.ijheatmasstransfer.2012.10.037.

[4] A. Kaggwa and J. K. Carson, “Developments and future insights of using nanofluids for heat transfer enhancements in thermal systems: a review of recent literature,” *Int. Nano Lett.*, vol. 9, no. 4, pp. 277–288, 2019, doi: 10.1007/s40089-019-00281-x.

[5] I. M. Mahbubul *et al.*, “Effect of Ultrasonication Duration on Colloidal Structure and Viscosity of Alumina − Water Nanofluid,” 2014.

[6] I. M. Mahbubul *et al.*, “Effect of ultrasonication duration on colloidal structure and viscosity of alumina-water nanofluid,” *Ind. Eng. Chem. Res.*, vol. 53, no. 16, pp. 6677–6684, 2014, doi: 10.1021/ie500705j.

[7] B. Ruan and A. M. Jacobi, “Ultrasonication effects on thermal and rheological properties of carbon nanotube suspensions,” *Nanoscale Res. Lett.*, vol. 7, pp. 1–14, 2012, doi: 10.1186/1556-276X-7-127.

[8] M. Sandhya, D. Ramasamy, K. Sudhakar, K. Kadirgama, and W. S. W. Harun, “Ultrasonication an intensifying tool for preparation of stable nanofluids and study the time influence on distinct properties of graphene nanofluids – A systematic overview,” *Ultrason. Sonochem.*, vol. 73, p. 105479, 2021, doi: 10.1016/j.ultsonch.2021.105479.

[9] M. Noroozi, S. Radiman, and A. Zakaria, “Influence of sonication on the stability and thermal properties of Alnanofluids,” *J. Nanomater.*, vol. 2014, 2014, doi: 10.1155/2014/612417.

[10] M. Leena and S. Srinivasan, “Synthesis and ultrasonic investigations of titanium oxide nanofluids,” *J. Mol. Liq.*, vol. 206, pp. 103–109, 2015, doi: 10.1016/j.molliq.2015.02.001.

[11] Y. Son, Y. No, and J. Kim, “Geometric and operational optimization of 20-kHz probe-type sonoreactor for enhancing sonochemical activity,” *Ultrason. Sonochem.*, vol. 65, no. January, p. 105065, 2020, doi: 10.1016/j.ultsonch.2020.105065.

[12] A. A. Green and M. C. Hersam, “Emerging methods for producing monodisperse graphene dispersions,” *J. Phys. Chem. Lett.*, vol. 1, no. 2, pp. 544–549, 2010, doi: 10.1021/jz900235f.

[13] A. Asadi, M. Asadi, M. Siahmargoi, T. Asadi, and M. Gholami Andarati, “The effect of surfactant and sonication time on the stability and thermal conductivity of water-based nanofluid containing Mg(OH)2 nanoparticles: An experimental investigation,” *Int. J. Heat Mass Transf.*, vol. 108,

pp. 191–198, 2017, doi: 10.1016/j.ijheatmasstransfer.2016.12.022.

[14] A. Asadi *et al.*, "Effect of sonication characteristics on stability, thermophysical properties, and heat transfer of nanofluids: A comprehensive review," *Ultrason. Sonochem.*, vol. 58, no. July, 2019, doi: 10.1016/j.ultsonch.2019.104701.

[15] H. Zhu, C. Li, D. Wu, C. Zhang, and Y. Yin, "Preparation, characterization, viscosity and thermal conductivity of $CaCO_3$ aqueous nanofluids," *Sci. China Technol. Sci.*, vol. 53, no. 2, pp. 360–368, 2010, doi: 10.1007/s11431-010-0032-5.

[16] B. Tajik, A. Abbassi, M. Saffar-Avval, and M. A. Najafabadi, "Ultrasonic properties of suspensions of TiO_2 and Al_2O_3 nanoparticles in water," *Powder Technol.*, vol. 217, pp. 171–176, 2012, doi: 10.1016/j.powtec.2011.10.024.

[17] I. M. Mahbubul, R. Saidur, M. A. Amalina, E. B. Elcioglu, and T. Okutucu-Ozyurt, "Effective ultrasonication process for better colloidal dispersion of nanofluid," *Ultrason. Sonochem.*, vol. 26, pp. 361–369, 2015, doi: 10.1016/j.ultsonch.2015.01.005.

[18] G. Xia, H. Jiang, R. Liu, and Y. Zhai, "Effects of surfactant on the stability and thermal conductivity of Al_2O_3/de-ionized water nanofluids," *Int. J. Therm. Sci.*, vol. 84, pp. 118–124, 2014, doi: 10.1016/j.ijthermalsci.2014.05.004.

[19] Z. Mingzheng, X. Guodong, L. Jian, C. Lei, and Z. Lijun, "Analysis of factors influencing thermal conductivity and viscosity in different kinds of surfactant solutions," *Exp. Therm. Fluid Sci.*, vol. 36, pp. 22–29, 2012, doi: 10.1016/j.expthermflusci.2011.07.014.

[20] P. D. Meshram, S. Shingade, and C. S. Madankar, "Comparative study of saponin for surfactant properties and potential application in personal care products," *Mater. Today Proc.*, vol. 45, pp. 5010–5013, 2021, doi: 10.1016/j.matpr.2021.01.448.

[21] R. K. Gouda, M. Pathak, and M. Kaleem Khan, "A biosurfactant as prospective additive for pool boiling heat transfer enhancement," *Int. J. Heat Mass Transf.*, vol. 150, p. 119292, 2020, doi: 10.1016/j.ijheatmasstransfer.2019.119292.

[22] D. S. Wen and B. X. Wang, "Effects of surface wettability on nucleate pool boiling heat transfer for surfactant solutions," *Int. J. Heat Mass Transf.*, vol. 45, no. 8, pp. 1739–1747, 2002, doi: 10.1016/S0017-9310(01)00251-4.

[23] M. Hemmat Esfe, S. Saedodin, A. Asadi, and A. Karimipour, "Thermal conductivity and viscosity of $Mg(OH)_2$-ethylene glycol nanofluids: Finding a critical temperature," *J. Therm. Anal. Calorim.*, vol. 120, no. 2, pp. 1145–1149, 2015, doi: 10.1007/s10973-015-4417-3.

[24] R. M. Mostafizur, M. G. Rasul, and M. N. Nabi, "Effect of surfactant on stability, thermal conductivity, and viscosity of aluminium oxide–methanol nanofluids for heat transfer applications," *Therm. Sci. Eng. Prog.*, vol. 31, no. November 2021, p. 101302, 2022, doi: 10.1016/j.tsep.2022.101302.

[25] Z. Sharifalhoseini, M. H. Entezari, and R. Jalal, "Direct and indirect sonication affect differently the microstructure and the morphology of ZnO nanoparticles: Optical behavior and its antibacterial activity," *Ultrason. Sonochem.*, vol. 27, pp. 466–473, 2015, doi: 10.1016/j.ultsonch.2015.06.016.

[26] M. Asadi and A. Asadi, "Dynamic viscosity of MWCNT/ZnO-engine oil hybrid nanofluid: An experimental investigation and new correlation in different temperatures and solid concentrations," *Int. Commun. Heat Mass Transf.*, vol. 76, pp. 41–45, 2016, doi: 10.1016/j.icheatmasstransfer.2016.05.019.

[27] K. S. Suganthi and K. S. Rajan, "Metal oxide nanofluids: Review of formulation, thermo-physical properties, mechanisms, and heat transfer performance," *Renew. Sustain. Energy Rev.*, vol. 76, no. February, pp. 226–255, 2017, doi: 10.1016/j.rser.2017.03.043.

[28] D. Zhu, X. Li, N. Wang, X. Wang, J. Gao, and H. Li, "Dispersion behavior and thermal conductivity characteristics of Al_2O_3-H_2O nanofluids," *Curr. Appl. Phys.*, vol. 9, no. 1, pp. 131–139, 2009, doi: 10.1016/j.cap.2007.12.008.

[29] K. Cacua, F. Ordoñez, C. Zapata, B. Herrera, E. Pabón, and R. Buitrago-Sierra, "Surfactant concentration and pH effects on the zeta potential

values of alumina nanofluids to inspect stability," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 583, no. July, 2019, doi: 10.1016/j.colsurfa.2019.123960.

[30] N. Guanhua *et al.*, "The effect of anionic surfactant (SDS) on pore-fracture evolution of acidified coal and its significance for coalbed methane extraction," *Adv. Powder Technol.*, vol. 30, no. 5, pp. 940–951, 2019, doi: 10.1016/j.apt.2019.02.008.

[31] D. Kumar and M. A. Rub, "Effect of anionic surfactant and temperature on micellization behavior of promethazine hydrochloride drug in absence and presence of urea," *J. Mol. Liq.*, vol. 238, pp. 389–396, 2017, doi: 10.1016/j.molliq.2017.05.027.

[32] S. A. Ebrahim, E. Pradeep, S. Mukherjee, and N. Ali, "Rheological behavior of dilute graphene-water nanofluids using various surfactants: An experimental evaluation," *J. Mol. Liq.*, vol. 370, p. 120987, 2023, doi: 10.1016/j.molliq.2022.120987.

[33] S. N. M. Zainon, "Recent Progress on Stability and Thermo-Physical Properties of Mono and Hybrid towards Green Nanofluids," pp. 1–35, 2021.

[34] S. Mukherjee, S. Jana, P. Chandra Mishra, P. Chaudhuri, and S. Chakrabarty, "Experimental investigation on thermo-physical properties and subcooled flow boiling performance of Al2O3/water nanofluids in a horizontal tube," *Int. J. Therm. Sci.*, vol. 159, no. July 2020, p. 106581, 2021, doi: 10.1016/j.ijthermalsci.2020.106581.

[35] A. Altun, O. Şara, and S. doruk, "SDS Surfactant Effects on Stability and Thermophysical Properties of Al_2O_3–Water Based Nanofluids," *Konya J. Eng. Sci.*, vol. 10, no. 3, pp. 599–612, 2022, doi: 10.36306/konjes.1019424.

[36] B. Mehta, D. Subhedar, H. Panchal, and K. K. Sadasivuni, "Stability and thermophysical properties enhancement of Al_2O_3-water nanofluid using cationic CTAB surfactant," *Int. J. Thermofluids*, vol. 20, no. June, p. 100410, 2023, doi: 10.1016/j.ijft.2023.100410.

[37] Y. Qiao, W. Sheng, C. He, C. Liu, and Z. Rao, "Experimental study on the effect of different surfactants on the thermophysical properties of graphene filled nanofluids," *Int. J. Energy Res.*, vol. 45, no. 7, pp. 10043–10063, 2021, doi: 10.1002/er.6497.

[38] A. R. Studart, E. Amstad, and L. J. Gauckler, "Colloidal stabilization of nanoparticles in concentrated suspensions," *Langmuir*, vol. 23, no. 3, pp. 1081–1090, 2007, doi: 10.1021/la062042s.