Stability analysis of Al₂O₃/water nanofluids

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ABSTRACT
This paper presents the stability analysis of Al₂O₃/water nanofluid. The stability is investigated with the help of zeta potential and visual inspection methods. The effects of pH and sonication time for the stability of nanofluids are studied in detail. The visual inspection method is used to calculate the stability period of nanofluids. The zeta potential is directly related to stability period of nanofluids; higher the absolute value of zeta potential, higher the stability period. The stability is also analysed by using sodium dodecyl sulphate, a surfactant, with respect to the time elapsed after the preparation of nanofluids.

KEYWORDS
zeta potential; sonication time; stability period; isoelectric point

1. Introduction
In the early stage of research, the millimetre and micron-sized solid particles were dispersed in the fluids. The thermal conductivity of suspension was observed to be increasing with the increase in particle concentration of solid particles. Maxwell [1] observed an appreciable increase in the thermal conductivity of suspension. The rapid settlement of the millimetre and micron-sized particles deteriorates the heat transfer capacity of the suspension. The other disadvantages of millimetre and micron-sized particles observed by Pradeep and Ashokreddy [2] were the erosion and clogging of the application area and increment in the pressure drop. The poor stability of millimetre and micron-sized particles forced the research towards a stable system. With the advent of nanotechnology, researchers were able to produce particles of nanometre size. The stable fluid formed by the dispersion of nanoparticles in the conventional fluids was called nanofluid by Choi.

The extreme stability and very high thermal conductivity made the nanofluids an efficient heat carrier fluid. Moreover, nanofluids are harmless working fluids and have low cost due to its reduced pumping power and negligible erosion and clogging.

Wu et al. [3] reported three types of stability: kinetic, dispersion and chemical stability. The strong Brownian motion prevents the sedimentation of the nanoparticles and increases the mobility of the nanoparticles. This is called kinetic stability. The aggregation of the nanoparticles with the elapsed time deteriorates the dispersion stability of nanofluids. When no chemical reaction takes place between the nanoparticles and base fluid, it is called chemical stability. The stability of the nanofluids is inversely proportional to the settling velocity of the suspended nanoparticles.
The stability of nanofluids depends on different aspects such as preparation of nanofluids, size and shape of nanoparticles, particle concentration, type of base fluid, additives and mechanical mixing, etc. Portinha et al. [4] observed that if the particles of cylindrical shape were dispersed in base fluid, a chain-like structure was formed and particles were stable for 40 days. The selection of nanoparticles and the base fluid depends on the dielectric constant with the aim to minimise the particle–particle interaction so that aggregation could be prevented. For minimum interaction between the particles, Koo and Kleinstreuer [5] suggested that the dielectric constant of the nanoparticles must be as near as possible to the base fluid’s dielectric constant. The mechanical mixing of the nanoparticles in the base fluid includes the ultra-sonication, magnetic stirring, etc. Hong et al. [6] found a reduction in the aggregated size of the nanoparticles with the increase in sonication time, which resulted in the higher stability of the nanofluids.

The addition of surfactant is the most popular way to improve the dispersion behaviour of nanofluids and to minimise particle aggregation. Surfactants can be defined as the chemical compounds added to lower the surface tension of liquids and increase the suspension time of particles. Surfactant addition is the very effective technique to enhance the stability of nanofluids. Zawrah et al. [7] employed sodium dodecyl benzene sulphonate surfactant to increase the stability of Al$_2$O$_3$/distilled water (DW) nanofluids. Stabilised nanofluids were observed by the authors from the zeta potential measurements. It should be pointed out that this technique cannot be applicable for nanofluids working in high temperature on account of probable damage of bonding between surfactant and nanoparticles. Although the addition of a surfactant is an effective way to increase the stability of nanofluids, but this may cause some problems. For example, Chen et al. [8] found the traces of foam on the heating surface as well as on the solid nanoparticles during the use of the surfactants and this activity may act as a thermal resistance to heat transfer.

Apart from the addition of the surfactant, the other techniques to improve the stability of nanofluids are surface modification technique, pH control and ultrasonic agitation. Surface modification technique is also called surfactant-free method because it does not require the need for the addition of any surfactant. In this technique, functionalised nanoparticles are employed to make nanofluids which overcome the drawback of surfactant. Yang and Liu [9] used functionalised nanoparticles and observed that the prepared nanofluids were highly stable with low viscosity and good fluidity.

Stability of nanofluids is directly related to its electro-kinetic properties. Therefore, the pH control of the fluid can increase stability due to strong repulsive forces. Samal et al. [10] measured the variation in zeta potential with the variation in pH of Al–Cu nanoparticles in water and reported that the dispersion stability of Al–Cu nanofluid was best at pH 10.30 and 4.96, corresponding to zeta potential values of $-27.70$ and $49$ mV, respectively.

While the addition of the surfactant, surface modification and pH control prevent clustering and agglomeration, the ultrasonic vibration is applied to break down agglomeration. Hwang et al. [11] observed the effect of various physical treatments like stirrer, the ultrasonic bath and the ultrasonic disruptor on the deagglomeration of Ag nanoparticles in silicon oil. The ultra-sonication was reported as an effective way to break the agglomeration of nanoparticles. Without any physical treatment, the particle size in the liquid was 335 nm. After physical treatment of stirrer, ultrasonic bath and ultrasonic disrupter, the particle sizes were 150, 90 and 40 nm, respectively. The magnetic stirrer or
ultra-sonication raises the temperature of nano-liquids which can diminish the thermal properties of nano-liquids [12]. Therefore, an optimum sonication time must be estimated for the superior stability and thermal properties of nano-liquids.

2. Techniques of stability analysis

The stability of nano-liquids influences the thermo-physical properties of the nano-liquids, hence, the investigation of the stability is crucial. Hanaor et al. [13] reported various methods, such as sedimentation method, zeta potential analysis, UV-vis spectrophotometer, transmission electron microscopy (TEM), scanning electron microscopy (SEM), sedimentation balance method, dynamic light scattering method, etc., to evaluate the stability of nano-liquids.

The sedimentation method is the simplest method to evaluate the stability of the nano-liquids with the elapsed time. When the concentration of supernatant particles does not change with the elapsed time, a stable nano-liquid occurs. In this method, the stability of nano-liquid is observed by taking the sedimentation photographs of nano-liquids in test tubes using a camera. The disadvantage of this method is long observation period to check the sedimentation of particles.

Zeta potential is the potential difference between the bulk fluid and the stationary layer of fluid attached to nanoparticles. Ghadimi et al. [14] showed that the high zeta potential (negative or positive) depicts the electrically stable suspension system, while the nano-liquids of lower zeta potential lead to faster sedimentation of nanoparticles. According to Vandsburger [15], nano-liquids are expected to be moderately stable if zeta potential is near to ±30 mV. If the zeta potential is near ±45 mV, the stability of nano-liquids is supposed to be good. The zeta potential above ±60 mV depicts an excellent stable nano-liquid system (Table 1).

Another efficient way to estimate the stability of suspension is spectral absorbency analysis. The UV-vis spectroscopy measures the absorbance of incident light by the nanoparticles. Zhu et al. [16] experimentally observed that the absorption is directly proportional to a number of suspended nanoparticles, therefore, higher absorbency results in the stable nano-liquids.

TEM and SEM are used to examine the shape, size and distribution of the nanoparticles. The size distribution and mean effective diameter of the nanoparticles suspended in the base fluid can also be determined by dynamic light scattering (DLS) method.

3. Preparation of nano-liquids

The white colour, spherical shape γ-Al₂O₃ nanoparticles (99.99% Al₂O₃ content) were purchased from the Nanoshel LLC, USA, having the mean diameter of 20 nm. The physical and chemical properties are summarised in Table 2. The purchased nanoparticles

| Zeta potential (±mV) | Stability                  |
|---------------------|---------------------------|
| 0                   | Little or no stability    |
| 15                  | Some stability but settling lightly |
| 30                  | Moderate stability        |
| 45                  | Good stability, possible settling |
| 60                  | Very good stability, little settling likely |
were in the dry state and agglomerated. The two-step method (Figure 1) was used to prepare the Al₂O₃–water nanofluids as follows:

1. The mass of nanoparticles for the desired volume concentration can be estimated using the density of both nanoparticles and base fluid, as given in following equation, proposed by Pak and Cho [17]:

\[
\phi = \frac{1}{\frac{m}{\rho_{np}} + 1} \times 100%
\]

where \( \phi \) is the volume concentration, \( m \) is the mass of the nanoparticles, \( \rho \) denotes the density (kg/m³) and subscript np and bf represent the nanoparticle and the base fluid, respectively. To prepare the nanofluids of different particle concentrations with higher accuracy, it is mandatory to measure the mass of nanoparticles with great attention. For that, the weight of Al₂O₃ nanoparticles was measured by Digital Analytical Balance (model – DAB 220; make – Wensar Weighing Scale Ltd., Chennai, India). The balance has the readability and repeatability of 0.1 and ±0.1 mg, respectively.

1. The nanoparticles were mixed with the DW, produced in the laboratory, to prepare the nanofluids of different concentrations.

Table 2. Physical and chemical properties of Al₂O₃ nanoparticles.

| Property                  | Value         |
|---------------------------|---------------|
| Particle size             | 20 nm         |
| Colour                    | White         |
| Crystal form              | Alpha         |
| pH value                  | 6.6           |
| Odour                     | Odourless     |
| Al₂O₃ content             | 99.99%        |
| Morphology                | Powder        |
| Density, g/cm³            | 3.77          |
| Specific surface area, m²/g | 79.57        |

Source: Certificate of analysis provided by the Nanoshel LLC, USA.

Figure 1. Set-up for preparation of nanofluids.
2. The mixture was shaken and stirred by hand for 10 minutes and then ultrasoundated to break any possible aggregation of nanoparticles in a Probe Sonicator (model – BMS-750T; make – Biomatrix, India). A uniform dispersion of nanoparticles occurred using the ultrasonic pulse of 19.2 ± 2 kHz at the power of 750 W.

In the present work, additives such as NaOH and HCl for the pH variation and sodium dodecyl sulphate (SDS) as the surfactant were used to improve the stability of the nano-fluids, which will be discussed in the forthcoming sections.

4. Method of stability analysis

In the present study, two techniques, visual inspection and zeta potential measurement of nano-fluids, were used to examine the stability of nano-fluids. The visual inspection method is used to measure the stability period of nano-fluids for different particle concentration, sonication time and pH values. The stability period is defined as the elapsed time after the preparation of nano-fluids, at which the traces of sedimentation are visible. The ultra-sonicated nano-fluids were kept in the test tubes after the variation of the pH and the transparency was visualised for the stability analysis.

The zeta potential values were measured using the Zetasizer Nano ZS90, Malvern Instruments Ltd, UK. The mentioned instrument works on the dynamic light scattering, laser Doppler micro-electrophoresis and static light scattering techniques in a single unit to measure the particle size, zeta potential and molecular weight of the suspension.

In general, the nano-fluids of very low particle concentration, 0.01 vol. %, were reported to be very stable, and same was observed in the present study. But, stability was observed to be decreasing with the increase in particle concentration. In the present study, two parameters were used to enhance the stability: sonication time (Sot) to break down the aggregates of nanoparticles dispersed in the base fluid, and variation of the pH after preparation of nano-fluids. The nano-fluids were prepared at three different sonication times: 60, 120 and 180 minutes, while the pH of prepared nano-fluids was varied from acidic region to the basic region.

HCl and NaOH of 0.1 normality were used for the pH adjustment in the Al₂O₃/water nano-fluid and the variation of zeta potential and particle sedimentation as a function of pH was investigated. The variation in the zeta potential (Z) and sedimentation periods (Stt) as a function of sonication time (Sot) and pH for the different particle concentrations (φ) is discussed herein.

5. Results and discussion

5.1. Effect of pH and sonication time

Table 3 shows the values of zeta potentials for different experimental combinations.

Figure 2 shows the variations of zeta potential with the particle concentration of Al₂O₃ in water at different sonication times without addition of acid/base. It is observed that the zeta potential is maximum at 0.1 vol. % and 60 minutes sonication time. At high concentration (0.5 vol. % and 0.8 vol. %), the value of zeta potential is maximum at 30 minute
Comparing particle concentrations (0.1, 0.5 and 0.8 vol. %), the zeta potential is maximum for 0.1 vol. % for all sonication times. Figures 3–5 depict the variation in the zeta potential with the pH value for the different particle concentrations and sonication times. It is observed that the zeta potential is higher on the higher sides of acid and basic regions of nanofluids. There is the presence of a large number of $H^+$ ions in the suspension due to acidic nature of the nanofluids when pH is

| Concentration (vol. %) | Sonication time (minutes) | Addition of acid/base | pH value | Zeta potential (mV) |
|------------------------|--------------------------|-----------------------|----------|---------------------|
| 0.01                   | 60                       | Acid                  | 2.47     | 40.35               |
|                        |                          | Acid                  | 5.41     | 28.85               |
|                        |                          | Base                  | 9.41     | 19.65               |
|                        |                          | Base                  | 11.07    | 27.65               |
| 0.1                    | 30                       | Nil                   | 6.25     | 32.3                |
|                        |                          | Acid                  | 3.43     | 40.90               |
|                        |                          | Acid                  | 4.94     | 38.08               |
|                        |                          | Nil                   | 7.55     | 36.68               |
|                        |                          | Base                  | 9.21     | 22.1                |
|                        |                          | Base                  | 11.14    | 30.7                |
|                        | 60                       | Acid                  | 3.04     | 38.80               |
|                        |                          | Acid                  | 4.66     | 34.17               |
|                        |                          | Base                  | 10.14    | 25.03               |
|                        |                          | Base                  | 11.09    | 33.87               |
|                        | 120                      | Acid                  | 3.38     | 43.40               |
|                        |                          | Acid                  | 5.56     | 34.63               |
|                        |                          | Nil                   | 7.71     | 24.70               |
|                        |                          | Base                  | 9.62     | 26.7                |
|                        |                          | Base                  | 11.06    | 33.83               |
|                        | 180                      | Acid                  | 3.03     | 50.07               |
|                        |                          | Acid                  | 4.56     | 43.22               |
|                        |                          | Nil                   | 7.77     | 6.87                |
|                        |                          | Base                  | 9.82     | 13.90               |
|                        |                          | Base                  | 11.46    | 26.40               |
| 0.5                    | 30                       | Nil                   | 6.39     | 25.5                |
|                        |                          | Acid                  | 2.74     | 37.93               |
|                        |                          | Acid                  | 5.06     | 29.23               |
|                        |                          | Nil                   | 7.50     | 18.25               |
|                        |                          | Base                  | 9.60     | 24.6                |
|                        |                          | Base                  | 11.58    | 16.2                |
|                        | 60                       | Acid                  | 2.72     | 26.30               |
|                        |                          | Acid                  | 4.85     | 19.23               |
|                        |                          | Base                  | 9.94     | 16.10               |
|                        |                          | Base                  | 11.23    | 22.50               |
|                        | 120                      | Acid                  | 3.03     | 50.07               |
|                        |                          | Acid                  | 4.56     | 43.22               |
|                        |                          | Nil                   | 7.77     | 6.87                |
|                        |                          | Base                  | 9.82     | 13.90               |
|                        |                          | Base                  | 11.46    | 26.40               |
|                        | 180                      | Acid                  | 3.17     | 45.61               |
|                        |                          | Acid                  | 4.72     | 41.09               |
|                        |                          | Nil                   | 7.88     | 8.11                |
|                        |                          | Base                  | 9.68     | 11.39               |
|                        |                          | Base                  | 11.32    | 21.2                |

and minimum at 180 minutes. Comparing particle concentrations (0.1, 0.5 and 0.8 vol. %), the zeta potential is maximum for 0.1 vol. % for all sonication times.

Figures 3–5 depict the variation in the zeta potential with the pH value for the different particle concentrations and sonication times. It is observed that the zeta potential is higher on the higher sides of acid and basic regions of nanofluids. There is the presence of a large number of $H^+$ ions in the suspension due to acidic nature of the nanofluids when pH is
less than 7. This increases the probability of positive ions in the electric double layer around the nanoparticles, which increases the zeta potential (positive) in magnitude. On the other hand, there is the presence of a large number of $\text{OH}^-$ ions in the suspension due to basic nature of the nanofluids when the pH is more than 7. The possibility of presence of $\text{OH}^-$ in the vicinity of nanoparticles increases. These negative ions are attracted to the positive ions present in the stern layer, which causes the zeta potential (negative) to increase in magnitude.

Figure 2. Zeta potential variations with the concentrations of $\text{Al}_2\text{O}_3$/water nanofluid at different sonication times without addition of acid/base.

Figure 3. Zeta potential variation with the pH value of $\text{Al}_2\text{O}_3$/water nanofluid of different particle concentrations and sonication time of 60 minutes.
The zeta potential of the nanofluids is higher in the acidic region than that of the basic region, at all the sonication times. The isoelectric point (IEP) (the point at which the zeta potential becomes zero) for all the particle concentrations is found at the pH value of 8.6 for sonication times of 120 and 180 minutes, whereas it varies between 8 to 9.4 for the sonication time of 60 minutes. Hence, the value of IEP does not vary much at higher sonication times for the concentration in the range discussed above. Zawrah et al. [7] also experimented with the variation of zeta potential of Al₂O₃/water nanofluid with pH. Authors reported that the IEP for Al₂O₃ lies at a pH of nearly 8. The increase in the pH value, after the IEP point, increases the ionic strength of the solution and decreases the

![Figure 4](image4.jpg)

**Figure 4.** Zeta potential variation with the pH value of Al₂O₃/water nanofluid of different particle concentrations and sonication time of 120 minutes.

![Figure 5](image5.jpg)

**Figure 5.** Zeta potential variation with the pH value of Al₂O₃/water nanofluid of different particle concentrations and sonication time of 180 minutes.
zeta potential, i.e., the zeta potential increases in the negative direction. On the other hand, when the pH is decreased from IEP point, there is an increase in the magnitude of zeta potential in a positive direction due to the decrease in the ionic strength of the nanofluids. It is also observed that the zeta potential increases with the decrease in the concentration in the basic region after the IEP point for both 120 and 180 minutes sonication times.

Figure 6 shows the variation of zeta potential and stability period with the pH value of Al₂O₃/water nanofluid at 0.8 vol. % particle concentrations and sonication time of 120 minutes.

Figure 7 shows the variation of stability period as a function of sonication time for different particle concentrations. It is observed that there is an optimum value of sonication...
time, where stability period is maximum. With the increase in particle concentration, the optimum sonication time also increases. During sonication, the ultrasonic waves of nearly 19 kHz frequency pass through the nanofluid to cause vibration to the agglomerated nanoparticles. This leads to the development of cavitation bubbles which grow gradually during several cycles until they attain a critical state. At this critical state, the bubbles collapse which causes a very high local pressure and temperature called hot-spots. These hot-spots are responsible for splitting up of the particle agglomerations [18]. Hence, nanofluids are more stable after proper sonication. On the other hand, if the time of sonication exceeds the optimum time, it accelerates the nanoparticles and increases the temperature of the colloidal suspension and hence the Brownian motion. This causes the high rate of collision of the nanoparticles and hence there is instability due to agglomeration of nanoparticles.

5.2. Effect of surfactant

Figure 8 depicts the effect of surfactant on the zeta potential of Al₂O₃/water nanofluids with increasing elapsed time (in days) for 0.01 vol. % concentration. The SDS is used as the surfactant and added to the nanofluids before sonication in the same amount to the nanoparticles.

Surfactants have the chain-like structure with a head and tail. The anionic surfactants (like SDS) have the positive functional group at head and negative tail. The positive head is attracted towards the nanoparticles and attaches to them. This increases the charge in electric double layer (which is the charge of tail-negative charge) and hence the zeta potential (negative) increases in magnitude. The measured zeta potential varies from $-30$ to $-26$ mV for the surfactant-dosed nanofluids, while from 14 to 2 mV for the nanofluids without surfactant. For freshly prepared nanofluids, the absolute value of zeta potential (positive or negative) is higher for both types of nanofluids. With the passage of time, the

![Figure 8. The variation in zeta potential with elapsed time, in days, for Al₂O₃/water nanofluid having the particle concentration of 0.01 vol. % and sonication time of 60 minutes.](image-url)
absolute value of zeta potential decreases, which indicates that the stability of nanofluids decreases with time.

6. Conclusion

The stability of nanofluids is analysed using two methods: zeta potential and visual inspection method. The zeta potential is varied with the addition of acid, base and surfactant, and also with the variations of sonication periods. It is observed that the zeta potential is higher on the higher sides of acidic and basic regions of nanofluids for both 120 and 180 minutes sonication times. It is also observed that the zeta potential increases with the decrease in the concentration in the basic region after the IEP point for both 120 and 180 minutes sonication time. The zeta potential is directly related to stability period of nanofluids; higher the absolute value of zeta potential, higher the stability period. It is also observed that the optimum value of sonication time (where stability period is maximum), increases with the increase in the concentrations of nanofluids.

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