Viscosity and rheological behavior of aqueous nanofluids containing TiO₂ nanoparticles

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Abstract. Nanofluids containing different concentration of TiO₂ nanoparticles were prepared. Their rheological behavior was investigated on LVDV III ultra-programmable Brookfield viscometer at different temperature and particles loading. Results show that rheological behavior of nanofluids is determined by the concentration of TiO₂ in base fluid, nanofluids shows good Newton behavior when nanoparticles loading is low, while shear thinning becomes evident when the volume fraction of particles was continuously increased. Besides, viscosity of nanofluids shows strong nanoparticles loading and temperature dependence, but quite differs from classical viscosity model, as the theory models severely underestimate the value of viscosity, which is attributed to electroviscous effect of nanoparticles in base fluids. The primary electroviscous coefficient is evaluated at different pH values. Modified primary electroviscous coefficient is in good agreement with Booth’s theory.

1. Introduction
Nanofluids are dispersions of nanomaterials in base fluids. Since the concept of “nanofluids” was coined by Choi in the year 1995, it has been studied in all fields include heat transfer in automobiles, nanolubrication, waste heat recovery and environment engineering. Viscosity is the resistance of fluid to flow, it is one of the important thermophysical parameters of nanofluids, while rheology is the study of how a fluid flows when external force are applied. They are both important factors for the potential application of nanofluids.

More recently, viscosity and rheology of nanofluids has been intensively investigated. These studies reveal that the viscosity of nanofluids is a function of temperature [1], concentration [2], shape and size [3] of nanoparticles. Zhou [4] deeply investigated temperature and shear rate dependencies of viscosity by analyzing alumina polyaphaolefins nanofluids, he found that the relative viscosity of alumina polyaphaolefins nanofluids decreases with an increased temperature. Baratpour [5] studied the dynamic viscosity of single wall carbon nanobubes in ethylene glycol at different temperature and solid volume fraction, he pointed out that the dynamic viscosity of SWCNTs/EG nanofluids increases with decreasing temperatures and increasing solid volume fractions.

Despite numerous experimental and theoretical researches have been put into practice, an effective or integrated theory to establish the mechanism of enhanced viscosity of nanofluids still remains ambiguous. The failure of the well-known models to predict the viscosity of nanofluids gives rise to various theoretical hypotheses and empirical formulas. Most scholars attribute it to the addition of
dispersant or pH value. However, it is not everyone thinks that was right. According to Rubiohernández [6], the phenomenon of viscosity enhancement is briefly summarized in two factors. Firstly, the flow field of base fluid is distorted with the appearance of solid particles, which would generate an increase in the energy dissipation. Secondly, additional energy dissipation is produced due to the electrical double layer (EDL) that surrounds the particles, which may exert an extra distortion on flow field.

This work aims at investigating the effect of volume fraction, temperature and shear rate on rheological behavior of aqueous nanofluids. It is believed that this research would be beneficial for deeply understanding the rheological behavior of nanofluids, and then perfecting the theoretical foundation for the development of nanofluids research.

2. Experimental methods

2.1. Preparation of TiO\textsubscript{2} nanofluids
The TiO\textsubscript{2} nanoparticles chosen in this experiment are purchased from Sinopharm group Co. Ltd, China, nanoparticles are analytical grade and used directly without any further treatment. Firstly, nanoparticles were dispersed in deionized water at different volume fraction, followed by vigorous stirring for 30mintes, and then the mixture was sonicated for 30 minutes to obtain stable nanofluids. No dispersant is involved during the whole process to avoid the effect of surfactant to viscosity of the nanofluids. A drop of nanofluids dropped on a copper grid coated by carbon and evaporated under ambient atmosphere, and then the morphology was evaluated by JEM 2010 TEM. Size distribution of nanoparticles in nanofluids was measured with Zetasizer ZS from Malvern as well.

2.2. Measurement of dynamic viscosity
Viscosity experiment will be conducted as soon as the nanofluids were prepared to reduce the error caused by aggregation. The dynamic viscosity was firstly measured under continuously increased shear rate from 1 to 1000 s\textsuperscript{-1} at different particles loading. Then the volume fraction dependence of the viscosity was performed at the stationary shear rate and temperature range from 20\textdegree C to 40\textdegree C. Relative viscosity was defined as \( \eta_{nf}/\eta_{bf} \) and made a comparison with well-known viscosity models.

3. Results and discussion

3.1. Characterization of as-prepared nanofluids
According to the results of Malvern Zetasizer ZS, The solid particles distribution of nanofluids containing 1 vol. % TiO\textsubscript{2} nanoparticles is presented in Fig. 1. Evidently, the average size of nanoparticles in nanofluids is approximately 30 nm, it is much larger than the primary size of 10nm, possibly due to the absence of dispersant, which arouse agglomeration among nanoparticles.

![Fig. 1 Particles-size distribution of nano- TiO\textsubscript{2}](image)

![Fig. 2 TEM images of TO\textsubscript{2} nanoparticles](image)

TEM image of nanofluids further demonstrates this phenomenon as presented in Fig. 2. It shows that there are still several agglomerates in the sample, indicates that nanoparticles in the deionized water are
difficult to be broken into primary particles completely with the absence of dispersant. However, all nanofluids are synthesized without the participation of dispersant, in addition, there are not obvious agglomeration appear. Thus, it is still effective to investigate the rheological behavior and enhanced viscosity mechanism.

3.2. Analysis of rheological behavior

As one of the most important rheological measurement, dynamic viscosity curve may evaluate the rheological behavior of the fluid intuitively and visually. The dynamic viscosity versus shear rate of TiO$_2$ nanofluids at different volume fraction are shown in Fig. 3. Evidently, the viscosity of nanofluids is little affected by shear rate when volume fraction of TiO$_2$ nanoparticles is lower than 1 vol.%, indicating relatively good Newtonian fluids properties. As the TiO$_2$ volume fraction increases, non-Newtonian behavior (shear thinning) begins to dominate. The phenomenon of shear thinning occurs for higher volume fraction, possibly due to realigning along the flow direction of nanoparticles under the imposed shear stress. An interesting phenomenon is found in Fig. 3, when nanoparticles loading is above 1 vol.%. The dynamic viscosity keeps approximately constant at a higher shear rate from 200 to 1000 $s^{-1}$, acts as Newton behavior. But it decreases obviously when shear rate is lower than 200 $s^{-1}$, behaves as evident shear thinning phenomenon. Previous study of SiC in ethylene glycol nanofluids also confirmed this phenomenon [7].

![Fig. 3. Viscosity of nanofluids as a function of shear rate](image)

![Fig. 4 Dynamic viscosity of nanofluids as a function of volume fractions](image)

Temperature is one of the important factors that affect the viscosity of nanofluids. Fig. 4 illustrates the viscosity of TiO$_2$ nanofluids as a function of temperature and volume fraction of nanoparticles. It’s observed a decrease in viscosity with increased temperature, as the increasing temperature weakens the intermolecular forces of the particles and base fluid itself. For example, dynamic viscosity of nanofluids containing 0.5 vol.% nanoparticles decreases 32% while temperature changed from 20$^\circ$C to 40$^\circ$C. Similar trends have been found in several other nanofluids as well. Fig. 4 also represents the viscosity of nanofluids with different solid loading. Due to the addition of nanoparticles, the viscosity of
nanofluids is higher than that of base fluid, furthermore, as the nanoparticles loading increase, the viscosity of nanofluids is also increased.

If the nanofluids viscosity is expressed by relative viscosity, which is defined as $\eta_{nf}/\eta_{bf}$, relevant data can be concluded in Fig. 5. It represents that the increase in viscosity is a function of particle loading but little dependent of temperature. Compared with the prediction by the well-known Einstein equation and Brinkman equation. It can be seen that both the Einstein and Brinkman equation greatly underestimated the value of viscosity of nanofluids at all volume fraction. Most scholars attributed it to the addition of surfactant or pH value. Anyway, no surfactant was involved in this experiment, pH dependent mechanism also maintains obscure. Thus, some deep connection is urgent to be explored.

![Fig. 5 Viscosity enhancement of nanofluids as a function of volume fraction of nanoparticles at given shear rates](image)

**3.3. Electroviscous effect of nanofluids**

Laminar flow in different conditions can be simplified by Fig. 6. As a pure liquid, laminar flow is only determinate by external factors such as shear rate. When solid particles are added, as shown in Fig. 6b, assume that these particles are neutral in the fluid, they will exert a distortion of laminar flow. In most cases, solid particles in fluid are always charged, thus an extra distortion appears (as Fig.6c), the distortion due to EDL will cause an additional energy dissipation and thus result in further increase in the viscosity. This effect is called electroviscous effect and first considered by Smoluchowski [8]. It can be written as Eqn. (1).

$$\frac{\eta}{\eta_0} = [1 + (2.5 + P)\phi]$$

(1)

![Fig. 6 Laminar flow sketch of (a) pure fluid; (b) neutral particle in fluid; (c) charged particle in fluid.](image)

Where P is the primary electroviscous coefficient. Obviously, it is not sensible to calculate the sum of all ions. Anyway, measurement of Zeta potential (also calledζ potential) provides a new idea to evaluate the electroviscous effect since the $K^{-1}$ depends on ζ potential in a large extent. It is supposed that at IEP surface charge is completely neutralized or screened and no EDL exist around the particles. There is same distribution at particles surface and into the bulk. Thus, P is declined to 0. Zeta potential of nanofluids with different pH value is analyzed to confirm the IEP, the results are shown in Fig. 7. It illustrates a decrease in Zeta potential with the increased pH, and when pH value is 5.5, Zeta potential declines to 0. Evidently, the IEP of TiO$_2$ nanofluids is pH 5.5.
**Fig. 7** Zeta potential of nanofluids at different pH value

Viscosity of nanofluids versus the volume fraction of the solid phase at 20°C is plotted in Fig. 8, for different pH values. Approximatively linear dependence is observed at all pH values, indicating that only primary electroviscous effect is taken into action. It is also found that the slope is large when pH value is far away from the 5.5, possibly due to Zeta potential is higher in that case and consequently the primary electroviscous effect will be more remarkable. The primary electroviscous coefficient at all pH values can be obtained by calculating the ratio of viscosity and volume fraction of solid particles. The experimental results were made a comparison with Booth’s model [9]. And they are shown in Fig. 9. As can be seen, there is qualitative agreement between experimental and theoretical model, while the quantitative agreement is poor. Evidently, primary electroviscous effect is severely underestimated by Booth’s theory. Attempt is made to explain this disagreement.

**Fig. 8** Relative viscosity as a function of particles loading at different pH (a) from 3 to 6 (b) from 6 to 9

It is plausible to predict that electroviscous effect is negligible in the vicinity of isoelectric point (pH=5.5), thus the primary electroviscous coefficient should be zero in this point. However, it is not the case in our experiment, as the experiment value P far exceeds to zero. The primary cause may be adsorption of hydrone on the surface of nanoparticles, forming a firm adsorbed film, which consists of an entity with nanoparticles. Volume fraction of nanoparticles is thus increased by this phenomenon indirectly. Besides, some other factors, for examples, instrumental error, also exert an extra influence. However, these factors exist in all case of our experiment. Assume that influence of these factors is constant, actual primary electroviscous coefficient curves should be shifted downwards until the value in pH 5.5 is Zero. As the red line shown in Fig. 9, surprising consensus can be found between modified experimental values with Booth’s theory.
4. Conclusion
Rheologic behavior of TiO$_2$ nanofluids is determinate by the concentration of TiO$_2$ in base fluid, and there is a transition from Newtonian to Non-Newtonian behavior when the concentration is continuously increased.

Viscosity of TiO$_2$ nanofluids shows strong nanoparticle content and temperature dependence. It was increased with increasing particles loading and decreased temperature.

There is a huge deviation between experiment value and well-known viscosity model. This deviation is mostly due to electroviscous effect of nanoparticles in base fluids. The primary electroviscous coefficient is evaluated by both experiment and theory calculation. Modified primary electroviscous coefficient is in good agreement with Booth’s theory.

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