Stability and rheology of dilute TiO₂-water nanofluids

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Abstract
The apparent wall slip (AWS) effect, accompanying the flow of colloidal dispersions in confined geometries, can be an important factor for the applications of nanofluids in heat transfer and microfluidics. In this study, a series of dilute TiO₂ aqueous dispersions were prepared and tested for the possible presence of the AWS effect by means of a novel viscometric technique. The nanofluids, prepared from TiO₂ rutile or anatase nanopowders by ultrasonic dispersing in water, were stabilized by adjusting the pH to the maximum zeta potential. The resulting stable nanofluid samples were dilute, below 0.7 vol.%. All the samples manifest Newtonian behavior with the fluidities almost unaffected by the presence of the dispersed phase. No case of important slip contribution was detected: the Navier slip coefficient of approximately 2 mm Pa⁻¹ s⁻¹ would affect the apparent fluidity data in a 100-μm gap by less than 1%.

Background
Bulk rheological properties of nanofluids (shear viscosity [1,2], yield stress [3-7], and complex modulus [8]) can be important factors for some applications (e.g., convective heat transfer [9,10], and filtration [5]) and can also provide some correlations with other properties, such as volumetric particle concentration [1,2], thermal conductivity [11,12], or ζ-potential [3-6].

On the other hand, there are processes with a dominant microscopic length scale, such as small Nernst diffusion thickness in heat/mass transfer [13], small hydraulic radius in microfluidics [14-17], small pore diameter in filtration [5], etc., where the bulk rheology characteristics should be completed using another kind of information. In some cases, two-scale description (particle size or inter-particle distance vs. hydraulic radius) is useful [15]. In other cases, an additional macroscopic interfacial property, like apparent wall slip (AWS) velocity [18,19], could provide the missing information.

In this study, we examine experimentally the AWS effect in dilute TiO₂-water nanofluids, using a novel AWS viscometric technique [19].

Experimental procedure
Preparation and stability of the samples
Sample nanofluids were prepared by dispersing a nanopowder in an aqueous electrolyte solution (the base solution). The TiO₂ nanopowders (A1, A2, A3, R1, and R2) used in this study are specified in Table 1. The base solutions with adjusted pH values were prepared by adding HCl or NaOH to demineralized water with a possible content of dissolved gases.

In preliminary experiments, 0.02 g of a nanopowder was added into 25 mL of each base solution. The flask with a suspension was treated for 30 min in a 40-kHz ultrasonic bath with a nominal acoustic power of 30 kW m⁻³. The samples were then tested using DLS technique (Zetasizer Nano ZS - Malvern Instruments) to determine the zeta potential, ζ. Actual values of pH, see Figure 1, slightly differ from idealized log-linear estimates (dotted line in Figure 1) even for a series of the base solutions. This difference is caused by dissociation of water and hydrated TiO₂, as well as by the presence of dissolved CO₂ (around c_{NaOH} = 10⁻⁵ mol/L). The resulting ζ-potentials dependent on the actual measured pH values are plotted in Figure 2.

Assuming that the maximum stability of a TiO₂-water dispersion, i.e., the highest resistance against sedimentation, can be achieved at the extreme values of ζ-potential [1], further ten samples (A1±, A2±, A3±, R1±, and R2±), were prepared to examine their particle size distribution using again the DLS technique; see also Table 2. The preparation of these samples differs from the preliminary procedure only in the utilization of a larger primary amount of nanopowder (2.5 g in 100 g of dispersion) and a longer ultrasonication time (24 h). An external cooling system was employed to keep the sample at a constant temperature of 23°C during ultrasonic treatment. After keeping the sample aside for next 8 h, the sediment
coarse clusters, whereas the rutile dispersions (R1- and R2-) become finer. As a matter of fact, the coarser dispersions (A1-, A2-, A3-, R1+, and R2+) settle rather fast, while the finer dispersions (A1+, A2+, A3+, R1-, and R2-) are stable for a few days. Only the stable dispersions were further subjected to rheological examinations using the AWS rotational viscometry.

**AWS rotational viscometry**

The concept of AWS effect from the viscometric viewpoint [17-19] is illustrated in Figure 4 for the simple shear flow between two mutually sliding parallel plates. A possible near-wall flow anomaly, resulting in a nonlinear velocity profile under constant shear stress \( \tau \), is represented by the apparent slip velocity \( u \). The only experimentally available kinematic quantity, the sliding velocity \( U \), determines the apparent shear rate \( \dot{\gamma}_{\text{app}} \equiv \frac{U}{h} \) (or \( \dot{\gamma}_{\text{app}} = \frac{\Omega R}{h} \) for the Couette flow in a narrow gap \( h \) between two coaxial cylinders), which is expressed as a sum of the bulk flow and wall slip contributions, as follows:

\[
\dot{\gamma}_{\text{app}} = \dot{\gamma} + 2\frac{u}{h} = (\phi \sigma) + 2\chi \frac{\sigma}{h} \sigma
\]  

(1)

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Table 1 Nanopowders used for the preparation of nanofluids

| Powder | Mineral | Source          | Density (g cm\(^{-3}\)) | Max. size (nm) |
|--------|---------|-----------------|--------------------------|----------------|
| A1     | TiO\(_2\) anatase | Aldrich         | 3.90                     | 25             |
| A2     | TiO\(_2\) anatase | ICPF \(^a\)     | 3.90                     | 40             |
| A3     | TiO\(_2\) anatase | ICPF \(^a\)     | 3.90                     | 20             |
| R1     | TiO\(_2\) rutile  | Aldrich         | 4.17                     | 100            |
| R2     | TiO\(_2\) rutile  | Precheza \(^b\) | 4.17                     | 100            |

\(^a\)ICPF - nanopowder for photocatalytic application supplied by Department of Catalysis of ICPF ASCR, Prague.

\(^b\)Precheza - commercial pigment, produced by Prerov Chemical Works, Czech Republic.

(ranging from 5 to 90% of the original content of nanopowder) was withdrawn and weighed to determine the final real particle concentration, shown in Table 2.

The resulting particle size distributions, Figure 3, show remarkable differences in the behaviors of anatase- and rutile-based dispersions. While the anatase dispersions display the maximum content of the finest particles in acid media (A1+, A2+, and A3+), the rutile dispersions in acid media (R1+ and R2+) are much more coarse. In alkaline media, on the contrary, the anatase dispersions (A1-, A2-, and A3-) display a remarkable shift toward

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**Figure 1** Titration curves of the tested samples. Dotted line shows an idealized titration curve. Deviations for the individual samples are due to dissociation of hydrated TiO\(_2\) and dissolved CO\(_2\).
Two material functions, the bulk fluidity $\phi[\sigma] \equiv \gamma/\sigma$ and the Navier slip coefficient $\chi[\sigma] \equiv u/\sigma$, are constant in many cases [17-19]. The flow and slip effects can be distinguished through a series of viscometric experiments, in which the gap thickness $h$ is systematically varied whereas the shear stress $\sigma$ is kept constant. This is the essence of AWS viscometry.

Rotational viscometer with a KK sensor

The experimental realization of AWS viscometry needs a series of sensors of different and well-calibrated hydraulic radii (tube radius in the capillary viscometry, gap thickness between cup and bob in the rotational viscometry, etc.). The novel KK-type sensor for the rotational AWS viscometry [19], shown in Figure 5 complies with this need by means of an axial shift facility for adjusting $\Delta z$ and, subsequently, the gap thickness $h$ is given by

$$h = h_0 + \Delta z \sin(\theta)$$

where $h_0$ corresponds to $h$ at the starting position $\Delta z = 0$. Both the working surfaces of the sensor are the coaxial

![Figure 2 Acidobasic adjusting of $\zeta$-potential. Individual nanopowders are specified in Table 1.](image)

Table 2 Parameters of the stable nanofluids

| Sample | Powder | Base solution | pH  | $\zeta$ (mV) | Conc. TiO$_2$ (wt.%) | Conc. TiO$_2$ (vol.%) |
|--------|--------|---------------|-----|--------------|----------------------|-----------------------|
| A1+    | A1     | $10^{-2}$ M HCl | 2.4 | 69.4         | 1.2                  | 0.31                  |
| A1-    | A1     | $10^{-3}$ M NaOH | 12.4 | -42.7       | 0.8$^b$              | 0.2$^a$              |
| A2+    | A2     | $10^{-2}$ M HCl | 2.4 | 81.2         | 2.4                  | 0.65                  |
| A2-    | A2     | $10^{-3}$ M NaOH | 12.4 | -44.3       | 1.2$^*$              | 0.3$^*$              |
| A3+    | A3     | $10^{-2}$ M HCl | 2.4 | 87           | 1.4                  | 0.36                  |
| A3-    | A3     | $10^{-3}$ M NaOH | 12.4 | -44.5       | 0.8$^*$              | 0.2$^*$              |
| R1+    | R1     | $10^{-2}$ M HCl | 2.4 | -            | 0.2$^*$              | 0.05$^*$             |
| R1-    | R1     | $10^{-2}$ M NaOH | 12.4 | -65.2       | 0.2                  | 0.05                 |
| R2+    | R2     | $10^{-2}$ M HCl | 2.4 | 34.9         | 0.2$^a$              | 0.05$^a$             |
| R2-    | R2     | $10^{-2}$ M NaOH | 12.4 | -61.6       | 0.3                  | 0.07                 |

Volumetric concentrations were calculated using the densities from Table 1.

*Unstable samples with rough estimates of particle concentration.
cones of the same cone angle $\theta$, as in a Morse clutch. The gap thickness can be adjusted over a broad range of $100$-$2500 \mu m$ with substantially (ten times) higher accuracy than for the plate-plate (PP) sensor. At the same time, the KK sensor displays much lesser edge effects and better reproducibility. In many applications, it is important to note that the measurements with a varied gap thickness can be made without refilling samples.

The fully automated rotational rheometer HAAKE RS 600 has been used both for driving the KK sensors and for data acquisition. When operating the KK sensor under HAAKE software RheoWin, it is appropriate to identify it with a PP-type sensor. Primary data in the text files, generated by the HAAKE RheoWin software, were further treated using a home-made software AWS-Work, described in [19].

**Correction on centrifugal effects in AWS rotational viscometry**

The original theory [19] of the KK sensors ignores possible inertia effects at the edges of rotating spindle. An additional correction $E$ of the shear stress on inertia was until now considered only for the standard cylinder-cylinder Z40 DIN sensor [20]. This result can be
rearranged to a local edge correction for a single semi-infinite cylinder by radius $R$ rotating with a speed $\Omega$ in an infinite coaxial cylindrical vessel by radius $R + h = R (1 + \kappa)$, filled with a Newtonian liquid of kinematic viscosity $\nu = 1/(\rho \eta)$:

$$E(Re, \kappa) \equiv a x Re^2/(1 + b Re^{3/2})$$  \hspace{1cm} (3)

where $\kappa \equiv h/R$, $Re \equiv \Omega R^2/\nu$, $a = 7.0 \times 10^{-4}$, and $b = 2.7 \times 10^{-4}$.

For a KK-type conical spindle, the local edge effects are related to different radii at the both fronts, $R$ and $\lambda R$, respectively, with a common $h$ and $\lambda = 1 - \tan(\theta) H/R$, $\theta$ Figure 5. The final correction on centrifugal effects can be approximated for Newtonian liquids by the formula:

$$\sigma_{\text{primary}}/\sigma_{\text{corrected}} = \psi_{\text{corrected}}/\psi_{\text{primary}} = 1 + E(Re, \kappa) + E(\lambda^2 Re, \kappa/\lambda).$$  \hspace{1cm} (4)

**Results and discussion**

**Stability and texture of dilute nanofluids**

All the TiO$_2$ dispersions, prepared in the described way, were partially settling down. The concentrations of the final stable dispersions depend on the base solution used, individual nanopowder, and dispersion procedure.

The series of images in Figure 6 illustrates the influence of the dispersion procedure and base solution on the texture of several dispersions of the nanopowder A3. The photographs were obtained using the SEM imaging technique (Camceca SX100), applied to the samples of the dried drops. In conclusion, the particles of the nanopowder A3 were better dispersed in the acidic solution than in the neutral or alkaline one (compare Figure 6a, b, c). The clusters remaining in the acid dispersion were broken up during the ultrasonic treatment (compare Figure 6c, d).

The influence of pH on the quality of dispersions was observed for all the tested dispersions via DLS technique. It can be seen from the number and volume-weighted particle size distributions (Figure 3) that anatase nanopowders disperse better in the acid solutions while rutile ones in the alkali solutions. The finer the dispersion the higher the concentration in the final stable samples.

**AWS rotational viscometry**

Rheological measurements were conducted using the AWS rotational viscometry on the HAAKE RS 600 commercial instrument with a series of home-made KK sensors. Basic characterization of the examined samples is given in Table 2. As the AWS effect can depend on the material type and roughness of confining surfaces of the sensors, four different KK sensors were used, see Table 3. For the each combination sample - KK sensor, a series of individual viscometric measurements was made, covering the range of shear stress $\sigma$ of 0.05-5 Pa and the range of gap thickness $h$ of 150-500 $\mu$m. In the final data treatment, including the inertia correction according to Equations 3 and 4, the primary data with $\sigma > 1$ Pa or $h > 300$ $\mu$m were disregarded (errors due to inertia effects over 5%). Uncorrected AWS data on $\phi$ and $\gamma$, not shown here,

| Sensor  | Material         | $h_0$ (μm) |
|---------|------------------|------------|
| KK01    | Stainless steel  | 173.5 ± 2  |
| KK02    | Titanium         | 134.5 ± 2  |
| KK03    | Eloxed dural     | 131.5 ± 2  |
| KK04    | Sand-blasted stainless steel | 150.6 ± 2 |

All sensors share the nominal dimensions $R = 17.5$ mm; $H = 60$ mm; $\cot \theta = 10$. The minimum gap thicknesses $h_0$ were determined by calibrations with water.

### Table 4 Results of rheological measurements at 23°C

| Sample | Fluidity $\phi$ (Pa$^{-1}$ s$^{-1}$) |
|--------|--------------------------------------|
|        | Avg | Dev | Avg | Dev | Avg | Dev | Avg | Dev | Avg | Dev |
| KK01   | 1.032 | 0.016 | 1.026 | 0.047 | 1.049 | 0.010 | 1.031 | 0.011 | 1.036 | 0.010 |
| KK02   | 1.045 | 0.010 | 1.041 | 0.016 | 1.045 | 0.010 | 1.041 | 0.010 | 1.043 | 0.002 |
| KK03   | 1.001 | 0.010 | 1.028 | 0.018 | 1.022 | 0.018 | 1.009 | 0.010 | 1.015 | 0.012 |
| KK04   | 1.018 | 0.019 | 1.031 | 0.022 | 1.060 | 0.013 | 1.069 | 0.014 | 1.045 | 0.024 |
| R1+    | 1.042 | 0.010 | 1.045 | 0.031 | 1.073 | 0.012 | 1.030 | 0.045 | 1.048 | 0.018 |
| R2-    | 1.033 | 0.017 |

Avg & Dev, average and standard deviation for a given data series.
display remarkable dependence on $\sigma$, evoking a shear-thickening behavior. However, the correction of primary data on inertia effects shows that this dependence is only an experimental artifact.

The AWS data were further treated to separate the flow and slip contributions and to identify the corresponding material functions $\phi[\sigma]$ and $\chi[\sigma]$. The resulting fluidities, given in Table 4, do not deviate from that of pure water by more than 3%. Statistical estimates of the slip extrapolation length $\beta$ [19],

$$\beta[\sigma] = \chi[\sigma]/\varphi[\sigma]$$

(5)
given in Table 5, indicate the mean values about zero with uncertainty about $\pm 2$ μm. This is in a good agreement with the estimate of instrumental uncertainty $\Delta h$ of the adjustable gap thickness $h$, given in Table 3. Possible slip effects in all the studied samples are therefore quite negligible in comparison with the instrumental uncertainty.

The absence of slip effect is illustrated also in Figure 7, where the AWS data are fitted on two different constitutive models according to Equation 1, for details on the parametric filtration see [19]. Figure 7a shows the results obtained for the model with no-slip assumption, $\chi = 0$, while the Figure 7b shows those for the model with adjustable but constant $\chi$. Comparing of the both approaches shows that they provide nearly same estimates of the fluidity.

Conclusions
AWS rotational viscometry with KK-type sensors represents a novel technique suitable for testing microdisperse fluids in the presence of slip effects.

Several dilute TiO$_2$-water stable nanofluids with an optimized pH (via $\zeta$-potential) are used to demonstrate the capability of this instrumentation to detect possible slip effects even in low-viscosity liquid samples. The

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Table 5 Results of rheological measurements at 23°C

| Sample | Slip extrapolation length $\beta = \chi[\phi] (\mu m)$ |
|--------|--------------------------------------------------------|
|        | KK01         | KK02         | KK03         | KK04         |
|        | Avg | Dev | Avg | Dev | Avg | Dev | Avg | Dev |
| A1+    | 2   | 2   | 0   | 2   | 6   | 2   | 0   | 2   |
| A2+    | 2   | 2   | 0   | 2   | 2   | 2   | 2   | 2   |
| A3+    | 5   | 5   | 1   | 2   | 3   | 3   | 5   | 5   |
| R1-    | 3   | 3   | 5   | 3   | 5   | 5   | 5   | 5   |
| R2-    | 6   | 4   | 9   | 2   | 7   | 3   | 4   | 4   |
| Water  | 0   | 2   | 0   | 2   | 0   | 2   | 0   | 2   |

Avg & Dev, average and standard deviation for a given data series.
tested stable colloidal samples differ in the nominal volumetric concentrations of nanoparticles, ranging from 0.07 to 0.7 vol.%.

The sensitivity of the AWS viscometric instrument on slip effects depends on the minimum available gap thickness and the accuracy of its adjustment. Within the given instrumentational limits, no slip effect was detected for the nanofluid samples examined for this investigation.

Abbreviations

AWS: apparent wall slip.

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Authors’ contributions

VP carried out experiments, and evaluations, including development of special software. JT participated as a consultant both in rheology and nanotechnologies. OW developed KK-sensors and the related theory. All the authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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