The Effect of Surfactants on the Stability of TiO$_2$ Aqueous Suspension

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ABSTRACT. To produce TiO$_2$ nanoparticles suspension for coating applications, it is vital that the nanoparticles are well dispersed in liquid media and remain stable without sedimentation for a certain time. In this study, TiO$_2$ suspensions were dispersed in aqueous media using ultra-sonication in the presence of various types of surfactants; Sodium dodecyl sulfate (SDS), Hexa-decyltrimethylammonium bromide (CTAB) and Pluronic F-127 (PF-127). Three parameters were investigated; amount of surfactant, time-dependent stability and effect of charges (ions) on the TiO$_2$ dispersion and the suspension stability behavior. The addition of surfactant produced more dispersed and stable TiO$_2$ in aqueous suspension. 2.5 wt.% of all type surfactant was found to produce the most stable suspension with high turbidity and measurable particle size. CTAB was found to provide more stable TiO$_2$ suspension than SDS and PF-127 attributed from electro-steric stabilization.

Keywords: TiO$_2$, Stability, Surfactant, Turbidity, Zeta potential;

1.   INTRODUCTION

Titanium dioxide (TiO$_2$) can be used in various industries, such as for environment and health-care. For environment, it is widely used as self-cleaning coating [1], water treatment [2] and materials for air purification [3]. In health-care, it is used as antibacterial [4] and anti-cancer [5]. These two applications require TiO$_2$ nanoparticles (NPs) to be dispersed in aqueous environment and enter the aquatic ecosystem. The outcomes of TiO$_2$-NPs in aqueous environment depend on their physical and chemical properties such as surface characteristics and sizes and other chemical species in water. To prepare the TiO$_2$ dispersion it requires deagglomeration of NPs clusters to represent individual particles with size as smallest as possible and stabilizing these NPs in the suspension for a certain time. The main problem with TiO$_2$-NPs is they typically insoluble in aqueous medium, hence obstructing its utilization as colloidal dispersion or stable suspension. The NPs have strong tendency to agglomerate due to large surface are as compared to submicron particles. Generally, the agglomeration is caused by Van der Waals attraction forces between particles. In the case of TiO$_2$-NPs, the surface is hydrophobic in nature, while the electrostatic interaction between NPs in aqueous medium resulting accumulation and agglomeration of TiO$_2$ to size larger than 3 μm [6].

The aggregation of TiO_2 NPs plays a key role in their fate in aqueous environment. It is explained why the commercial TiO_2-NPs are often shipped as dry powders; for easy handling because storage these NPs in dispersed water could not be kept in nanoscale range. In coating industries especially for photoactive and UV-blocking, the uniform and transparent coating is essential which relies on the ability of TiO_2-NPs to have minimum degree of agglomeration and the NPS can be distributed homogeneously or in desired patterns [7]. While in medicine, the agglomeration can lead to misleading interpretation of the toxicology and the uptakes of Nps into the biological system [8]. There are several methods to suppress the agglomeration or to deagglomerate the NPs in colloidal state such as by counterbalanced of electrostatic and steric stabilization [9-13]. Stability of NPs in aqueous environment is determined by the pH of solution and surface charges of the NPs in water [10]. Deagglomeration proceeds through the break-up of bonds between single NPs crystallites in the aggregates. These can be achieved by creating an electrical double layer at the solid-liquid interface or by adsorbing polymers or surfactants on the NPs surfaces [14]. A stable colloid solution needs some type of inter-particle repulsion to overcome the nature of van der Waals attraction. Electrostatic stabilization is achieved by addition of charge (ion) to NPs so that they can repel each other and this is often occurs under influence of pH. Steric stabilization is achieved by adsorption of polymer to the surface of NPs forming a thin layer which prevents the NPs from agglomeration [15]. Addition of polyelectrolyte into a NPs suspension will generate a combination of electrostatic and steric stabilization termed as electro-steric [16,17]. Steric stabilization or polymer-induced interactions arise from the adsorbed polymer chain of the surfactant that protrude into the solvent and provide protective layer on the NPs surfaces [15]. There are three main factors brought to the efficient stabilization; the adsorbed layer should be thick enough to avoid the van der Waals attraction, the adsorbed molecules should be adsorbed strongly to the entire NPs surfaces and the chains that protrude into solvent should be in good solvent conditions [18].

To disperse TiO_2-NPs in aqueous medium, an external force is needed to overcome the van der Waals attractions. Sonication is commonly used to break up agglomerated NPs in a solvent because the oscillation of liquid cause nucleation and collapse of solvent bubbles; bubble formation and collapse at the surface of solids can be very effective in chopping solids [19]. In this work three types of surfactants with various functional groups were used as stabilizing agent to stabilize the TiO_2 aqueous suspension. The aim is to study the behaviour of TiO_2-NPs when dispersed in aqueous medium in the mean of turbidity, zeta potential and particle size. The main objective is to determine the most suitable surfactant to stabilize TiO_2 in aqueous media.

2.   MATERIALS AND METHODS

The readily synthesized anatase TiO_2 particles were prepared as described by previous study [20]. To prepare the TiO_2 suspension, 0.025 g of TiO_2 NPs was dispersed in 50 mL of distilled water using ultrasonic homogenizer equipped with temperature controller (Ultrasonic Elma, E15H) for 30 min. Three types of surfactants were used; Sodium Dodecyl Sulfate (SDS) molecular weight (Mw) of 288.372 $gmol^{-1}$, Hexadecyltrimethylammonium bromide (CTAB) Mw of 364.45 $gmol^{-1}$ and PluronicF-127 (PF-127) Mw of 12 600 $gmol^{-1}$. The required amount of dispersant from 0 to 3 wt.% was added into the TiO_2 suspension followed by further sonication for 30 min. The suspensions were then aged overnight at room temperature. Prior to characterization, the suspensions were re-dispersed using the same homogenizer for 3 min. The suspensions were characterized using UV-Visible spectrometer (Lambda 35, Perkin Elmer) to measure the turbidity of the suspension over time (1 to 4 hours). Turbidity is relative to the ability of the TiO_2-NPs to remain dispersed in the suspension. Zeta potential analyser (Zeta Plus, Brookhaven Instruments) was used to measure the zeta potential which indicates the surface charge of the NPs in the suspension. Particle size was measured using Nanophox (Sympatec).

3.   RESULTS AND DISCUSSION

To demonstrate the stability of TiO_2 NPs in aqueous solution, time dependent % transmittance (%T) was measured by UV/Vis spectrometer. The %T was converted to turbidity value using Beer Lambert Law equation as stated in Eq. 1;Turbidity = 100 - %T   (1)

3.1 Effect of surfactant concentration. The % transmittance data was recorded after 1 hour from the re-dispersion time (after overnight aging). Fig. 1 shows the trend of the turbidity as a function of surfactant concentration for all type of surfactants. In this study, turbidity value is used to determine the ability of the TiO_2-NPs to remain dispersed in the suspension. High turbidity reflects the dispersion of NPs in suspension while low turbidity means most NPs are sediment to the bottom of suspension. Among all, CTAB shows highest turbidity while PF-127 is the lowest. CTAB has higher turbidity in all concentration range compared to control sample. In contrast, SDS and PF-127 show lower turbidity than control sample at surfactant < 2.5 wt.%. All TiO_2-NPs suspensions show that 2.5 wt.% of surfactant concentration has the highest turbidity which is about 40–50. Turbidity starts to decrease at 3.0 wt.% for CTAB and SDS but slightly increase for PF-127.
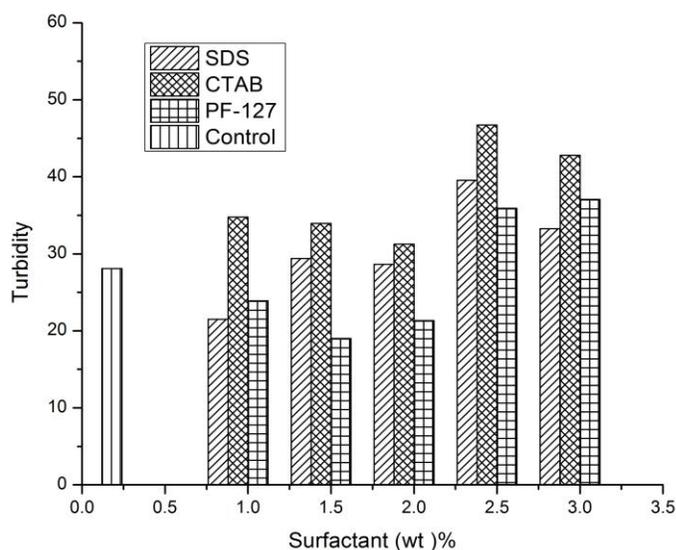
Fig. 1 Turbidity of TiO_2 suspensions as a function of surfactant concentration

3.2 Effect of sediment time. The stability of the TiO_2 NPs to remain disperses in aqueous media with and without surfactant was monitored with time. Turbidity was measured at 1, 2, 3 and 4 hours from re-dispersion time to get a complete time dependent measurement, respectively. Fig. 2 depicts the turbidity of all TiO_2 suspensions as a function of time to show the degree of stability of NPs. It shows that at 2.5 wt.% of surfactant, turbidity of all suspensions is in the range of 35 to 45 at 1 hour measurement. These suspensions are more turbid compared to control sample (TiO_2 suspension without surfactant) and surfactant solution. This means that in the presence of surfactant most NPs are remain stable to disperse in aqueous media but without surfactant NPs are easily sediment to the bottom. After 2 hours, the turbidity decreases to about 10 to 20 for SDS and CTAB and about 10 to 15 for PF-127. These values remain unchanged for the third and fourth hour. This indicates most NPs are settled to the bottom of suspension after 2 hours, leaving the surfactant-stabilized NPs to remain disperse in the suspension.

3.3 Effect of surfactant type. The stability of TiO$_2$ suspensions was further characterized with measurement of zeta potential (ZP). Zeta potential represents the potential stability of the suspension and indicates the degree of repulsion between adjacent, similarly charged particles in the suspension. It is a function of the surface charge of the particles [17]. In dispersions where value of the ZP is close to zero (isoelectric point), particles tend to agglomerate. The higher the magnitude of ZP, the more stable of the suspensions can be [9]. At highly negative or positive values of ZP (more than 30 mV or less than -30 mV [21]) particles in dispersions tend to repel each other, thus no agglomeration occurs. Fig. 3 shows the chemical structure of the SDS, CTAB and PF-127. The chemical structure helps to understand how surfactant can contribute to the potential stability of TiO$_2$ suspension.

Fig. 2 Turbidity of TiO$_2$ suspensions containing different surfactants as a function of time

Fig. 3 Chemical structure of three different surfactants; SDS, CTAB and PF-127

Table 1 shows the ZP and particle size range of all suspensions as a function of surfactant concentration. TiO$_2$ suspension without surfactant shows low ZP and the particle size is out of range of measurement. This can be explained by the agglomeration of TiO$_2$ NPs which caused the suspension to easily sediment to the bottom. The addition of surfactants to TiO$_2$ suspensions leads to higher ZP and attainable particle size attributed to more stable TiO$_2$ NPs in aqueous solution. Among all surfactants, PF-127 shows the lowest ZP

which stands the reason for low turbidity. As a zwitterionic surfactant, PF-127 has less positive charges compared to CTAB. It is also a long carbon chains polymer that can adsorb onto the TiO_2 surfaces and bond them with each other causing flocculation of NPs that result in destabilization of the suspensions [22].

   The presence of CTAB in TiO_2 suspensions leads to the change of magnitude of ZP from negative to positive, indicating possible electrostatic interaction between cationic CTAB and TiO_2. The electrostatic interaction could occur between the OH^- groups of TiO_2 with the cetrimonium (hexadecyltrimethylammonium) cations of CTAB. At 2.5 wt.% surfactant, suspension with CTAB has the highest ZP (48.74 mV) which explained why it has the highest turbidity and particle size is in the range of 1 nm to 2 μm. At 3 wt.% CTAB, the ZP is slightly decreases which indicating the excess amount of CTAB weaken the stability of suspension, probably due to the adsorption of polymer chain to the NPs surfaces that may lead to flocculation [22]. This is agreed with the decreasing of turbidity and increasing of particle size up to 6 μm. Suspension containing SDS although show higher ZP than CTAB but seems to have lower turbidity probably because it has insufficient repulsive forces to overcome the van der walls attractions between TiO_2 NPs [15].
   This is also supported by the larger particle size for TiO_2 added with SDS than CTAB. SDS is an anionic surfactant with sulfate groups as the active site for interactions. Since there is no electrostatic interaction between SDS and TiO_2, the stabilization might come from the strong adsorption of this surfactant to TiO_2 surface due to the multiplicity of sulfate groups in the whole polymer [23]. Thus, this study suggests TiO_2-NPs suspension is stabilized better by the repulsive forces from excess cationic attributed from electrostatic interaction between TiO_2 and CTAB and also from steric repulsion of CTAB. These results are in agreement with previous studies done by Naeini et al. [24] that reported the TiO_2 suspension added with NH_3 was stabilized up to 360 min attributed from the OH^- which has larger space size than H^+ groups. The suggested that the TiO_2 suspension added with NH_3 was stable due to the repulsive forces between similar charges and an extra steric repulsion from the NH_3.

Table 1 Zeta potential (ZP) and particle size range for TiO_2-NPs suspension with and without surfactant

Surfactant (wt.%)	Zeta potential (mV)			Particle size range (nm)		
	SDS	CTAB	PF-127	SDS	CTAB	PF-127
0.0	-10.19	-10.19	-10.19	Nil	Nil	Nil
1.0	-64.04	38.09	-22.59	1.01 - 2013.30	311.06 - 3660.8	Nil
1.5	-58.12	51.94	-28.97	1.01 - 1147.04	167.2 – 2502.63	Nil
2.0	-50.41	45.88	-16.08	1.01 - 3105.16	757.08 – 3166.88	Nil
2.5	-31.53	48.74	-13.29	104.6 - 3167.0	1.01 – 2013.30	Nil
3.0	-47.64	44.33	-8.33	54.9 - 3042.94	4.30 – 6242.69	Nil
Surfactant	Nil	3.4	-8.77	Nil	Nil	Nil

4.   SUMMARY

This study demonstrates that colloidal suspension of TiO_2-NPs was stabilized at high turbidity up to 1 hour, sufficient for observation of particles aggregation and surface charge studies. CTAB shows better dispersion and stability of TiO_2-NPs than SDS and PF-127.

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