Electrophoretic mobility of different sizes synthesized titanium dioxide (TiO$_2$) based microemulsion

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ABSTRACT

Effects of different particle sizes of titanium dioxide on electrophoretic mobility were investigated. Methodology to synthesize different sizes of titanium dioxide were carried out with varying molar ratio, w$_\text{o}$, ≈[H$_2$O]/[Surfactant] values, which later hydrolyzed by Tetrapropyl orthotitanate (TPOT) based with sol-gel microemulsions techniques. Synthesized TiO$_2$ demonstrated the increase in sizes as the molar ratio of water over surfactant increased. Electrophoretic mobility of TiO$_2$ with different sizes was measured in different pH range from 4 to 10, temperatures from 15°C to 60°C and applied voltages varied from 10 V to 60 V. Results showed that the optimum electrophoretic mobility was observed at pH 6 for all the particles sizes. Buffer for pH 6 with less hydrogen ion increased the electrophoretic mobility. Meanwhile, electrophoretic mobility of TiO$_2$ at temperatures below 60°C did not show any significant changes for all sizes of particles, unless 60°C. This indicated that higher temperatures increased kinetic energy of charged particles which led to a random movement of particles and reduced electrophoretic mobility. In different applied voltages, the electrophoretic mobility of the biggest size of TiO$_2$ increased proportionally as increase in voltages. The higher applied voltage provided a greater electrostatic force to the particles. The smallest size of TiO$_2$ recorded higher electrophoretic mobility. This indicated that the smallest TiO$_2$ possessed denser negative charges on its surface and experienced lesser frictional force contributed to greater mobility.

INTRODUCTION

Titanium dioxide has been used in many applications such as special optic properties and high catalytic activity[1]. A promising method to synthesize TiO$_2$ is to use sol-gel process[2,3], which sol based with microemulsion generates nanoparticles to provide a microhetero

genous medium[4]. This is important to prepare the homogenous powder of TiO$_2$[5]. Study showed that formation of TiO$_2$ by controlling the hydrolysis of TiCl$_4$ in an aqueous cores concluded that the preparation of the microemulsion with the ratio of [water]/[Surfactant] is strongly influence the physical properties of these nanoparticles[6]. Some investigations reported that wa-

KEYWORDS

Electrophoretic mobility; Sol-gel process; Microemulsion; Titanium dioxide; Molar ratio.
Electrophoretic mobility of different sizes synthesized (TiO$_2$) nanomaterials can be employed to obtain ultrafine particles\cite{7}. Furthermore, understanding on the surface charge of TiO$_2$ leads to better applications of it in the future. For instance, the mobility of particles in solutions can be monitored to avoid agglomeration with appropriate conditions. The information on surface charge properties of TiO$_2$ can also be a guide on clearing the bacteria from the storage of waste, food, and medical tools.

Surface charge of synthesized TiO$_2$ is studied with electrophoresis system. When external electric field is supplied, charged particles would migrate toward the electrode. This system is famous in plenty of investigations on studying surface charges of rigid colloidal particles and even bacteria\cite{8,9}. It is essential to gain more information on surface charge of colloidal particles and also bacteria. This encourages more usage on them. The theory of the electrophoretic mobility is known as a movement of particle with charges under the influence of an external electric field, $\mu$ is defined as followed.

$$\mu = \frac{v}{E}$$

where the $v$ is the rate of migration (m/s) and $E$ is external voltage on separation distance (V/m). Besides, the mobility also depends on other physical properties such as particle size and the surface charges and the properties of electrolyte solution which might involve pH, ionic strength and permittivity. The equation is given by Smoluchowski\cite{10},

$$\mu = \frac{\varepsilon \sigma \zeta}{\eta} = \frac{\sigma \chi}{\eta}$$

which the $\varepsilon$ is dielectric constant, $\sigma$ is permittivity of the free space, $\zeta$ is zeta potential and $\eta$ is viscosity of the solution. This is followed by $\sigma$, charge density of the surface charge and $\chi$ is effectiveness of ionic double layer surrounding the surface.

This research is to study how the size properties of TiO$_2$ influence the surface charge in different conditions such as pH (4-10), temperature (10°C - 60°C) and applied voltages (10 V-60 V). There are three different sizes of TiO$_2$ is investigated. These particles were synthesized with microemulsion of a sequence increase in molar ratio.

**MATERIALS AND METHODS**

**Chemicals**

Cyclohexane was purchased from Sigma-Aldrich which was used as an organic solvent and surfactant of Triton X-45 (Sigma-Aldrich) was selected. Tetrapropyl orthotitanate (Ti(OC$_3$H$_7$)$_4$) from Fluka and sodium hydroxide (HmbG chemical) were used. Buffer at pH 7 was prepared with Sodium Phosphate Monobasic Dihydrate (H$_2$NaO$_4$P.2H$_2$O) from Fluka, assay $>99.0\%$ and Sodium Phosphate Dibasic Dihydrate (HNa$_2$O$_4$.P.2H$_2$O) with a purity up to 98% was also purchased from Fluka.

**Instrument**

The water content of the cyclohexane and Triton X-45 are measured with titrator (Mettler Toledo DL38, Karl Fisher Titrator). The particle size and electrophoretic mobility is measured with zetasizer series nano-ZS which purchased from Malvern Instrument. The stirrer is used which has the labeled of HTS-1003 LMS.

**Preparation of TiO$_2$**

The calculation of molar ratio, concentration of water over concentration of surfactant ($w_o$=[H$_2$O]/[Surfactant]) which varied the sizes of the synthesized TiO$_2$ was determined. Nanosized TiO$_2$ particles were prepared by controlled the hydrolysis Tetrapropyl orthotitanate (TPOT) with 0.5 M of sodium hydroxide in deionized water. Triton X-45 was mixed with cyclohexane as it is dissolvable in organic solvent. The solution of microemulsion was kept stirring for ten minutes and the size of the microemulsion was measured with zetasizer, nano-ZS. On the other hand, the TPOT was mixed in cyclohexane and was added dropwise to the microemulsion. The solution was stirred throughout the process for overnight. Ethanol (95%) was added into the solution in the ratio of 3:2 (Ti(OH)$_4$: ethanol) and stirred for another 30 minutes to damage the emulsion and solubilize the surfactant. The solution was dried at 60°C for 24 hours and followed by calcination at 550°C for 4 hours. Sizes of the dried fine powder of the synthesized TiO$_2$ were then examined.

**RESULT AND DISCUSSION**

The sizes of microemulsion were prepared by determining the $w_o$ value\cite{7}, which showed in figure 1. TiO$_2$ was synthesized with size of microemulsion range from 4 nm to 21 nm. The sizes of TiO$_2$ were effected by the
transferring rate of TPOT to microemulsion solutions due to TPOT was easy to hydrolyze and solidify. Furthermore, oxidation of TPOT also contributed to the enlargement of particle sizes. From TABLE 1, results showed that particle size of TiO$_2$ was directly influenced by microemulsion which prepared with different molar ratio. This was also reported by the same observation related to the effects of lower water contents on controlling sizes of particles.$^{[11]}$

Figure 2 shows particle size measurement. The intensity distribution for TiO$_2$ for three different sizes (A, B, and C) obtained a rather even dispersity. This can be observed through width of intensity distribution.

Two results are shown in figure 3. The conductivity of pH increased from low pH to high pH. This is because of the increase in hydroxyl ions in buffer has increased negative ions which contributes to increase the conductivity of pH buffer. Meanwhile, All sizes of TiO$_2$ indicated that the electrophoretic mobility increased from low pH buffer to higher pH range but reduced slightly as pH increased in alkaline range. Buffer pH 4 obtained the lowest electrophoretic mobility for three different sizes of TiO$_2$. This is due to the excessive hydrogen ions in buffer which neutralizing negative charges of TiO$_2$, thereby retarded the movement of particles. As hydrogen ions reduces, increasing the electrophoretic mobility. However, there was an increase in hydroxyl ions in buffer as pH range increase in alkaline region. The increase of negative ions in buffer caused the elevation in conductivity but retarded the migration rate of particles. This was due to the share of current of net negative charges on particles were overcome by surrounding ions. On the other hand, the electrophoretic mobility of three different sizes of TiO$_2$ in pH buffer did not show any significant difference.

The electrophoretic mobility of TiO$_2$ showed slight increased as temperatures increased. There was an obvious reduction in the electrophoretic mobility at 60°C for all sizes of TiO$_2$ as shown in figure 4. The increase in temperatures had provided a higher thermal energy to charged particles moving faster toward electrode. At higher temperatures, diffuse double layer was thickening and decreased net charges on surface of particles, thereby increased the electrophoretic mobility. The decrease in mobility at highest temperatures for this range showed TiO$_2$ moved randomly as internal energy of particles increased. This energy has overcome the attraction of forces to electrode, subsequently a drop in mobility of charged particles were recorded.
For the same range of temperatures, the smaller sizes of TiO$_2$ obtained a higher electrophoretic mobility. However, the smaller particle size of TiO$_2$ obtained lower electrophoretic mobility. This was due to smaller particles absorbing more thermal energy and move more random in high temperatures.

Different applied voltages had increased the electrophoretic mobility of charged particles and showed in figure 5. The increase in applied voltages has provided a greater electrostatic force on charged particles which enhance the mobility of charged particles. Meanwhile, the increase in particle sizes of TiO$_2$ showed a decrease in electrophoretic mobility. The smaller particle size of TiO$_2$ labeled A and B experienced minimal frictional forces acting on it during the applied voltages were supplied. On the other hand, the biggest particles labeled C barely showed any changes throughout the increment of applied voltages.

CONCLUSION

The electrophoretic mobility of TiO$_2$ was depended on pH, temperatures and applied voltages. The optimum result of electrophoretic mobility was obtained at pH 6. Different sizes of TiO$_2$ were less influenced by the change of pH. Besides, temperatures increased the electrophoretic mobility of particles. As particles absorbed excessive thermal energy, reducing the electrophoretic mobility and temperature at 60°C showed the drastic decreased. At last, applied voltages increased the electrostatic force on particles enhanced the electrophoretic mobility of charged particles. Sizes of TiO$_2$ were more influenced by different range of temperatures and applied voltages. The smaller particles recorded a higher electrophoretic mobility as the frictional forces on it were lesser.

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REFERENCES