Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 3893–3900

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Stability of titania nano-particles in different alcohols

M. Farrokhi-rad [a,1], M. Ghorbani [a,b,*]

[a] Department of Materials Science and Engineering, Sharif University of Technology, Tehran P.O. Box 11356-8639, Iran
[b] Institute For Nanoscience and Nanotechnology, Sharif University of Technology, Tehran, Iran

Received 3 December 2011; accepted 17 January 2012
Available online 26 January 2012

Abstract

The alcoholic suspensions of titania nano-particles were prepared using the methanol, ethanol, isopropanol and butanol as the solvents as well as triethanolamine (TEA) as an dispersant. The colloidal stability of suspensions, both in the absence as well as presence of TEA, was studied by measuring the zeta potential, sedimentation, pH and electrical conductivity of suspensions, dispersant adsorption and particles size distribution. Results showed that in the absence of TEA, the stability of the suspensions increases with the molecular size of alcohol (from methanol to butanol), while the zeta potential decreases. It was also observed that with the addition of TEA up to the optimum dosage (4 mL/L and 1.33 mL/L for isopropanolic and butanolic suspensions, respectively), the stability of isopropanolic and butanolic suspensions increases; however, its addition into the methanolic and ethanolic suspensions, even at very low concentrations in the order of 0.1 mL/L, results in the quick settling of the particles in the suspension. It was found that the mechanism of TEA action as a dispersant, in the isopropanolic and butanolic suspensions, is its protonation and then adsorption on the titania nano-particles, which yields an electrostatic and some steric stabilization mechanisms.

Keywords: A. Suspension; Titania nano-particles; Triethanolamine (TEA); Methanol; Ethanol; Butanol

1. Introduction

Due to their unique properties, titania nano-particles [1–4] and nano-structured coatings [5–7] have acquired large number of applications including photocatalysis, self cleaning, solar cells and so on [8,9]. The preparation of titania colloidal suspensions [10,11] or substrate-supported coatings [12,13] is required for its photocatalysis applications.

Electrophoretic deposition [14,15] and tape casting [16,17] processes which preferably use non-aqueous solvents [16–19] (often alcohols) for suspension preparation have been widely used to produce titania coatings. The degree of the dispersion of titania nano-particles in the suspension has a great influence on their photocatalytic efficiency in colloidal state [10] as well as in titania coatings produced from it [12]; so the preparation of well dispersed suspension of titania nano-particles is of great importance. Nano-particles have large surface area and high tendency to agglomeration, so their stabilization in the suspensions is very difficult [20]. Under the influence of short range Van der waals attractive forces, nano-particles may be flocculated in the suspension. According to the classical Derjaguin, Landau, Verwey and Overbeek (DLVO) theory [21,22], by generating the similar surface charge on the surfaces of particles, the repulsion force is developed between them (electrostatic stabilization mechanism). There is also another stabilization mechanism based on the adsorption of high molecular weight polymers on the particles which act as physical barrier between them (steric stabilization) [23]. Due to low dielectric constant of organic solvents, the surface charge on the particles in non-aqueous suspensions is usually very low; so the electrostatic repulsion force between particles suspended in them is not strong enough to yield the stable suspension; so that to enhance their stability, the efficient dispersants must be added at appropriate concentrations. Usually high molecular weight polymers [23–28] are added to non-aqueous suspensions to enhance their stability by steric stabilization mechanism; however this is with the risk of deteriorating the finale product properties; so in non-aqueous colloidal processing, the use of low molecular weight electrostatically stabilizer dispersants can be very useful. Triethanolamine (TEA) is an

---

* Corresponding author. Tel.: +98 21 66165219; fax: +98 21 66005717.
E-mail addresses: Morteza_farrokhi_rad@yahoo.com (M. Farrokhi-rad), ghorbani@sharif.edu (M. Ghorbani).

[1] Present address: Materials Engineering Department, Faculty of Engineering, Tarbiat Modares University, 1411713114, Tehran, Iran.

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2012.01.041

organic base with relatively low molecular weight which can be used as an additive to enhance the stability of ceramic colloidal suspensions [19,29–31].

In this study the stability of titania nano-particles in different alcohols (methanol, ethanol and butanol) as well as the effect of TEA additive on the suspensions stability were investigated.

2. Materials and methods

2.1. Materials

Titania nano-powder (Aldrich Corporation) with an average particles size of 5 nm was used as raw particles. Methanol (99.99%, Merck, Germany), ethanol (99.8%, Merck, Germany), isopropanol (99.9%, Merck, Germany) and butanol (99%, Merck, Germany) were used as the solvents. The properties of these alcohols are presented in Table 1 [32]. TEA (reagent grade, Merck, Germany) was also used as an additive to enhance suspension stability.

2.2. Suspension preparation

Suspensions were prepared by adding the different volumes of TEA into 50 mL of alcohols, stirring for 1 h, then adding 2 g of titania nano-powder to them followed by stirring again for 24 h and finally ultrasonification for 20 min (Sonopuls HD 2200, 30 kHz, Bandelin Co, Germany).

2.3. Suspensions characterization

The sedimentation test was used to determine the optimum concentrations of TEA in the suspensions. The prepared suspensions were purred into 10 mL graduated cylinders and were allowed to sediment during 30 days. The volume of the suspension region was recorded against the time. The electrical conductivity of the alcohols and corresponding suspensions, with different concentrations of TEA, was measured by conductivity meter (EDT Company, model: RE387TX, United Kingdom).

The zeta potential and the particles size distribution of titania nano-particles, were measured (Malvern instrument, Worcestershire, United Kingdom) in the suspensions with different TEA concentrations. Fourier Transform Infrared (FTIR) spectroscopy analysis was used to study the adsorption of TEA at titania nano-particles surfaces.

Table 1
Properties of the alcohols used in this study [32].

Alcohol	Density (g/cm^3)	Viscosity ($cP = 10^{-3}$ N.s.m^{-2})	Relative dielectric constant
Methanol	0.791	0.557	32.63
Ethanol	0.789	1.0885	24.55
Isopropanol	0.786	2.0439	19.92
Butanol	0.810	2.5875	17.51

3. Results and discussion

3.1. Stability of suspensions without TEA

The volume of suspension region after 30 days of sedimentation and the zeta potential of titania nano-particles in the suspensions without TEA additive, are listed in Table 2.

The results show the negative values for the zeta potential of titania nano-particles; imply that the titania nano-particles acquire negative surface charge in the pure alcohols.

For titania nano-particles, depending on pH, the following surface reactions can occur in the suspension [33]:

$$\equiv \mathrm{TiOH} + \mathrm{H}^+ \Leftrightarrow \equiv \mathrm{TiOH}_2^+ \tag{1}$$

$$\equiv \mathrm{TiOH} \Leftrightarrow \equiv \mathrm{TiO}^- + \mathrm{H}^+ \tag{2}$$

Titania is an amphoteric oxide; titania particles act as base at low pH and take H^+ from alcohol molecules (reaction (1)); While they act as acid at high pH and releases H^+ (reaction (2)) into the alcohol. Titania has the point of zero charge (PZC) of about 5.8 [34].

The pH values of the alcohols used in this study were higher than 5.8; thus according to reaction (2) titania nano-particles developed negative surface charge. The mechanism of titania nanoparticles charging in butanol (the mechanism is similar for all 4 alcohols) is schematically shown in Fig. 1.

Similar to the mechanism proposed by Damodaran and Moudgil [35], the reaction (2), probably, consists of a mechanism as follow: two alcohol molecules are adsorbed on the surface of titania nano-particles (Fig. 1(a)), ionize and form RO^- and ROH_2^+ (Fig. 1(b)), then RO^- captures proton from the surface of titania and is converted into ROH (Fig. 1(c)); followed by the ROH and ROH_2^+ desorption into the bulk of the suspension (Fig. 1(d)).

Small molecular size alcohols have larger dielectric constant (Table 1) as well as higher tendency to ionization on the surface of titania nano-particles (step b in Fig. 1) than large molecule ones [36]; so they form more easily the electrical double layer structure on the titania nano-particles surfaces; on the other hand with increasing the molecular size of the alcohol the adsorption of generated ROH_2^+ on the particles surface increases (due to weaker interaction between large molecules alcohol and ROH_2^+) which neutralize some amount of negative surface charge; so the developed negative surface charge and zeta potential are larger for small size molecule alcohols. Jimmy C. Yu et al. [36] also measured the zeta potential of titania nano-particles in different alcohols (methanol, ethanol,

Table 2
The results of sedimentation test after 30 days and the zeta potential of titania nano-particles in the alcohols without TEA additive.

Type of suspension	Suspension volume after 30 days (mL)	Zeta potential (mV)
Methanol	2	−15
Ethanol	2.7	−11
Isopropanol	4	−8
Butanol	6	−5

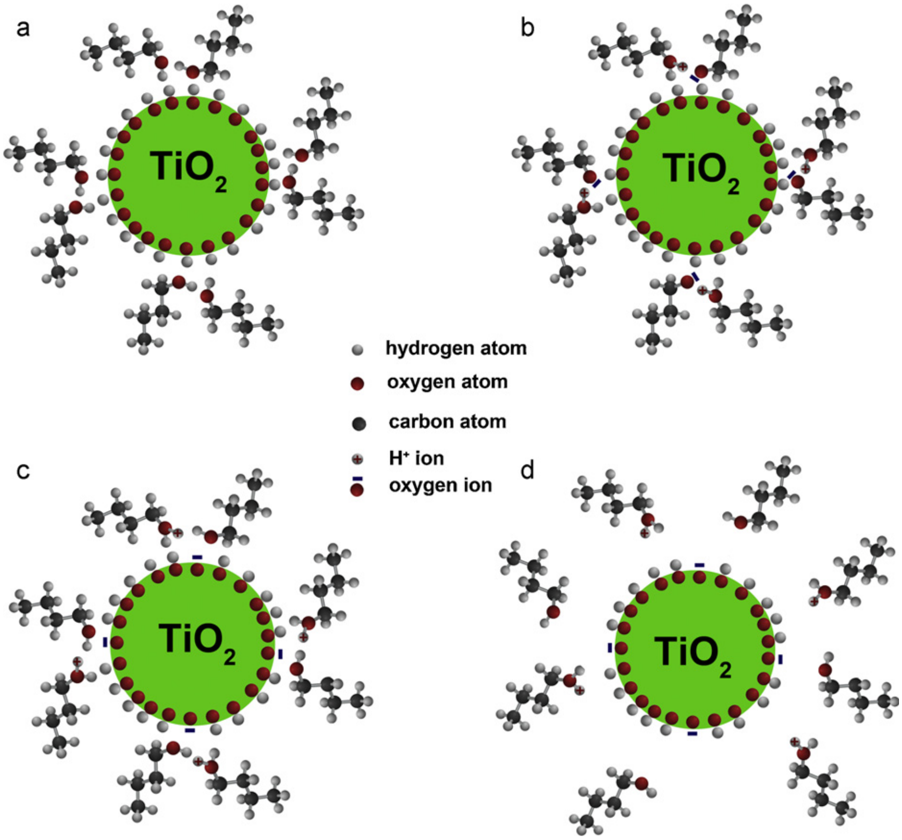

Fig. 1. Mechanism of titania nanoparticles charging in butanol.

propanol, iso-propanol, and butanol) and found that the zeta potential decreases with increasing the molecular size of the alcohols.

It can also be seen from the results of Table 2 that, with increasing the molecular size of the alcohol (from methanol to butanol) the suspensions stabilities increase while the absolute values of the zeta potential decrease. Xiao and Liu [29] prepared the suspensions of hydroxyapatite nano-particles in various alcohols (methanol, ethanol, n-propanol and n-butanol) and similarly observed that the stability of the suspensions increase with increase in the molecular size of the alcohols.

The zeta potential of particles is a criterion for the charge developed on their surface in a suspension; so the higher the zeta potentials, the higher the electrostatic repulsion force between the particles and so the suspension stability. While here, stability decreases with increasing in the zeta potential.

The sedimentation velocity of particles in a suspension is obtained by following equation:

$$v = \frac{d^2 \Delta\rho g}{18\eta} \tag{3}$$

This equation shows that the sedimentation velocity of particle in a suspension increases with particle size (d) (with power 2) and difference between the density of particle and solvent ($\Delta\rho$); while it decreases with the viscosity of solvent (η). In this equation (g) is the gravitational acceleration. According to Eq. (3), it can be concluded that the higher stability of the suspension prepared from the alcohol with larger molecular size (butanol) is due to the higher viscosity of its solvent (Table 1). This claim is only valid in the circumstances where the size of the agglomerates formed in the suspensions with different solvents would be nearly in the same range; since according to Eq. (3), the sedimentation velocity of particles is proportional to their size by second power. Particles in the suspension undergo randomized brownian motion, which arises from their collision with solvent molecules [37]. Brownian motion is very size dependant and becomes considerable for particles size smaller than 1 μm [38,39]. The diffusion sufficient of colloidal particles in a suspension can be obtained by fundamental Einstein's equation [40]:

$$D = \frac{kT}{3\pi\eta d} \tag{4}$$

In this equation k is Boltzmann's constant, T is absolute temperature, η is the viscosity of medium and d is the particle diameter. According to Eq. (4), colloidal particles have larger diffusion coefficient in the media with lower viscosity than those with higher one (the viscosity of alcohols are given in Table 1). Since the zeta potentials of titania nano-particles in these pure alcohos are relatively low (Table 2), the collision between particles due to Brownian motion is more probable; so the titania nano-particles can diffuse more rapidly and collide with each other more frequently in the suspensions with the order of: methanol, ethanol, isopropanol and butanol. Therefore the agglomerates growth rate in the suspension increases in the mentioned order; so while the absolute value of the zeta

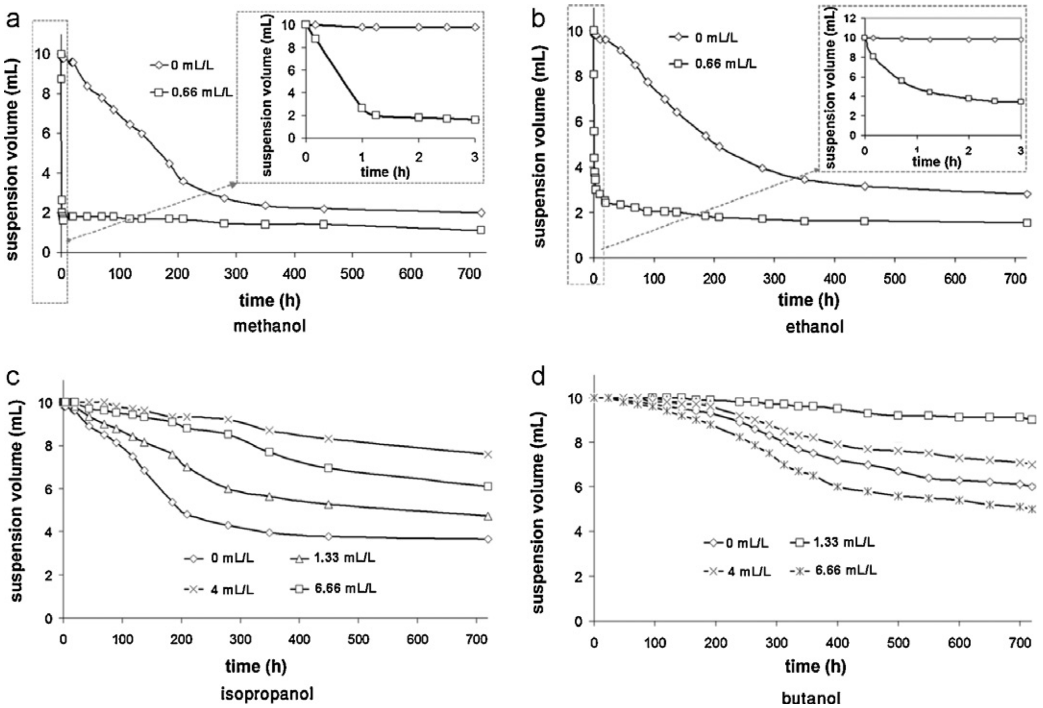

Fig. 2. Suspension volume against time for (a) methanolic, (b) ethanolic, (c) isopropanolic and (d) butanolic suspensions.

potential decreases in the order: methanol, ethanol, isopropanol and butanol, the suspensions stability increases according to this order (Table 2).

3.2. Effect of TEA addition on the stability of suspensions

In this section the effect of TEA additive on the stability of the alcoholic suspensions has been discussed. The results obtained from sedimentation test at various concentrations of TEA, are shown in Fig. 2. As can be seen, the addition of TEA into the suspension prepared from methanol and ethanol, results in the quick settling of particles, but its addition at optimum dosages of 4 mL/L and 1.33 mL/L into the suspensions prepared from isopropanol and butanol, respectively, results in higher stability.

The variation of electrical conductivity of the alcohols and the corresponding suspensions with TEA concentration are shown in Fig. 3. As can be seen, in all cases, except the butanol, the electrical conductivities of the alcohols and the corresponding suspensions increase continuously with the TEA addition.

Due to the lone pair electron on the nitrogen atom, TEA has basic characteristics and can take proton from alcohol molecule according to following reactions:

$$\mathrm{ROH} + \mathrm{ROH} \Leftrightarrow \mathrm{RO}^- + \mathrm{ROH}_2^+ \tag{5}$$

$$\mathrm{ROH}_2^+ + \mathrm{N(C_2H_4OH)_3} \Leftrightarrow \mathrm{ROH} + \mathrm{NH^+(C_2H_4OH)_3} \tag{6}$$

$$\mathrm{ROH} + \mathrm{N(C_2H_4OH)_3} \Leftrightarrow \mathrm{RO}^- + \mathrm{NH^+(C_2H_4OH)_3} \tag{7}$$

Reaction (5) is identified as autoprotolysis reaction, and its equilibrium constants for methanol, ethanol, isopropanol and butanol are $10^{-17.2}$, $10^{-18.88}$, $10^{-20.8}$ and $10^{-21.56}$, respectively [41]. This means that the larger the alcohol molecular size, the lower its tendency to autoprotolysis reaction. In reaction (6), TEA takes proton from ROH_2^+ ions generated through the autoprotolysis reaction of alcohols molecules. Reaction (7) is the net reaction and explains the alcohols electrical conductivity increasing with TEA addition into them.

Reaction (7) proceeds in the cases of ethanol and specially methanol to higher extents than isopropanol and butanol, which is due to their relatively larger equilibrium constants for the autoprotolysis reactions; therefore the conductivity increasing as a result of TEA addition is also larger for them. The addition of titania nano-powder into pure alcohols (without TEA), results in conductivity increasing. According to reaction (2), the conductivity increasing is because of the H^+ releasing from the surface of titania nano-particles into them. In the suspension prepared from butanol, with the addition of TEA up to 1.33 mL/L, the electrical conductivity decreases and reach a minimum value, and then increases at higher concentrations of TEA. The mechanism of TEA action as a dispersant for butanolic suspensions (also for the suspension prepared from isopropanol) is schematically shown in Fig. 4. As mentioned previously, the tendency of butanol to the autoprotolysis reaction is much lower than methanol and ethanol, thus with the addition of TEA to butanolic suspension, TEA preferably takes proton from ROH_2^+ ions generated through catching the proton from titania nano-particles surfaces (reaction (2), Fig. 4(b) and (c)) and generates $\mathrm{NH^+(C_2H_4OH)_3}$ species (Fig. 4(c)). The affinity of these species towards titania nano-particles surface is higher than theirs towards butanol molecules, so they are adsorbed (Fig. 4(d)) on the surface of previously negatively charged titania nano-particles and convert their

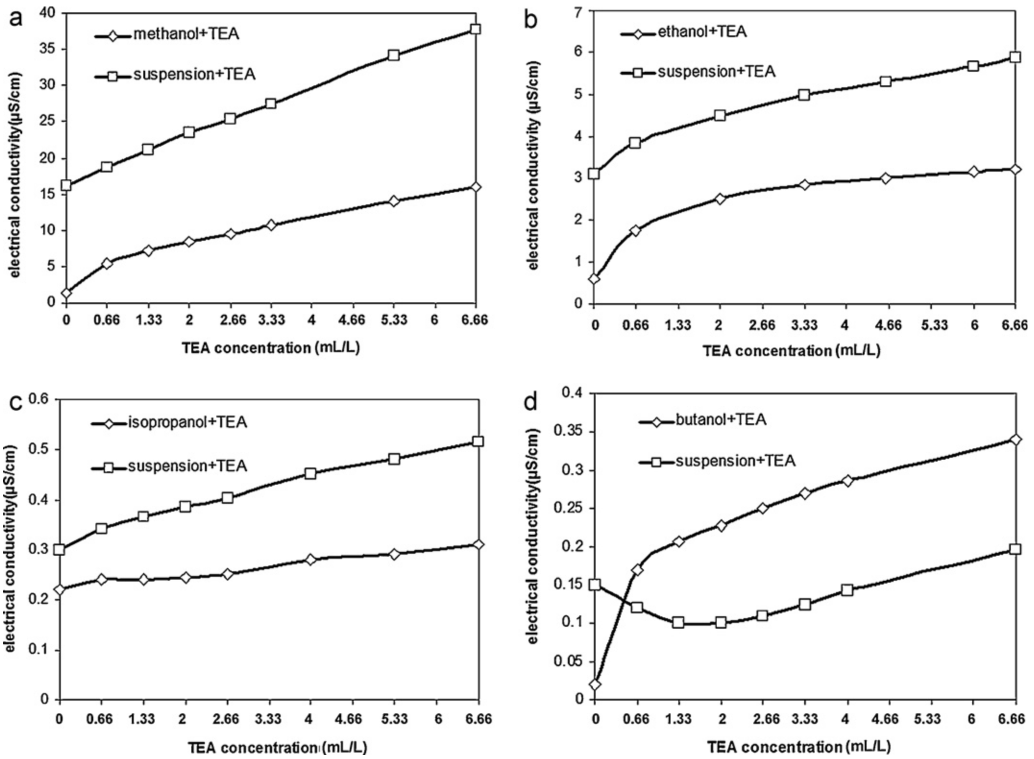

Fig. 3. The electrical conductivity of alcohols and corresponding suspensions against TEA concentration (a) methanol, (b) ethanol, (c) isopropanol and (d) butanol.

charge into positive (as proved by FTIR analysis, Fig. 5). Since the mobility of free ions in the suspension (protonated TEA) is higher than charged particles (particles with adsorbed protonated TEA), the electrical conductivity decreases until 1.33 mL/L TEA. It is more probable that the surfaces of titania nanoparticles are saturated from TEA at the concentration of 1.33 mL/L; so that the electrical conductivity of butanolic suspension initiates to increase at this concentrations.

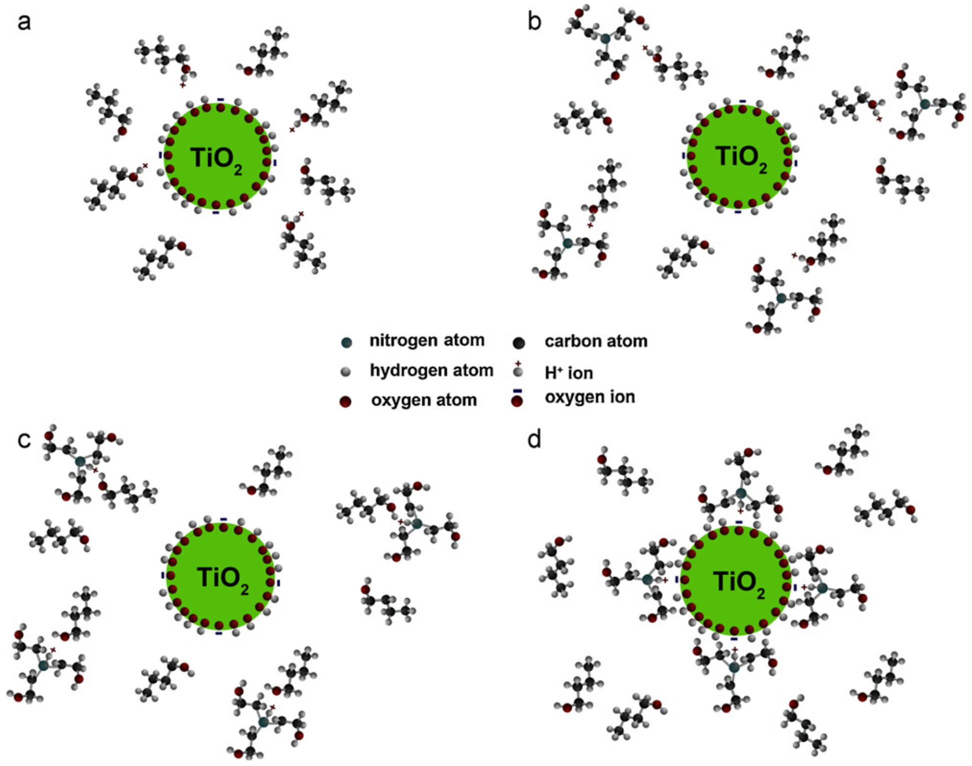

Fig. 4. Schematic presentation of TEA action as a dispersant in butanolic suspension (a) negatively charged titania particles in pure butanol (b) adding TEA to the suspension (c) proton transfer from ROH_2^+ to TEA and (d) protonated TEA adsorption on the titania nano-particle.

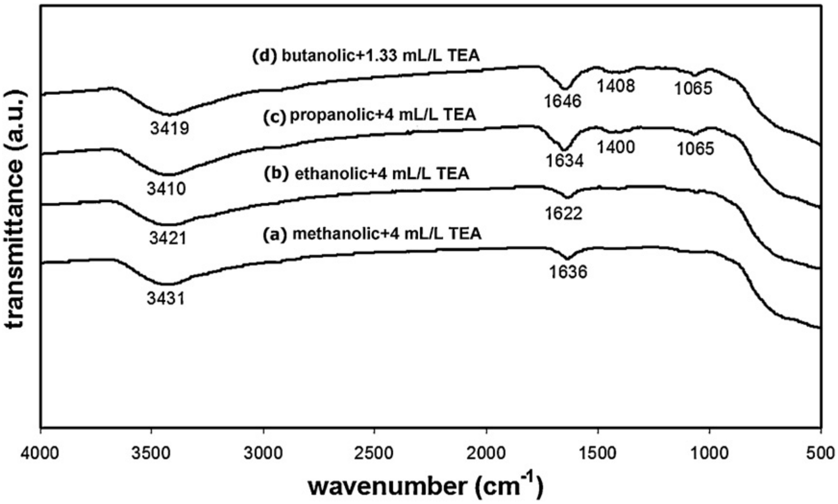

Fig. 5. The results of FTIR analysis obtained for powder removed and dried from suspensions with TEA (a) methanolic, (b) ethanolic (c) isopropanolic and (d) butanolic.

In contrast to butanolic suspension, the electrical conductivities of the suspensions prepared from methanol, ethanol and isopropanol continuously increase with the addition of TEA; because in these alcohols, TEA protonation is relatively easy and also the affinity of protonated TEA to adsorption on the surface of titania nano-particles is not as high as in butanol. In fact, with increasing the molecular size of the alcohol, the solvation interaction between the protonated TEA and the alcohol molecules becomes weaker, and therefore affinity of these species towards titania nano-particles surfaces increases. Thus, the adsorption of protonated TEA on the surfaces of titania nano-particles in suspension increases in the order of methanol, ethanol, isopropanol and butanol.

The results for FTIR analysis are shown in Fig. 5. As can be seen, the spectra obtained for titania nano-powder removed from methanolic and ethanolic suspensions with 4 mL/L TEA dose not show any peak related to TEA. Two peaks at 1615 and 3413 cm^{-1} are assigned to H–O–H bending vibration and O–H stretching vibration, respectively [42,43]; indicate that titania nano-powder samples contain physically adsorbed water. While in the spectra of titania nano-powders dried from the suspensions prepared from isopropanol and butanol containing 4 and 1.33 mL/L TEA (optimum concentrations), respectively, in addition to these two peaks, two other peaks are also appeared at about 1070 and 1400 cm^{-1} which are belong to C–N and O–H stretching vibrations, respectively [44], prove that TEA efficiently adsorbs on the surface of titania nano-particles in these suspensions.

The zeta potential of titania nano-particles in the suspensions with various TEA concentrations, are shown in Fig. 6. As can be seen, the zeta potential of particles increases with TEA addition. With increasing the TEA concentration in the suspensions, the concentration of protonated TEA adsorbed on the nano-particles surfaces increases, causes in the increase in the zeta potential values with TEA concentration. The excessive addition of TEA results in some drop in the zeta potential, which can be due to the enhancement in the ionic strength of the suspension [45].

It is very interesting to note that in the butanolic suspension, the concentration of TEA (1.33 mL/L) at which the suspension conductivity is minimum (Fig. 3(d)), is equivalent to the one at which the maximum value of the zeta potential (Fig. 6) and the highest stability (Fig. 2(d)) occurs, which can be a good reason for the claim that nano-particles surfaces are saturated from TEA at this concentration.

In the case of suspensions prepared from methanol and ethanol, TEA protonation occurs more easily as well as its adsorption efficiency on the particles is low; so the addition of TEA even at low concentrations results in the reduction in the absolute value of the zeta potential as well as strong enhancement in the ionic strength of the suspension and so intensive decrease in its stability.

Although the majority of TEA action as a dispersant in the suspensions prepared from isopropanol and butanol is based on electrostatic stabilization mechanism, but its aliphatic chains may also contribute to some steric stabilization mechanism

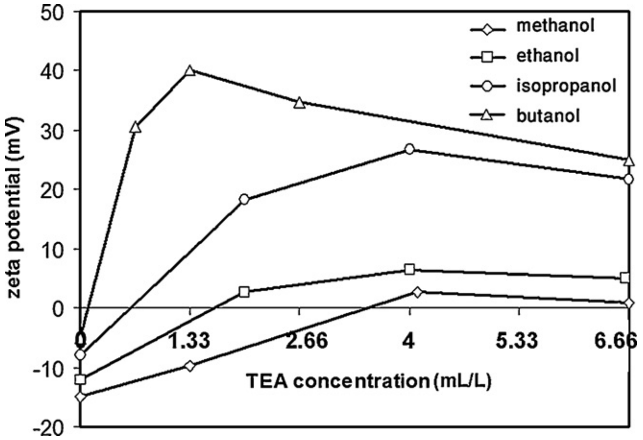

Fig. 6. The zeta potential of titania particles against TEA concentration in different suspensions.

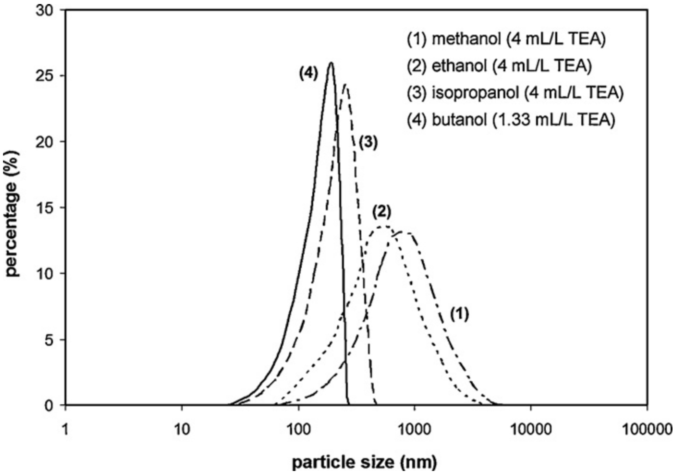

Fig. 7. The particles size distribution in the suspensions prepared from different alcohols containing the optimum concentration of TEA for butanolic (1.33 mL/L) and isopropanolic (4 mL/L) suspensions and 4 mL/L for methanolic and ethanolic suspensions.

(Fig. 4(d)). Ping Xiao et al. [31] also used the TEA additive to adjust the operational pH of the yttria stabilized zirconia (YSZ) suspension in acetylacetone for electrophoretic deposition; similarly, they found that the TEA can increase the suspension stability by capturing proton from acetylacetone followed by adsorption on the YSZ particles which increase their positive surface charge.

Fig. 7 shows the particles size distribution of suspensions prepared from different alcohols and containing the optimum concentration of TEA after 30 days of preparation. As can be seen, suspensions prepared from butanol and isopropanol have smaller and narrower particles size distribution (average particles size of about 190 nm and 270 nm, respectively for butanol and isopropanol) than those prepared from methanol and ethanol (average particles size of about 640 nm and 950 nm respectively for ethanol and methanol). As mentioned previously, the addition of TEA to methanolic and ethanolic suspensions even at low concentrations, results in the intensive particles agglomeration.

4. Conclusion

The alcoholic suspensions of titania nanoparticles were prepared in the presence and absence of TEA. It was observed that in spite of decreasing the zeta potential, the stability of titania nanoparticles increases with increasing alcohol molecular size (from methanol to butanol). It was also observed that TEA is an effective dispersant to increase the stability of titania nano-particles in isopropanol and butanol; however it intensively decreases the stability of methanolic and ethanolic suspensions. The mechanism of TEA action as a dispersant in the ethanolic and butanolic suspensions consists of protonation and then adsorption on the titania nano-particles surfaces, which generate high positive surface charge and so high suspension stability by electrostatic stabilization mechanism. Although the aliphatic chains of TEA may also contribute to some steric stabilization mechanism.

References

[1] A. Hagfeldt, M. Gratzel, Light-induced redox reactions in nanocrystalline systems, Chem. Rev. 95 (1995) 49–68.
[2] S. Sakthivel, H. Kisch, Daylight photocatalysis by carbon-modified titanium dioxide, Angew. Chem. Int. Ed. 42 (2003) 4908–4911.
[3] L. Reijnders, Hazard reduction for the application of titania nanoparticles in environmental technology, J. Hazard. Mater. 152 (2008) 440–445.
[4] J. Robertson, T.J. Bandosz, Photooxidation of dibenzothiophene on TiO_2/hectorite thin films layered catalyst, J. Colloid Interface Sci. 299 (2006) 125–135.
[5] U. Diebold, The surface science of titanium dioxide, Surf. Sci. Rep. 48 (2003) 53–229.
[6] L. Gao, Q. Li, Z. Song, J. Wang, Preparation of nano-scale titania thick film and its oxygen sensitivity, Sensor. Actuator. B. Chem. 71 (2000) 179.
[7] A. Fujishima, X. Zhang, D.A. Tryk, TiO_2 photocatalysis and related surface phenomena, Surf. Sci. Rep. 63 (2008) 515–582.
[8] K. Nagaveni, G. Sivalingam, M.S. Hegde, G. Madras, Solar photocatalytic degradation of dyes: high activity of combustion synthesized nano TiO_2, Appl. Catal. B: Environ. 48 (2004) 83–93.
[9] H. Bieber, P. Gilliot, M. Gallart, N. Keller, V. Keller, S. Begin-Colin, C. Pighini, N. Millot, Temperature dependent photoluminescence of photocatalytically active titania nanopowders, Catal. Today 122 (2007) 101.
[10] J. Xu, L. Li, Y. Yan, H. Wang, X. Wang, X. Fu, G. Li, Synthesis and photoluminescence of well-dispersible anatase TiO_2 nanoparticles, J. Colloid Interface Sci. 318 (2008) 29–34.
[11] A.R. Caamal-Parra, R.A. Medina-Esquivel, T. Lopez, J.J. Alvarado-Gil, P. Quintana, Optical study of the photoactivation time of a sol–gel titania suspension in ethanol, J. Non-Cryst. Solids 353 (2007) 971–973.
[12] A.G.G. Toh, R. Caib, D.L. Butler, The influence of surface topography on the photocatalytic activity of electrophoretically deposited titanium dioxide thin films, Wear 266 (2009) 585–588.
[13] J.H. Yum, S.S. Kim, D.Y. Kim, Y.E. Sung, Electrophoretically deposited TiO_2 photo-electrodes for use in flexible dye-sensitized solar cells, J. Photochem. Photobiol. A: Chem. 173 (2005) 1–6.
[14] L. Besra, M. Liu, A review on fundamentals and applications of electrophoretic deposition (EPD), Prog. Mater. Sci. 52 (2007) 1–61.
[15] N. Ogata, J. Van Tassel, C.A. Randall, Electrode formation by electrophoretic deposition of nanopowders, Mater. Lett. 49 (2001) 7–14.
[16] K.H. Zuo, D.L. Jiang, J.x. Zhang, Q.L. Lin, Forming nanometer TiO_2 sheets by nonaqueous tape casting, Ceram. Int. 33 (2007) 477–481.
[17] Zh. Jingxian, J. Dongliang, L. Weisensel, P. Greil, Deflocculants for tape casting of TiO_2 slurries, J. Eur. Ceram. Soc. 24 (2004) 2259–2265.
[18] M.F. De Riccardis, D. Carbone, A. Rizzo, A novel method for preparing and characterizing alcoholic EPD suspensions, J. Colloid Interface Sci. 307 (2007) 109–115.
[19] M. Farrokhi-Rad, M. Ghorbani, Electrophoretic deposition of titania nanoparticles in different alcohols: kinetics of deposition, J. Am. Ceram. Soc. 94 (2011) 2354–2361.
[20] B.H. Kear, J. Colaizzi, W.E. Mayo, S.C. Liao, On the processing of nanocrystalline and nanocomposite ceramics, Scr. Mater. 44 (2001) 2065–2068.
[21] B.V. Derjaguin, L. Landau, The theory of stability of highly charged lyophobic sols and coalescence of highly charged particles in electrolyte solutions, Acta Physicochim. USSR 14 (1941) 633–652.
[22] E.J.W. Verwey, J.T.G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam, New York, 1948.
[23] T. Sata, R. Ruch, Stabilization of Colloidal Dispersion by Polymer Adsorption, Dekker, New York, 1984.
[24] R.E. Johnson, W.H. Morrison, Ceramic powder dispersion in non-aqueous systems, in: G.L. Messing, K.S. Mazdiyasni, J.W. McCauley, R.A. Haber (Eds.), Advances in Ceramics, Volume 21: Ceramic Powder Science, American Ceramic Society, Columbus, 1987 , p. 323.

[25] G.H. Hsiue, L.W. Chu, I.N. Lin, Optimized phosphate ester structure for the dispersion of nano-sized barium titanate in proper non-aqueous media, Colloids Surf. A: Physicochem. Eng. Aspects 294 (2007) 212–220.

[26] S. Bhattacharjee, M.K. Paria, H.S. Maiti, Polyvinyl butyral as a dispersant for barium titanate in a non-aqueous suspension, J. Mater. Sci. 28 (1993) 6490–6495.

[27] H.S. Al-Lami, N.C. Billingham, P.D. Calvert, Controlled structure methacrylic copolymers as dispersants for ceramics processing, Chem. Mater. 4 (1992) 1200–1207.

[28] T. Kakui, T. Miyauchi, H. Kamiya, Analysis of the action mechanism of polymer dispersant on dense ethanol alumina suspension using colloidal probe AFM, J. Eur. Ceram. Soc. 25 (2005) 655–661.

[29] X.F. Xiao, R.F. Liu, Effect of suspension stability on electrophoretic deposition of hydroxyapatite coatings, Mater. Lett. 60 (2006) 2627.

[30] Sh. H. Zhang, B. Xie, F.Y. Li, Dispersion and electrophoretic deposition of titania particles, Key Eng. Mater. 336 (2007) 1953–1955.

[31] H. Xu, I.P. Shapiro, P. Xiao, The influence of pH on particle packing in YSZ coatings electrophoretically deposited from a non-aqueous suspension, J. Eur. Ceram. Soc. 30 (2010) 1105.

[32] H. Negishi, H. Yanagishita, H. Yokokawa, Electrophoretic deposition of solid oxide fuel cell material powders, in: Proceedings of the electrochemical society on electrophoretic deposition: fundamentals and applications, vol. 2002-21, Pennington, USA, (2002), p. 214.

[33] V.S. Lusvardi, M.A. Barteau, W.S. Dolinger, W.E. Farneth, Influence of surface hydroxyls on the adsorption and reaction of ethanol on polycrystalline titania, J. Phys. Chem. 100 (1996) 18183–18191.

[34] S.G.J. Heijman, H.N. Stein, Electrostatic and sterical stabilization of TiO_2 dispersions, Langmuir 11 (1995) 422–427.

[35] R. Damodaran, B.M. Moudgil, Electrophoretic deposition of calcium phosphates from non-aqueous media, Colloids Surf. A: Physicochem. Eng. Aspects. 80 (1993) 191–195.

[36] J.C. Yu, Z.T. Jiang, H.Y. Liu, J. Yu, Influence of solvation interactions on the zeta potential of titania powders, J. Colloid Interface Sci. 262 (2003) 97–100.

[37] Robert J. Hunter, Introduction to Modern Colloidal Science, Oxford University Press, New York, 1993.

[38] W.B. Russel, Review of the role of colloidal forces in the rheology of suspensions, J. Rheol. 24 (1980) 287.

[39] H.A. Barnes, J.F. Hutton, K. Walters, An Introduction to Rheology, Elsevier, Amsterdam, 1989.

[40] S. Chandrasekhar, Stochastic problems in physics and astronomy, Rev. Mod. Phys. 15 (1943) 1–89.

[41] Ch. Reichardt, Solvent and Solvent Effects in Organic Chemistry, 3rd edition, Wiley-VCH, Weinheim, 2003.

[42] J.B. Paul, R.A. Provencal, C. Chapo, K. Roth, R. Casaes, R.J. Sakally, Infrared cavity ringdown spectroscopy of the water cluster bending vibrations, J. Phys. Chem. A 103 (1999) 2972–2974.

[43] Y. Shen, P. Wu, Two-dimensional ATR–FTIR spectroscopic investigation on water diffusion in polypropylene film: water bending vibration, J. Phys. Chem. A 107 (2003) 4224–4226.

[44] D.L. Pavia, G.M. Lampman, G.S. Kriz, Introduction to Spectroscopy, Thomson Learning Inc., New York, USA, 2001.

[45] B.P. Singh, S. Bhattacharjee, L. Besra, Factorial design of experiments on the effect of surface charges on stability of aqueous colloidal ceramic suspension, Colloids Surf. A.: Physicochem. Eng. Aspects 204 (2002) 175–181.