J. Phys. Chem. A **2007,** *111,* 8139−8146

Effect of pH on the Viscosity of Titanium Dioxide Aqueous Dispersions with Carboxylic Acids

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Received: February 19, 2007; In Final Form: June 19, 2007

Dispersions of titanium dioxide nanoparticles with terephthalic acid, isophthalic acid, salicylic acid, benzoic acid, and pyridine-2,5-dicarboxylic acid were prepared by aqueous grinding. The pH of the dispersions was adjusted by adding either HCl or NaOH, and the viscosity of the dispersions was measured. It was found that the viscosity of the system depends strongly on pH. The qualitative interpretation of the results based on the DLVO theory is presented. The evidence of the effect of bridging interactions on the viscosity of titanium dioxide−dicarboxylic acid dispersions is discussed.

Introduction

Titanium dioxide (TiO_2) is among the fifty most used chemicals in the world. Around three billion pounds of TiO_2 are produced annually.[1] TiO_2 dispersions are used in preparing a variety of applications ranging from pigments to photocatalysts and solar energy devices. The ability to control the rheological properties of TiO_2 dispersions using minor amounts of additives, such as to fine-tune their viscosity, is desirable, allowing their properties to be tailored to a specific application.[2,3] This ability to tailor properties can be beneficial from a green chemistry perspective. Understanding the structure−activity relationship between additives and dispersion properties (such as viscosity) can allow for redesign of processes to use less energy and fewer materials and therefore decrease waste and emissions.

The viscosity of a dispersion depends largely on interparticle interactions. These interactions can be divided into two broad groups. Van der Waals attraction and electric double layer repulsion belong to the first group: being present in most of the dispersion systems, they are well understood and described by DLVO theory.[4,5] The interactions governed by the specific chemistry of the particles and molecules of which the dispersion consists belong to the second group. These interactions are noncovalent, such as hydration forces that can be either attractive or repulsive, or covalent, resulting from chemisorption of solution species on the particles. These specific interactions are less predictable and are responsible for the endless variability in dispersions properties.

It was long established that carboxylic acids readily adsorb on TiO_2 surfaces under suitable conditions.[6,7] Recently, this phenomenon was harnessed in the design of dye-sensitized solar cells, where the sensitizing dye molecules are provided with multiple carboxylic acid functionalities to ensure dye chemisorption on TiO_2.[8,9] More specifically, transitional metal−polypyridyl dyes are being anchored onto TiO_2 surfaces via carboxylic acid functionalized pyridine ligands. A number of studies on the structure of pyridine adsorption and binding onto TiO_2 were published recently.[10−18]

It was previously demonstrated that adsorption of carboxylic acids on TiO_2 occurs more readily for stronger acids such as salicylic acid ($pK_a = 3$) than for weaker acids such as benzoic acid ($pK_a = 4.2$).[10,19] To explain this, one needs to consider the surface charge of TiO_2 particles as well as the state of the acid molecules. The surface of TiO_2 is known to be amphotheric.[20,21] At low pH a significant number of surface sites are protonated and the surface is positively charged. As the pH increases the surface charge decreases and reaches zero at $pH_{zpc} \sim 4-6$. If the pH continues to increase, the surface acquires a negative charge. One can expect maximum adsorption at the pH levels when the TiO_2 surface has a positive charge and the majority of acid molecules are deprotonated and carry a negative charge. Therefore, one can expect the most efficient adsorption for acids whose pK_a is lower than the pH_{zpc} of TiO_2. One also has to take into account that in the absence of additives the TiO_2 surface in aqueous dispersions is partially protonated and the pH is lower than the pH_{zpc}. Therefore if the pH of the titanium dioxide−carboxylic acid−water system is not adjusted, the pK_a of the acid should be lower than the natural pH of the TiO_2 dispersion.

Information about the structure of TiO_2−carboxylic acid complex can be obtained from spectroscopic studies. Three major bonding schemes or coordination modes of metal carboxylate complexes, namely unidentate, bidentate chelating, and bidentate bridging,[22] are presented in Figure 1. Infrared spectroscopy can be used to distinguish between the three modes. The characteristic IR bands of free carboxylic acids are C=O stretching at about 1700 cm^{-1} and C−O stretching coupled with O−H deformation at about 1300 cm^{-1}. Deprotonation of the acid results in disappearance of these bands and appearance of two new bands at about 1600 and 1400 cm^{-1} corresponding to the asymmetrical and symmetrical vibrations of COO^- group, respectively.[23] In unidentate metal carboxylates the difference between the frequencies of asymmetric and symmetric COO^- group vibrations $\Delta\nu = \nu_{asym} - \nu_{sym}$ is typically higher than that of corresponding ionic species. It should be noted here that $\Delta\nu$ can be lowered if the carbonyl group is hydrogen bonded.[22] Bidentate complexes typically exhibit lower $\Delta\nu$ than unidentate complexes. For bidentate bridging complexes $\Delta\nu$ is close to

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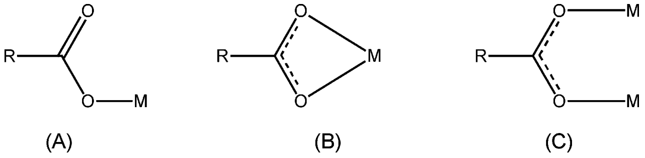

Figure 1. Coordination modes of metal carboxylate complexes: (A) unidentate; (B) bidentate chelating; (C) bidentate bridging.

those of ionic carboxylates, and for bidentate chelates $\Delta\nu$ is even lower.[7,13]

The adsorption of benzoic acid on TiO_2 has been studied extensively.[7,13,19] The COO^- group vibrations of benzoic acid adsorbed on a TiO_2 surface were observed at 1513 and 1404 cm^{-1} ($\Delta\nu = 109$ cm^{-1}), and the corresponding vibrations of the COO^- group in a free benzoate anion were observed at 1542 and 1388 cm^{-1} ($\Delta\nu = 154$ cm^{-1}). Because the $\Delta\nu$ of adsorbed benzoic acid was significantly lower than that of free benzoate anion it was concluded that benzoic acid is most likely adsorbed as a bidentate chelate, although the lack of resolution for the peak corresponding to the asymmetric vibration of COO^- group of adsorbed benzoic acid did not allow for the exclusion of the possibility of other coordinating modes as well.[7] Similar observations, i.e., $\Delta\nu = 109$ cm^{-1} for benzoic acid adsorbed on TiO_2 and $\Delta\nu = 156$ cm^{-1} for free benzoate have been reported.[19] In another study[13] the bands at 1535 and 1505 cm^{-1} in the IR spectrum of benzoic acid adsorbed on TiO_2 surface were assigned to asymmetric vibrations of COO^- group and the bands at 1418 and 1405 cm^{-1} to symmetric vibrations of COO^- group. Splitting of the bands was attributed to the existence of two different coordination sites. The largest observed separation $\Delta\nu = 130$ cm^{-1} for the adsorbed benzoic acid was lower than that of the benzoate anion ($\Delta\nu = 1559$ $cm^{-1} - 1378$ $cm^{-1} = 181$ cm^{-1}), which led to the conclusion that benzoic acid adsorbs on TiO_2 as a bidentate complex, either chelating or bridging. The results of the above studies are pointing at the bidentate chelate binding mode, as shown in Figure 2A, as being most likely, but by no means the only possible coordination mode of benzoic acid on the TiO_2 surface. This is in agreement with the studies that demonstrate the existence of different adsorption sites on TiO_2 surfaces.[6,24]

Although benzoic acid adsorbed on TiO_2 can be used as a model for more complex systems such as the transition metal polypyridyl dyes used in construction of the dye-sensitized solar cells,[13] it is important to note that some substituted aromatic acids were demonstrated to adsorb on TiO_2 in the coordination modes different from that of benzoic acid. When a salicylic acid molecule adsorbs on the TiO_2 surface, it was proposed that the added functionality participates in the coordination of the titanium atom, as presented in Figure 2B.[7,19] This structure was deduced from the infrared spectra of the adsorbed salicylic acid, which on one hand does not contain the phenolic C−O−H bending band, indicating deprotonation of the hydroxyl group, and on the other hand exhibits $\Delta\nu = 168$ cm^{-1} lower than that of salicylate ion ($\Delta\nu = 233$ cm^{-1}), which points to the unlikelihood of an ester-like linkage such as presented in the Figure 1A.

Similar ring-shaped surface complexes were proposed for adsorption of cationic (or rather zwitterionic) nicotinic[10] and anthranilic[7] acids on TiO_2 and are shown in the Figure 2C,D, respectively. In both cases it was suggested that the nitrogen atom can interact with a surface site on the TiO_2 surface. In the former case the formation of hydrogen bond between the protonated pyridinic nitrogen and the surface hydroxyl group was suggested,[10] whereas in the latter case the formation of a weak N−Ti bond was proposed.[7] Adsorption of 4-(dimethylamino)benzoic acid on TiO_2 was observed to occur by two different adsorption schemes.[25] Although the majority of the adsorbed molecules were coordinated in the bidentate bridging mode, the rest of the adsorbate molecules (protonated) formed hydrogen bonds between the carbonyl and surface hydroxyl groups.

In the studies dedicated to the adsorption modes of larger carboxylic acid substituted pyridines the results vary greatly with the system. Bignozzi and co-workers studied adsorption of $[Ru(2,2'\text{-bipyridine})_2(4,4'\text{-dicarboxy-}2,2'\text{-bipyridine})](PF_6)_2$, *cis*-$[4,4'\text{-dicarboxy-}2,2'\text{-bipyridine})]_2Ru(X)_2$, and *cis*-$[5,5'\text{-dicarboxy-}2,2'\text{-bipyridine})]_2Ru(X)_2$.[14,15] In both studies, though ester-like linkages (Figure 1A) between the adsorbates and the surface were observed, additional coordination modes were observed as well, namely either H-bonding[14] or bidentate.[15] Murakoshi et al. studied adsorption of one of the dyes used in construction of Graetzel solar cells, namely *cis*-bis(thiocyanato)-*N*,*N'*-bis-(2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium(II), on TiO_2 from an ethanol solution and observed both ester-like and bidentate chelate coordination modes.[18] Reflux conditions were reported to be especially beneficial for ester-like bond formation. Duffy et al. studied adsorption of the same dye on TiO_2 from an aqueous solution and found no evidence of ester-like linkages. The only coordination mode observed was bidentate bridging (Figure 1C).[17] Finnie et al. reported the results of their IR and Raman studies of the same dye adsorbed on TiO_2, which are consistent with either bidentate chelate or bridging coordination modes.[13] Vapor deposition of bi-isonicotinic acid (2,2′-bipyridine-4,4′-dicarboxylic acid) on TiO_2 was studied by X-ray photoelectron spectroscopy and by near edge X-ray adsorption fine structure.[12] The results revealed that the oxygen atoms in the adsorbates are equivalent, which is inconsistent with ester-like link formation. The bidentate bridging coordination mode was found to be consistent with the observations. Weisz et al. studied adsorption of nicotinic acid on TiO_2.[10] The proposed surface complex where the carboxylic acid group is coordinated to the Ti atom via an ester-like bond while protonated pyridinic nitrogen forms a hydrogen bond with a surface hydroxyl is shown in Figure 2C. In a recent study,[16] pyridine-3,4-dicarboxylic acid used in construction of a dye-sensitized heterojunction was proposed to be anchored to TiO_2 via both carboxylate groups, each in a bidentate chelate coordination mode. However, quantum chemical computations point at the unidentate, ester-like bond as energetically preferable for pyridine-4-carboxylic acid adsorption on the TiO_2 surface.[11]

The viscosity of the titanium dioxide−carboxylic acids aqueous dispersion is governed by the interparticle forces. The dispersion viscosity increases as the attraction between the particles increases, dominating over the electric double layer repulsion. The adsorption of molecules on the TiO_2 surface affects the van der Waals interactions between the particles, and if the molecules are charged, the electric double layer repulsion is affected as well. Moreover, when the adsorbed molecules are bifunctional, such as dicarboxylic acids, they may adsorb simultaneously on two TiO_2 particles, serving as bridges. This makes the interaction between the particles especially strong and induces flocculation accompanied by the abrupt increase in viscosity. The importance of such interactions was demonstrated in the previous work where the effect of aromatic dicarboxylic acid structure on the viscosity of titanium dioxide dispersions was investigated.[26] Although the acidities of the three dicarboxylic acids are about the same (phthalic acid $pK_{a1} = 3.0$, $pK_{a2} = 5.4$; isophthalic acid $pK_{a1} = 3.6$, $pK_{a2} = 4.6$;

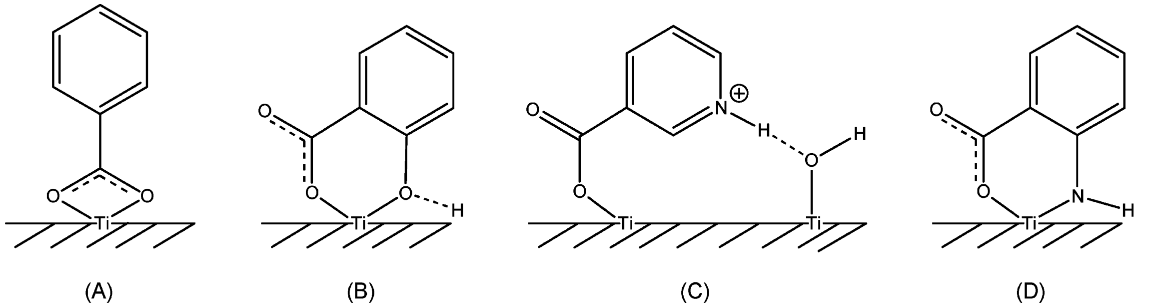

Figure 2. Adsorption of aromatic monocarboxylic acids on a TiO_2 surface: (A) benzoic acid (adapted from Tunesi et al.[7]); (B) salicylic acid (adapted from Tunesi et al.[7]); (C) nicotinic acid (adapted from Weisz et al.[10]); (D) anthranilic acid (adapted from Tunesi et al.[7]).

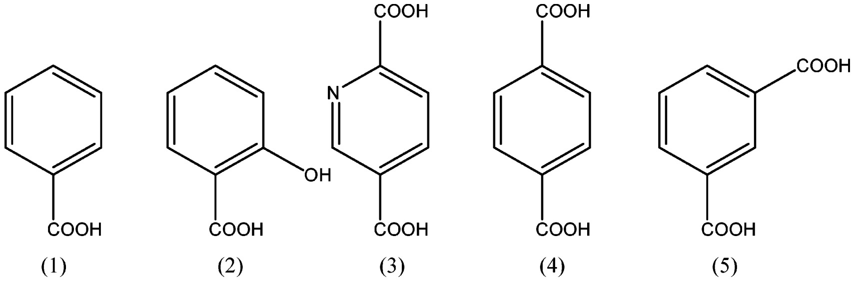

Figure 3. Benzoic acid (1), salicylic acid (2), pyridine-2,5-dicarboxylic acid (3), terephthalic acid (4), and isophthalic acid (5).

terephthalic acid $pK_{a1} = 3.5$, $pK_{a2} = 4.5$), the effect of adding these acids to TiO_2 dispersions varies. The smallest effect was observed for phthalic acid and the largest for terephthalic acid. The results were easily rationalized from steric considerations; terephthalic acid is most likely to link two TiO_2 particles together, and phthalic acid is least likely to serve as such a link.

The adsorption of pyridinedicarboxylic acids is especially interesting. These molecules have two carboxylic acid groups that allow “bridging” between two TiO_2 particles. Also, the third functionality, the ring nitrogen (protonated or deprotonated depending on the pH), allows for either creating a more stable surface complex with one of the particles, or participating in a hydrogen bond with another acid molecule. The effect of the heteroatom on the dicarboxylic acid−titanium dioxide dispersion viscosity needs to be elucidated. From the application point of view, it is interesting to note that in the dye-sensitized solar cells design, the dye molecules are chemically similar to the additives, which could be used to control viscosity. This is due to the necessity for both of them to anchor onto the TiO_2 surface. If inexpensive ways of synthesizing the dyes are found, these dyes can be used for producing good quality coatings in one step. Understanding the structure−activity relationships, namely the effect of the structure of the additive on the rheology of the dispersion, would help create a dye additive that could be used in miniscule amounts so as to avoid quenching, without compromising the film quality.

In the present work, we investigated the effects of adding five different mono- and dicarboxylic acids to TiO_2 aqueous dispersions: benzoic acid (1), salicylic acid (2), pyridine-2,5-dicarboxylic acid (3), terephthalic acid (4), and isophthalic acid (5) (Figure 3). The concentration of the acids was 1% by weight of TiO_2; this concentration was demonstrated in the previous work to have maximum effect on the dispersion viscosity.[26] The viscosity of the dispersions was monitored as a function of pH. It was shown that the viscosity of the TiO_2 dispersion can be controlled by selecting the additive and the pH of the dispersion. It was also shown that the viscosities of the dispersions containing pyridine-2,5-dicarboxylic acid are lower than the viscosities of the dispersions containing terephthalic or isophthalic acids. Two possible explanations are proposed, one based on the geometry of the complex formed between the TiO_2 surface and the adsorbed acid molecule, and another based on the impact of repulsive electric double layer forces.

Experimental Methods

Materials and Instruments. Benzoic acid, salicylic acid, terephthalic acid, isophthalic acid, and pyridine-2,5-dicarboxylic acid were purchased from ACROS and used as received. Titanium dioxide nanoparticles (mean diameter 21 nm, specific surface area 50 ± 15 m^2/g) Degussa P25 were received from Degussa and also used as received. Millipore water was used for the preparation of aqueous dispersions, which had resistivity above 15 MΩ cm and a pH of 6.2. The ball mill grinder, ceramic jars, and beads used for grinding the TiO_2 dispersions were manufactured by U.S. Stoneware (New Palestine, OH). Viscosities of the grinds were measured by the LVF Brookfield viscometer using spindle number 3. The pH of each dispersion was measured by the Omega PHB-209 pH meter. Infrared spectra were taken in attenuated total reflection (ATR) mode using a Nicolet 4700 FTIR spectrometer equipped with a Smart Orbit ATR attachment containing a single-bounce diamond crystal. The incidence angle was 45°.

Preparation of Titanium Dioxide Aqueous Dispersions. Titanium dioxide (15 g, total surface area 750 m^2), carboxylic acid (benzoic acid, salicylic acid, isophthalic acid, terephthalic acid, or pyridine-2,5-dicarboxylic acid) (150 mg), water (85 mL) and various amounts of either 1 M HCl or 1 M NaOH (0−0.27 mL) were added to a ceramic jar along with 20 ceramic beads. The jar was sealed and placed on a ball mill grinder to be rotated at 85 rpm for 18 h.

Characterization of Titanium Dioxide Aqueous Dispersions. The dispersions were allowed to equilibrate for 3 min without stirring and the pH of each dispersion was measured. Three readings were taken for each dispersion and the average of the three readings was taken. The viscosity of each dispersion was then measured at 30 rpm. The readings were recorded after 1 min of rotation. The viscosity measurements were performed in triplicate and then averaged.

Infrared Spectroscopy Measurements. The dispersions were dried under nitrogen at room temperature for 48 h. The resulting

TABLE 1: Viscosity and pH of TiO_2 Dispersions with Mono- and Dicarboxylic Acids (without HCl or NaOH)

carboxylic acid	viscosity (cPs)	pH	pK_{a1}[a]
none (control sample)	13	4.60	N/A
benzoic acid	73	3.47	4.2
salicylic acid	16	2.95	2.97
terephthalic acid	3800	3.40	3.61
isophthalic acid	1880	2.92	3.50
pyridine-2,5-dicarboxylic acid	1600	3.80	

[a] pK_{a1} values from Weisz et al.[10]

powders were placed on the ATR crystal and the spectra were taken. The spectrum of the dried TiO_2 aqueous slurry (not containing acids) was used as the background.

Results and Discussion

A control sample was first prepared where no acids were added in the preparation of the aqueous dispersion. No signs of sedimentation were observed in this control sample, therefore indicating that the grinding process was effective and the particles in suspension did not aggregate into large (micron-sized) clusters. To stay in suspension, the ratio of gravitational to Brownian forces $a^4\Delta\rho g/k_BT$ (where a is the particle radius, $\Delta\rho$ is the density difference between the particle and the liquid medium, $g = 9.8$ m/s^2, and $k_BT = 4.1 \times 10^{-21}$ J at 298 K) should be less than unity.[5] For TiO_2 $a^4\Delta\rho g/k_BT$ reaches unity at $a \approx 1.65$ μm. which is significantly larger than the radius of TiO_2 P25 particles ($a \approx 10$ nm, $a^4\Delta\rho g/k_BT \approx 1 \times 10^{-7}$). The viscosity of the dispersion (15% TiO_2 by weight or ~4% TiO_2 by volume) was measured and found to be 13 cPs, which is larger than could be expected from Einstein's formula for suspensions of hard spheres $\eta = \eta_s(1 + 2.5\phi)$, where η is the viscosity of the suspension, η_s is the viscosity of the solvent, and ϕ is the volume fraction of the spheres.[5] This can be attributed to the effect of particle charge. Because charged particles repel each other (especially in low ionic strength medium) the surface charges increase the effective particle diameter and subsequently the effective volume fraction of the particles and finally the viscosity. The pH of the dispersion was measured and found to be 4.6. The pH_{zpc} for Degussa P25 is about 6.3;[27] under our experimental conditions the particles indeed do carry positive charge and the viscosity measurements are consistent with the pH measurements.

The dispersions of TiO_2 with mono- and dicarboxylic acids were prepared. The pH and viscosity of each dispersion were measured. The results are presented in the Table 1.

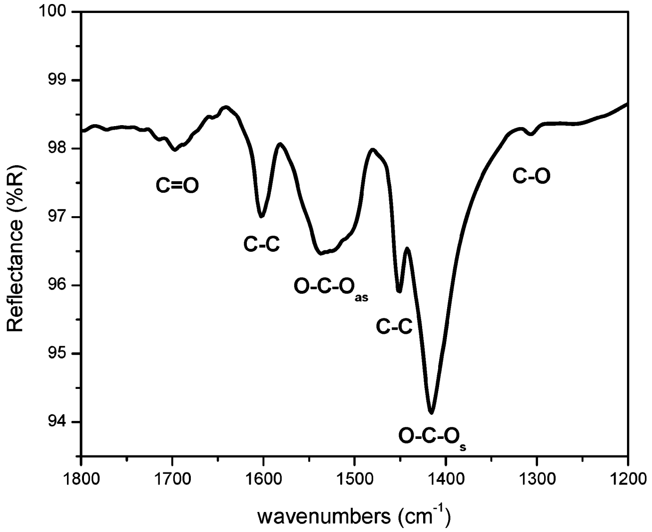

Figure 4. FTIR ATR spectrum of dried TiO_2−benzoic acid aqueous dispersion.

The dispersion of TiO_2 with benzoic acid was first studied. The viscosity of the dispersion was found to be 73 cPs, of the same order of magnitude as that of the control sample without acid additives. This is in agreement with our previously published results[26] and can be explained if one takes into account that benzoic acid does not contain a second functionality, and therefore cannot adsorb on two TiO_2 particles simultaneously and link them together. The IR spectrum of the dried dispersion was taken, and it is presented in Figure 4. The assignments were given to the IR bands in accordance to the previous studies.[7,13,19] The bands at 1602 and 1451 cm^{-1} were assigned to the aromatic ring C═C vibrations.[7] The strong band at 1415 cm^{-1} was assigned to COO^- symmetric vibration and the wide band (possibly consisting of two or three unresolved peaks) at 1538 cm^{-1} to COO^- asymmetric vibration. This results in $\Delta\nu = 1538$ cm^{-1} − 1415 cm^{-1} = 123 cm^{-1}, which is lower than that of the benzoate anion and is in agreement with the bidentate coordination of the benzoic acid molecules on the TiO_2 surface. The shoulders, which can be observed on the wide COO^- band, suggest different adsorption modes, most likely both bidentate chelate and bidentate bridging. The weak bands at 1697 and 1306 cm^{-1} were identified as C═O stretching and C−O stretching, respectively, and could belong to benzoic acid, which either is in the unidentate coordination or is attached to the TiO_2 substrate via hydrogen bonding. It is unlikely that these bands belong to residual benzoic acid not adsorbed on the TiO_2, because the spectrum of neat benzoic acid (not shown) exhibits the C═O band at 1678 cm^{-1}. Comparing the intensities of the COO^- and C═O bands leads us to the conclusion that the majority of the adsorbed benzoic acid is in a bidentate coordination mode, which is in agreement with the other studies.[7,13,19] It should be noted here that the coordination in the aqueous dispersion may be different from that in the dried sample. However, as we were unable to obtain quality spectra of the benzoic and other acids in aqueous dispersions with TiO_2, we are compelled to use the dried dispersions as proxies and to assume that the coordination modes are the same in both cases, i.e., before and after drying.

To test the hypothesis that the monocarboxylic acids do not increase the viscosity of the TiO_2 aqueous dispersions because they cannot serve as bridges between TiO_2 particles, the salicylic acid−TiO_2 dispersion was prepared. Salicylic acid ($pK_a = 2.97$), which is stronger than benzoic acid ($pK_a = 4.2$), was observed to adsorb readily on the TiO_2 surfaces.[10,12] The pH of the titanium dioxide−salicylic acid dispersion was found to be 2.95; therefore a significant fraction of the salicylic acid molecules are dissociated. The efficient adsorption of salicylic acid on the TiO_2 should result in increased attraction between the particles due to increased radius and also in decreased repulsion due to the lower surface charge on the TiO_2 particles. Also, the salicylate ions remaining in solution increase the ionic strength of the medium, thus decreasing the repulsion between the particles. Therefore if the van der Waals and electric double layer repulsion forces determine the dispersion rheology, adding salicylic acid should result in increased viscosity. Nevertheless, the viscosity of the dispersion was found to be 16 cPs, close to that of the control sample. As shown in Figure 2B, although salicylic acid has two functional groups, it cannot be attached to two TiO_2 particles simultaneously and serve as a link to increase the viscosity.

The titanium dioxide dispersions with dicarboxylic acids were prepared and studied. The viscosity of the terephthalic acid-

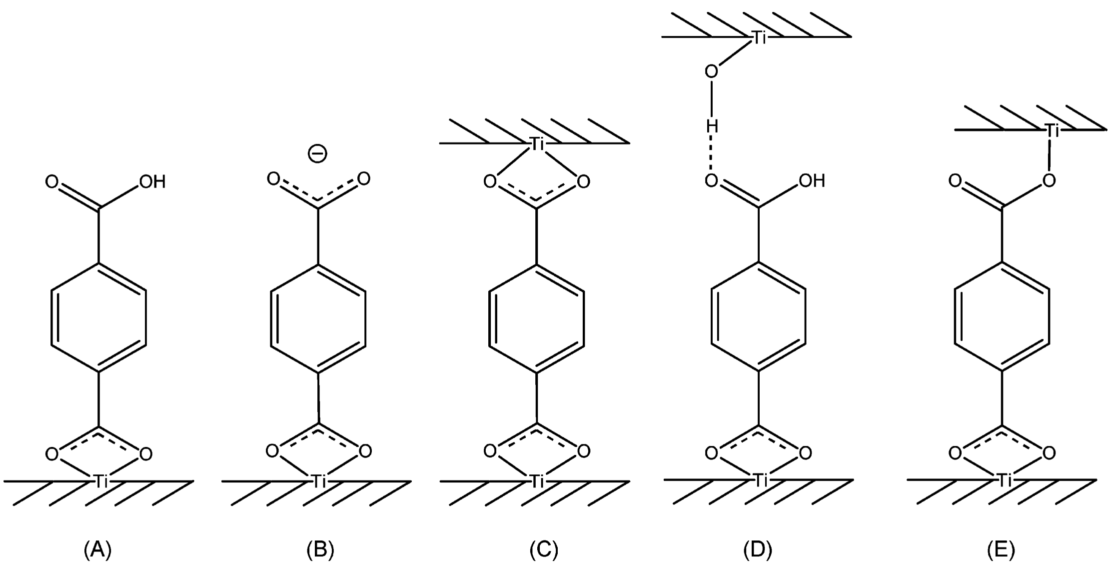

Figure 5. Adsorption of terephthalic acid on a TiO_2 surface.

TiO_2 dispersion was found to be about 3800 cPs, which is close to the value found in the previous study.[26] The pH of the dispersion was found to be 3.4. This is close to the pK_{a1} of terephthalic acid, meaning that the acid molecules in solution are either not dissociated at all or only partially dissociated. These partially dissociated molecules (anions with a charge of $-e$) are likely to be attracted to the positively charged TiO_2 particles. This can result in chemisorption of the acid molecule and formation of a surface complex, for example, such as the structure presented in Figure 5A.

Let us consider the effects of adding terephthalic acid to the dispersion and subsequent chemisorption on the interactions between TiO_2 particles. First, the van der Waals attraction will be affected. The adsorbed layer increases the radius of the particle, thus decreasing the distance between them and increasing attractive forces. However, because the refractive index of terephthalic acid is between that of water and TiO_2, the effect is reduced. The electric double layer repulsion is going to be affected more significantly. The adsorption of anions on the positively charged TiO_2 particles is likely to decrease the surface charge and thus repulsion between the particles is expected to decrease. However, adding terephthalic acid to the solution, where it is partially dissociated, increases the ionic strength of the medium and also causes the repulsion to decrease. Because both TiO_2 and terephthalic acid are quite hydrophilic, it is unlikely that hydration forces between the particles will change significantly as terephthalic acid is being added. These effects may cause van der Waals attraction forces to take over the decreased electric double layer repulsion and cause coagulation of the particles.

However, if all these effects combined would significantly affect the viscosity of the TiO_2 aqueous dispersion, a similar effect would be observed when either salicylic or benzoic acid was used as an additive. Thus the 300-fold increase in viscosity resulting from adding terephthalic acid to the dispersion cannot be explained by these effects alone.

A force that might play a more significant role is the attractive "bridging" force. When the attraction between suspended particles is increased as a compatible polymer is added to the system, due to the ability of one polymer chain to interact with two different particles forming a "bridge", the resulting interaction is referred to as bridging force.[4] In the recent work[26] we suggested that a similar effect takes place in the TiO_2-carboxylic acid systems. It should be pointed out that although in solution at pH 3.4 the second carboxylic acid group of the terephthalic acid is protonated, this is not necessarily the case for chemisorbed terephthalic acid molecules. It was demonstrated that acid dissociation constant can differ at surfaces from that in the solution;[28] Holmes-Farley et al. found that carboxylic acids chemisorbed on the functionalized polyethylene surface have values of pK_a that are lower than those in aqueous solution. This effect was attributed to the difficulty of ionization at the interface having a low dielectric constant. The interaction with TiO_2 particles having a dielectric constant comparable to that of water and, moreover, positively charged can decrease the pK_{a2} so that the chemisorbed molecule will be fully deprotonated, as shown in Figure 5B. At this state, the negatively charged carboxylate group can chemisorb onto the surface of another TiO_2 particle, forming a bridge, as shown in Figure 5C. As a result of these interactions all the particles in the dispersion are connected into a three-dimensional network and the viscosity of such a flocculated system is significantly higher than that of the system consisting of isolated particles suspended in the medium. If the second carboxylic acid group is not ionized, the terephthalic acid molecule can serve as a bridge between two TiO_2 particles if a hydrogen bond is formed between the carboxylic acid group and the surface hydroxyl, as shown in Figure 5D.

The IR spectrum of the dried terephthalic acid$-TiO_2$ dispersion is presented in Figure 6. The assignments of the observed bands was performed in accordance with the previously published studies on IR spectra of aromatic dicarboxylic acids[29] and their dipotassium salts.[30] The peaks at 1589 and 1507 cm^{-1} were assigned to the aromatic C=C vibrations. The strong band at 1389 cm^{-1} and the doublet at 1556 and 1539 cm^{-1} were assigned to symmetric and asymmetric vibrations of the carboxylate group respectively. These assignments result in $\Delta\nu = 167$ cm^{-1} or $\Delta\nu = 150$ cm^{-1}, both of which are lower than that of the dipotassium terephthalate ($\Delta\nu = 195$ cm^{-1}),[30] which is in agreement with the bidentate coordination of the terephthalic acid molecules on the TiO_2 surface, either chelating, as presented in Figure 5A, or bridging. As was suggested previously for benzoic acid,[7,13] a number of different coordination modes are possibly present. The bands at 1698 cm^{-1} and at 1283 cm^{-1} are assigned to C=O and C$-$O vibrations, respectively. These bands are significantly stronger than the corresponding bands in the spectrum of benzoic acid presented in Figure 4. Taking into account that the pK_{a2} of terephthalic acid

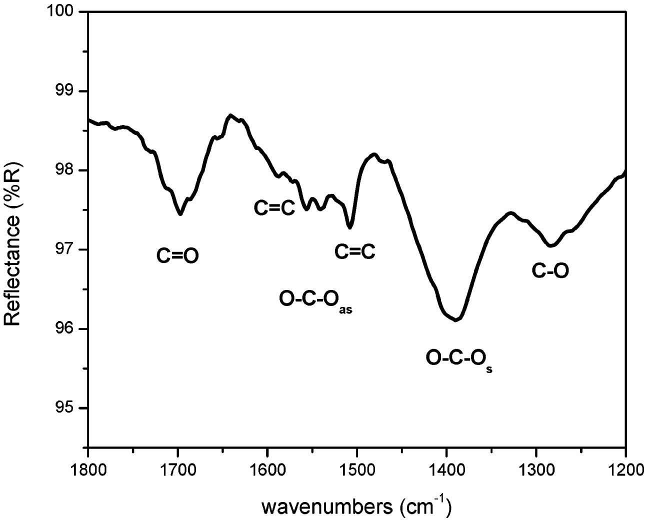

Figure 6. FTIR ATR spectrum of dried TiO_2−terephthalic acid aqueous dispersion.

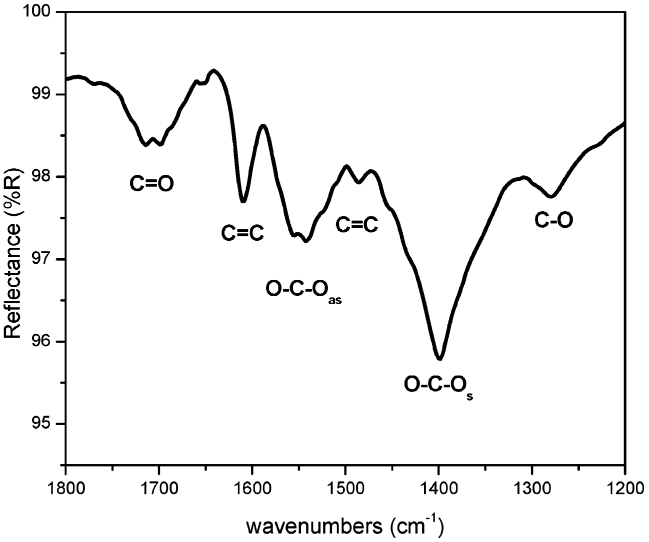

Figure 7. FTIR ATR spectrum of dried TiO_2−isophthalic acid aqueous dispersion.

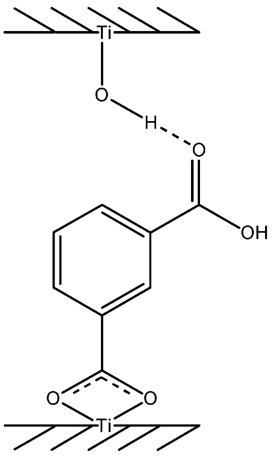

Figure 8. Isophthalic acid molecule serving as a link between two TiO_2 particles.

is significantly higher than the pH of the dispersion, these bands are likely to be due to the protonated carboxylic acid functional group. Thus the IR spectrum is in line with the bonding scheme presented in the Figure 5D rather than with that presented in the Figure 5C. Another possibility is the situation where one carboxylic acid group is chemisorbed on the TiO_2 surface in a bidentate mode and the other in a unidentate mode, as shown in Figure 5E. However, this structure is less likely because the unidentate coordination of the aromatic carboxylic acids on the TiO_2 surface was rarely observed in aqueous systems.

The viscosity of the isophthalic acid−TiO_2 dispersion was 1880 cPs, about half of that of terephthalic acid, and the pH was 2.92. The IR spectrum of the dried dispersion is presented in Figure 7. The spectrum is similar to that of the terephthalic acid−TiO_2 dispersion, namely the splitting between the bands corresponding to carboxylate asymmetric and symmetric vibrations $\Delta\nu = 1541\ \mathrm{cm}^{-1} - 1399\ \mathrm{cm}^{-1} = 142\ \mathrm{cm}^{-1}$, which is lower than that of the dipotassium isophthalate for which $\Delta\nu = 184\ \mathrm{cm}^{-1}$.[30] The results are indicative of bidentate coordination, either chelating or bridging. The band at 1541 cm^{-1}, assigned to the asymmetric vibration of the carboxylate group, is wide and seems to result from a few unresolved peaks, which may indicate different coordination modes, different adsorption sites, or both. As in the spectrum of the terephthalic acid−TiO_2 dispersion, the intensities of the C═O and C−O bands are comparable to those of the carboxylate group, which suggests that only one of the carboxylic acid groups per isophthalic acid molecule is deprotonated. The strong effect of adding isophthalic acid to the TiO_2 dispersion may be due to isophthalic acid molecules serving as links between the TiO_2 particles, as shown in Figure 8. From the steric considerations, it is clear that terephthalic acid is a better "bridging" agent when compared to the isophthalic acid because it allows for larger separation between two linked particles. This explains the viscosity of the terephthalic acid−TiO_2 dispersion being twice as high as that of the isophthalic acid−TiO_2 dispersion.

Measurements were then performed for the pyridine-2,5-dicarboxylic acid−TiO_2 dispersion. The pH was 3.8, similar to that of the terephthalic acid−TiO_2 dispersion. The pK_a's of the pyridine-2,5-dicarboxylic acid could not be found in the literature, but judging by the available pK_a's of other pyridinedicarboxylic acids, the pK_{a1} is estimated to be in the range 2−3 and the pK_{a2} in the range 4−5. Therefore, at a pH of 3.8, the acid molecules most likely have one deprotonated and one protonated carboxylic acid group and the pyridinic nitrogen is likely to be protonated. The result is the structure shown in Figure 9A with the total charge of the zwitterion being zero. Due to the formation of zwitterions rather than anions, as in the case of terephthalic acid, the change in the ionic strength of the medium would be significantly smaller than when terephthalic acid is added. Also adsorption of zwitterions on the charged TiO_2 surface should not affect the total charge on the particle (unless subsequent dissociation of the second carboxylic group occurs). Because neither ionic strength nor particle charge is affected as strongly as in the example with terephthalic acid, one would expect the effect on viscosity to be less pronounced. The measured viscosity was about 1600 cPs, which is about half of the terephthalic acid−TiO_2 dispersion viscosity and slightly lower than that of isophthalic acid−TiO_2 dispersion, but 2 orders of magnitude higher than that of the control TiO_2 dispersion. Such a significant increase of viscosity relative to the control dispersion, with no significant decrease in the electric double layer repulsion forces, is expected, prompting us to consider the difference of respective "bridging" abilities of terephthalic acid and pyridine-2,5-dicarboxylic acid. On the basis of the structures proposed for nicotinic acid[10] and anthranilic acid[7] adsorption on TiO_2 surfaces, which are presented in Figure 2C,D, respectively, we consider two possible geometries of pyridine-2,5-dicarboxylic acid complexes with the TiO_2 surface presented in Figure 9B,C.

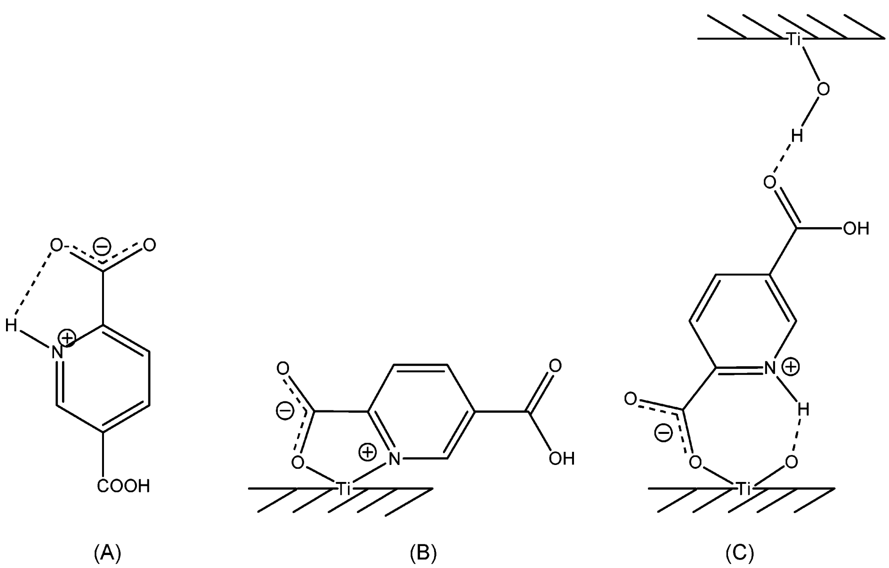

Figure 9. Proposed structures of pyridine-2,5-dicarboxylic acid: (A) as a zwitterion in solution; (B) adsorbed on a TiO_2 surface, but unable to serve as link between two TiO_2 particles; (C) adsorbed on a TiO_2 surface and serving as link between two TiO_2 particles.

The advantage of the geometry in Figure 9B is that it could be stabilized if an additional hydrogen bond is created between the second (protonated) carboxylic acid group and the TiO_2 surface (not shown). However, this geometry is unfavorable for creating a link between two TiO_2 particles. The geometry presented in Figure 9C resembles the proposed geometry of the isophthalic acid−TiO_2 complex presented in Figure 8 and therefore should allow linking two particles together. The geometry of the pyridine-2,5-dicarboxylic acid−TiO_2 surface complex is closer to that of isophthalic acid adsorbed on TiO_2 rather than to that of terephthalic acid, as presented in Figure 5 due to the presence of the pyridinic nitrogen participating in the chelating complex. The viscosity of the pyridine-2,5-dicarboxylic acid−TiO_2 dispersion is also similar to that of the isophthalic acid−TiO_2 dispersion, being slightly lower possibly on account of the fraction of the acid molecules adsorbed, as shown in Figure 9B, which are unable to serve as bridges between two particles.

Finally, the effect of pH on the viscosity of the suspensions was studied. HCl or NaOH was added prior to the ball-mill grinding. Both viscosity and pH were measured for each dispersion. The results of the study are presented in Figure 10. It was observed that as the pH decreased (by adding HCl), the viscosity of the dispersions with benzoic, isophthalic, and terephthalic acids decreased dramatically. This effect can be attributed to the growing positive charge on the TiO_2 particles, which must increase the repulsion between them. Also, the adsorption of the dicarboxylic acids on the TiO_2 surface (and therefore "bridging") should become less efficient, first due to the protonation of both carboxylic acid groups at $pH < pK_{a1}$ and a resulting decrease in electrostatic attraction between the particles and the acid molecules, and second due to competition between Cl^- anions and the carboxylic acid anions for the surface sites.[27] Such a sharp decrease in viscosity was not observed in salicylic acid and pyridine-2,5-dicarboxylic acid dispersions. Presumably, the competition with the chloride anions is less important in the species, which can use two functionalities to chelate the titanium atoms.

Adding small amounts of NaOH causes an increase of viscosity. This may be caused by a decrease of the initially positive pH dependent surface charge (as $pH \rightarrow pH_{zpc}$) as well as complete deprotonation (at $pH > pK_{a2}$) of the dicarboxylic acids, both of which result in decreased electric double layer repulsion between the particles. At the same time, deprotonation of the dangling carboxylic acid group of the chemisorbed molecules should increase the efficiency of "bridging". As the concentration of NaOH (and pH) increased further, the viscosity of the dispersions with dicarboxylic acids decreased, slightly for terephthalic and isophthalic acids and abruptly for pyridine-2,5-dicarboxylic acid. The slight decrease can be explained by considering the electrostatic repulsion between now negatively charged TiO_2 particles and dicarboxylic acid anions, which should render "bridging" less efficient. It was reported previously[27] that adsorption of carboxylic acids on TiO_2 becomes less efficient as the pH increases above pH_{zpc} and pK_a. The abrupt decrease of the viscosity of pyridine-2,5-dicarboxylic

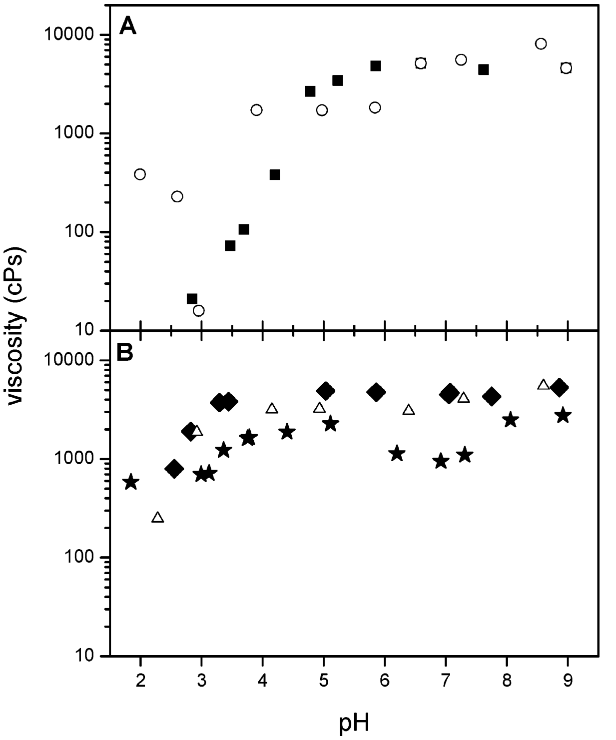

Figure 10. Viscosity vs pH in (A) monocarboxylic acid−TiO_2 dispersions [(■) benzoic acid; (○) salicylic acid] and (B) dicarboxylic acid−TiO_2 dispersions [(◆) terephthalic acid; (Δ) isophthalic acid; (★) pyridine-2,5-dicarboxylic acid].

acid−TiO_2 dispersions can be rationalized if we take into account that as pH increases the pyridinic nitrogens are becoming deprotonated. It is likely that the pyridine-2,5-dicarboxylic acid with deprotonated pyridinic nitrogen would preferentially chemisorb according to Figure 9B, which is unsuitable for "bridging". Finally at higher, basic, pH values the viscosity of the dispersions increases again. This effect was reported previously by a number of groups[20,21] and was attributed to increased ionic strength of the medium and therefore decreased electric double layer repulsion.

Conclusions

Understanding the role of a variety of factors determining the rheological properties of dispersions would allow for the creation of new materials with desired properties. Investigations of the structure−activity relationships in titanium dioxide−ligand systems may prove useful in the dye-sensitized solar cells design as well as in a variety of other applications. The present work concentrated on the effects of substituting a benzene ring for pyridine in the dicarboxylic acid additives intended to control viscosity of TiO_2 nanodispersions. The pH dependence of the viscosity of these materials was investigated.

Acknowledgment. We thank SAPPI Ltd. for generous financial support and Dr. Roger Boggs for helpful discussions.

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