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Adsorption studies on nano-zirconia in water and a water-1,2-propanediol mixture

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The adsorption of an electrosteric (polyacrylic acid, PAA), an electrostatic (triammonium citrate, TAC) and a steric dispersant (2-(2-(2 methoxy ethoxy) ethoxy)acetic acid, TODA) onto nanozirconia particles in deionized (d.i.) water and in a 75 wt% water-25 wt% 1,2-propanediol mixture was investigated. The amount of dispersant in d.i. water yielding the lowest apparent viscosity was measured via rheology. For PAA this was determined to be 6 wt%, for TAC 2 wt% (which corresponds to ≈ 0.43 mg/m²) and for TODA also 2 wt% (corresponding to ≈ 0.34 mg/m²). In the water-propanediol mixture the minimum viscosity was measured and the adsorbed amount was determined by adsorption isotherms using the depletion method. For TAC this was ≈ 0.076 mg/m², which is five times less than the value in pure water. Furthermore, zeta-potential measurements were performed to confirm the dispersion mechanism. Zirconia particles in water showed the same zeta-potential as in water-propanediol, although in water-propanediol less TAC molecules were adsorbed on the surface. For TODA the adsorbed amount was calculated to be ≈ 0.4 mg/m², which fits well to the value determined in water. Propanediol seems not to influence the adsorption in that case.

Key words: adsorption, zeta potential, nano-particles, zirconia, steric stabilization.

Introduction

Dispersing nano-sized ceramic particles in a slurry to achieve high solids loadings is still a challenge. On the one hand, dispersants are to be found, which supply a sufficient dispersing force to overcome van-der-Waals forces. On the other hand, this dispersing force needs to be very short range to allow dense packing of the particles and thus reach the desired high solids loading. Therefore, the right choice of dispersants and dispersion mechanism (electrostatic, steric, electrosteric) is crucial. Furthermore, the dispersing medium is known to influence the interparticle forces. Thus, a stable slurry may only be produced if the dispersing medium and dispersants are tailored to the surface chemistry of the ceramic particles which are to be processed. Recently, we have investigated the dispersing quality of electrostatically and sterically stabilized particles using the colloid probe technique [1]. The dispersing medium was varied between a pure d.i. water system and a 75 wt% 1,2-propanediol/25 wt% water mixture. The dispersing force created by the steric dispersant was

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strongly influenced by changing the dispersing medium. These results raised questions about the adsorption mechanisms of dispersants onto zirconia within water-propanediol mixtures. Here we present adsorption studies of an electrostatic, steric and an electrosteric dispersant onto zirconia surfaces. There are several methods available to determine the amount of adsorbed dispersant or the optimum dispersant level, respectively, in a slurry. Fukuda et al. [2] used the apparent viscosity of the suspensions as a function of added dispersant to determine this level. Greenwood and Bergström combined rheological experiments and adsorption isotherms [3], which was also used by Liu [4]. For rheological experiments usually suspensions are prepared with low solids content. The amount of dispersant is then varied in these suspensions. The apparent viscosity will decrease with increasing amount of dispersant until a minimum is reached. The decrease corresponds to more dispersants being adsorbed yielding fewer adsorptive particle surface sites and therefore reduced attraction. Bridging or depletion flocculation will be reduced and a possible electrostatic barrier may increase, which decreases the apparent viscosity. However, if too much dispersant is given to the fluid phase, the stabilizing barrier may be compressed due to a large amount of counterions. This allows the built up of

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new flocks, which again leads to an increase in viscosity (η) .

Non-adsorbed dispersant in the liquid phase may also result in a higher viscosity. Therefore, usually the minimum detected in the viscosity-dispersant curve is taken to correspond to the optimum dispersant level. Bergström has shown that this minimum corresponds to a monolayer coverage of the surface [5]. Additionally, Zeta-potential measurements may be taken for electrostatically and electrosterically stabilized systems as suggested by Greenwood et al. [6]. Also, adsorption experiments may be used. Here the ceramic powder is mixed with dispersant and subsequently centrifuged. The supernatant is analyzed for remains of dispersants. Thus the amount of dispersant adsorbed on the surface can be determined directly and the optimum dispersant level is established. In this work we have combined zeta-potential measurements, adsorption experiments and rheological results. We investigated the adsorption behavior of different dispersants on nano-zirconia powder. As a new attempt we have varied the liquid phase and compared the different adsorption behavior of the dispersants in water and a 1,2-propanediol-water mixture. Triammonium citrate (TAC) was used as an electrostatic dispersant, 2-(2-(2-methoxy ethoxy) ethoxy)acetic acid (trioxadecanoic acid TODA) a steric stabilizer and low molecular weight polyacrylic acid (PAA) as electrosteric dispersant. TODA had been used in our colloid probe investigations and was therefore also utilized here. PAA and TAC are commonly used as standard dispersants. They were used in this investigation to gain a general overview of the influence of a water-alcohol mixture on the dispersing mechanisms.

Experimental

A. Zirconia Powder

Nano-zirconia powder was supplied by Degussa, Germany. The primary particle size determined from transmission electron microscope (TEM) pictures was 13 nm. Agglomerates were present, leading to a size distribution (determined by a Cilas analyzer) as follows: $d_{10}=68$ nm, $d_{50}=114$ nm, and $d_{90}=287$ nm. The surface area was 61 m²/g and the monoclinic phase proportion 26 wt%.

B. Reagents

1,2-propanediol, TAC, HCL (33 wt%), NaOH, (2-(2-(2-methoxy ethoxy) ethoxy) Acetic Acid (TODA)), and polyacylic acid (Mw = 2000 g/mol) were ordered from Sigma-Aldrich (analytical reagent grade) and used as delivered. All water used in the presented experiments was filtered by a Millipore water purification system ("Milli-Q"), which increases the resistance of the water to well above $10^{-16} \Omega/cm$.

C. Suspension Preparation and Rheology

For rheological analysis zirconia suspensions with a solids loading of 8 vol% were prepared. Zirconia powder and the chosen dispersant were milled in a dissolver (supplied by VMA Getzmann GmbH, Germany) together with d.i. water for at least 1 hour. The pH was adjusted to the appropriate value depending on the dispersant (using HCl or NaOH). Due to our colloid probe results [1] for suspension preparation PAA and TAC were used at pH=9.5, whereas TODA was used at pH=3.0. The dissolver was equipped with a double milling impeller made of polyamide. The speed of the agitator was set to 1000 rpm. Also zirconia milling balls (diameter 2 mm) were added according to the manufacturer's manual and the batch was processed in a double walled container, which was connected to a cooling device (15 °C). A Haake RS150 rheometer was used to record rheological data. A plate-plate system of 35 mm diameter was utilized. The rheometer was set to a controlled shear stress mode and the temperature to 20.5 °C. Prior to each measurement the samples were allowed to adjust to the temperature for 300s. The stress was subsequently increased from 0 to 600Pa and the viscosity was recorded as a function of the shear rate. For analysis the viscosity at a shear rate of 100 1/s was taken.

D. Zeta-Potential Measurements and Adsorption Isotherms

– d.i. water

The zeta-potential measurements in d.i. water were taken from suspensions with low solids loadings (2 vol%). The dispersing agents were also given to this fluid (PAA 6 wt%, TAC 2 wt%, and TODA 2 wt%) and the pH was adjusted (compare section II C) using HCl or NaOH. Then the particles were added according to the calculated content in one step. Subsequently the particles were dispersed using an ultrasonic finger (HD2200 supplied by Bandelin, Germany). The frequency of the ultrasonic wave was 20 kHz (giving a power of 200W) and the amplitude was set to 310 μ m. The ultrasonic treatment was applied to each sample for 10 minutes using pulse cycles (1 second intervals -0.9s work, 0.1s break). To avoid a temperature increase during the process, all samples were placed in a water bath. Control measurements of the total weight were taken to insure that no significant evaporation took place. The zeta-potential of the particles in these suspensions was determined using a Malvern ZetaSizer instrument. The suspensions were diluted prior to the experiments using water with an electrolyte concentration of 0.001 M NaCl and automatic titration was enabled using NaOH and HCl.

- water-propanediol mixtures

Again a liquid phase (25-75 wt% water-propanediol) was prepared initially. Two sets of samples were then made: one with dispersant TODA and the other one with TAC. For TODA the water and propanediol was

simply mixed, whereas for TAC additionally 0.001 M NaCl was added to get a controlled ionic strength in the solution (this was not necessary for TODA samples as the ionic strength was controlled by the pH). The ZrO₂ powder was mixed into the liquid phase (2 wt%) solids loading). These slurries were then pH adjusted (3.5 for TODA and 9.5 for TAC) and equilibrated by mixing with a magnetic stirrer over night. Subsequently they were placed in an ultracentrifuge for 30 minutes at 50,000 rpm. The clear supernatant was diluted 10 times with water for TAC, and 5 times for TODA and then titrated (using a 736GP Titrino, Methrom, with a combined LL pH glass electrode). The pH was first adjusted with 0.5 M HCl to the starting pH value of the titration, then 0.05 M NaOH was added stepwise. For samples containing TODA the titration was performed between pH 3.5 and 10.5, and for the ones containing TAC between pH 3 and 9. A calibration curve was also taken for both dispersants in a water-propanediol mixture. The zeta-potential of the TAC samples was also investigated. The potentials were measured on the Zetasizer 2000 (Malvern Instruments), which utilizes the microelectrophoresis method. The slurries from the adsorption experiments were used for the electrokinetic measurements. However, they were diluted in a waterpropanediol mixture (25%: 75%), to a solids loading of about 0.001 vol%. A pH of 9.5 was installed. Additionally 0.001 M NaCl was added to achieve a constant ionic strength within the solution. The time between dilution of the slurry and the measurement was typically two minutes. It was deliberately kept short to minimize the risk for desorption of the acid from the powder.

Results and Discussion

A. Zeta-Potential

Figure 1(a) shows the zeta-potential of unmodified zirconia in water. The isoelectric point (iep) is at pH \approx 7. The potential increases to +40 mV at pH=4 and decreases to -30 mV at pH=10. If PAA is adsorbed at the surface, the iep is shifted significantly to a much lower pH value (3-4). Also the minimum potential is lowered to ≈ -45 mV and is now constant over a much wider pH range (pH=6 to 10). This is very common plot for polyelectrolyte modified zirconia. Wang et al. [7] also stabilized zirconia particles by using PAA. The mean particle size was 40 nm (determined by TEM) and the powder had a BET area of 31.6 m^2/g . The PAA they used was of higher molecular weight Mw = 10000g/mol. Their zeta-potential showed a similar iep (pH= 2.5), but the minimum potential was not as low (-30)mV). Biggs et Healy used PAA of the same molecular weight as utilized in this work and found an identical iep [8]. The minimum potential, however, was similar to the one determined by Wang et al. [7]. Petterson et al. published a potential plot for PAA (3500 g/mol) on



Fig. 1. Zeta-Potential of zirconia (a) untreated, (b) PAA modified, (c) TODA modified, and (d) TAC modified.

zirconia (15.2 m^2/g), which is almost identical with the one measured in this work [9]. Taking into account the standard deviation of about 20% for such measurements these changes are not significant. If TODA is mixed to the powder, the zeta-potential course does not change significantly [1], which is shown in plot (c). Obviously TODA does not act in an electrostatic manner and thus may indeed be taken as a steric stabilisator. However, since the potential course is almost identical to untreated zirconia, the adsorption amount seems to be very low.

Plot (d) in Figure 1 exhibits the potential if the zirconia is modified by TAC. Again, the iep is shifted to a lower value (pH=4) compared to the untreated powder. The minimum potential is very similar to the one found for the PAA plot. It agrees well with the TAC data published by Biggs et al. They determined the same iep, but a slightly lower minimum potential [10]. Greenwood and Kendall published an even lower one [11]. This deviation may be explained by a relative low adsorption of TAC onto zirconia. This will be discussed in more detail in the next section.

Finally, for untreated zirconia, it was also investigated how the liquid phase composition affected the surface potential. For this the liquid phase was varied form 100% water to mixtures of 75 wt%-25 wt%, 50 wt%-50 wt%, and 25 wt%-75 wt% water -1,2 propanediol, respectively. The ESA results were presented elsewhere [1]. It was found that the iep was constant for all solutions. But the maximum and minimum potential (at pH=3 and pH=10) were decreased significantly if the propanediol content was increased. The conclusion was drawn that the surface potential and thus the size of the double layer depends strongly on the propanediol content.

For the TAC modified powder this was investigated further. The potential in a 25 wt% water/75 w% propa-



Fig. 2. Zeta Potential as function of the amount of TAC added to the zirconia. The background liquid was a 25 wt% water/75 wt% propanediol mixture at pH 9.5.

nediol mixture was recorded as a function of added TAC to the surface. Figure 2 shows this zeta-potential as a function of added TAC. The measurements were performed at pH=9.5. If no dispersant was added, a zeta-potential of -8 mV was detected. This confirms the earlier assumption of a reduced zeta-potential (taken from the ESA data). The initial potential decreased if TAC was added to the system. A similar behavior was reported by Pettersson et al. for a PAA system [9]. The maximum adsorption of TAC onto zirconia was achieved at a concentration of 500 mg/l TAC in the sample. For higher concentrations the zeta-potential levels at ≈ -85 mV. This potential value for TAC modified zirconia was also found by Biggs et al. in their work [10]. However, they investigated a 100% water system. This issue will also be discussed in the next section.

B. Adsorption of dispersants

- Rheology

Figure 3 shows the viscosity of 8 vol% zirconia suspensions as a function of added amount of PAA. The pH was set to 9.5. The increase and constant high viscosity at low PAA concentrations was due to bridging flocculation. The molecules could adsorb on differ-



Fig. 3. Apparent viscosity as a function of the dispersant (PAA) concentration (related to the weight of zirconia powder). The liquid phase was deionized water. The high values at low PAA content indicate bridging flocculation, which is overcome at 6 wt% PAA. The solids volume content was ≈ 8 vol%.



Fig. 4. Apparent viscosity as a function of dispersant (TAC) concentration (related to the weight of zirconia powder). The liquid phase is 100% deionized water. Optimum dispersant level here is 2.5 wt%. The solids volume content was ≈ 8 vol%.

ent particles at the same time. The amount necessary to avoid the forming of bridges was determined to be 6 wt% (related to the amount of zirconia powder used to prepare the suspensions).

Figure 4 exhibits the viscosity-dispersant curve for TAC in deionized water. Again, the solids volume content was ≈ 8 vol% and the pH was set to 9.5. A clear minimum is visible at a dispersant level of 2.5 wt%, which corresponds to 0.43 mg/m² of adsorbed dispersant. Biggs et al. also investigated colloidal zirconia with a lower specific surface area (15.1 m²/g) [10] and found at pH=9.0 a maximum adsorption of 0.20 mg/m². A reason for this much lower value might be an insufficient dispersing procedure in their work. It also remains unclear whether they used yttria stabilized zirconia. This would clearly influence the number of surface sites onto which TAC may adsorb.

The increase of η for higher dispersant levels in Fig. 4 was due to the compression of the double layer barrier. If TAC is added and not adsorbed onto the surface, the molecule will simply dissociate in the liquid phase. This increases the number of counterions and results in a smaller Debye length $(1/\kappa)$ and thus a compression of the electrostatic barrier. Once a critical concentration of counterions is exceeded the system may become unstable and show thixotropic behavior. As a result zirconia particles are forming flocks and liquid will be trapped inside them, leading to an increasing η .

- Adsorption Isotherms

In industrial applications of ceramic suspensions, a 100% aqueos phase is often undesired. Therefore, a water-propanediol mixture was investigated as a liquid phase. Figure 5 (left plot) shows the adsorption iso-therm measurement of TAC onto zirconia in 75 wt% propanediol-25 wt%water mixture (pH=9.5) The dotted line in that diagram represents 100% adsorption of the dispersant onto the zirconia surface. The right plot shows a Langmuir fit to these data. The Langmuir theory for adsorption assumes that dispersants may adsorb to the surface on certain functional sites, which



Fig. 5. The left plot shows the adsorption isotherm of TAC where a 75-25 wt% propanediol-water mixture was used as liquid phase (pH=9.5). The doted line in this diagram corresponds to 100% adsorption. The right plot shows a Langmuir fit to the data.

are all equal. Multilayer adsorption is not possible. Also, the adsorption process should not be influenced by the number of molecules, which are already at the surface. Usually the last criterion is not met for electrostatic dispersants since these molecules build up an electrostatic repulsion, which will hinder more molecules from approaching the surface. However, the amount of adsorbed TAC was very low. The Langmuir fit therefore may be taken as a first approximation. The maximum adsorption calculated from the fit is 0.076 mg/m² with a reliability of $R^2 = 0.983$. This corresponds well with an extrapolation of the linear plot (left diagram in Fig. 5). However, the maximum adsorption value is more than five times less than the one determined by rheology in 100% water (0.43 mg/m²), which is surprising. The reason for this may be found in the zeta-potential. Figure 2 shows the potential as a function of TAC concentration in a propanediol-water mixture. The maximum potential here is -70 mV, which corresponds well with the one found by Biggs et al. [10]. However, it is higher than the value presented in this work at pH=9.5 in the 100% water system (see Fig. 1). Obviously, between 60-70 mV is the maximum potential for a zirconia system. If this maximum is reached, the repulsive barrier becomes too high for further ions to approach the surface. Therefore, in such electrostatic systems the zeta-potential controls the amount of dispersant being adsorbed. Obviously, in the 75-25 wt% propanediol-water liquid phase the TAC ions could create this potential much more efficiently in 100% watery systems, since a lower TAC concentration resulted in the same potential strength as in pure water. However, since the molecules are believed to be fully dissociated at pH=9.5 in both systems it is not explicable what mechanism causes this efficiency.

Figure 6 represents the viscosity-dispersant plot for TODA for suspensions with 8 vol% solids content in 100% water. The pH was set to 3.5. The viscosity rose for low TODA concentrations (< 1 wt%) but decreased for higher TODA levels to a minimum at 2 wt%, which corresponds to 0.34 mg/m². Further addition of TODA had no influence on η . The increase may be due to a depletion flocculation process, which would indicate



Fig. 6. Apparent viscosity as a function of dispersant (TODA) concentration (related to the weight of zirconia powder). The liquid phase is 100% deionized water. Optimum dispersant level here is 2 wt%. The solids volume content was $\approx 8 \text{ vol}\%$.

that even at small concentrations not all of the dispersant molecules adsorb to the surface. However, if depletion mechanisms were also present at higher concentrations a decrease in η should have been detected with an increasing amount of TODA. This is clearly not the case. Further, an electrostatic stabilizing mechanism can be ruled out since this would have led to an increase of η once the optimum dispersant level was exceeded. Such a mechanism would also be detected by the zeta-potential measurement. This may be taken as a confirmation that TODA acted as a steric stabilizer, although the solid content (8 vol%) may have been too low to argue that way.

The adsorption process in a 75-25 wt% propanediolwater mixture at pH=3.5 was also investigated (Fig. 7). The left plot shows the adsorption isotherm. A doted line in this diagram represents 100% adsorption. It can be seen that for added amounts of TODA less than 200 mg/l, the dispersant was fully adsorbed. This is inconsistent with the rheological result. The data was fitted to a Langmuir function (not shown), but the reliability was rather low (R²=0.707). A fit to a Freundlich function (right plot in Fig. 7) resulted in a much better reliability (R²=0.839). The Freundlich theory does not presuppose that all adsorption sites are equal. Multilayered structures are also possible. The maximum



Fig. 7. Left plot shows the adsorption isotherm of TODA where a 75-25 wt% propanediol-water mixture was used as liquid phase (pH=3.5). The dotted line in this diagram corresponds to 100% adsorption. The right plot shows a Freundlich fit to the data.

amount found by extrapolation of the adsorption isotherm was $\approx 0.4 \text{ mg/m}^2$, which corresponds well with the rheological value (0.34 mg/m^2) . Therefore, the conclusion may be drawn that the liquid phase composition did not influence the adsorption mechanism. Calculating the covered area per TODA molecule at 0.4 mg/m² gives 0.8 nm²/molecule. Usually fatty acids occupy an area of 0.2 to 0.3 nm²/molecule [12]. Due to the low pH value (pH=3 to 3.5) the TODA molecule was fully associated (the pKa value of TODA in water was determined to be 4). An adsorption by the carboxylic group was therefore unlikely. The much lower density of TODA on the surface indicates that the molecules adsorbed in a flat conformation on the surface due to hydrogen bonding between the OH surface sites and the oxygen in the TODA backbone.

It may be possible that the non-adsorbed but dissolved TODA molecules stabilizes a slurry (and thus decreases the viscosity) via a depletion stabilization mechanism. Such a mechanism is usually discussed for long chain molecules [13]. However, Kulkarni et al. found a depletion effect for short chain polyethylene glycol molecules (which display a similar structure to TODA: [-(CH₂-CH₂-O)_n-]) with a molecular weight of only Mw=1000 g/mol (n \approx 23) [14]. This issue has been discussed in our recent paper [1] and the low adsorption of TODA may be a further indication for the discussed depletion stabilization mechanism.

Summary

The adsorption of the dispersants PAA, TAC, and TODA onto nano-zirconia particles in deionized water and 75 wt% water-25 wt% 1,2-propanediol mixture was investigated. The amount of dispersant in water was detected via rheology yielding 6 wt% for PAA, 2 wt% for TAC (which corresponds to 0.43 mg/m²) and also 2 wt% for TODA (corresponding to 0.34 mg/m²). In the water-propanediol mixture the adsorbed amount was determined by adsorption isotherm measurements. For TAC this was ≈ 0.076 mg/m², which is five times

less than the value in pure water. Zeta-Potential measurements confirmed that the zirconia particles showed the same zeta-potential in water as in water-propanediol. This means that in water-propanediol mixtures the potential can be achieved with less adsorbed amount of TAC molecules. For TODA the adsorbed amount was calculated to be $\approx 0.4 \text{ mg/m}^2$, which fits well to the value determined in water. The adsorption of TODA therefore seems not to be influenced by propanediol.

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