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Influence of dispersant structure on the rheological properties of highly-concentrated zirconia dispersions

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Abstract

Twelve dispersants with different molecular structure features have been compared for their ability to produce low-viscosity suspensions of yttria-stabilised zirconia in organic media. The relationship between the molecular structures and their influence on the rheological properties of YSZ was studied. The effectiveness of a dispersant is mainly determined by its ability to adsorb onto the surface of the powder dispersed in the organic medium, and adsorption of a dispersant was found to be strongly promoted if a chelate ring could be formed with the powder surface. Rheological measurements showed that Solsperse3000, a pentastearic acid oligomer, was the best dispersant for the powder in question. This is explained in terms of the longer chain length of the surfactant molecule. The effectiveness of this dispersant was investigated in five different organic media. Solid loadings up to 52.5 and 55 vol.% with submicron- and micron-powder, respectively, could be reached using Solsperse3000 as the dispersant and terpineol as the organic medium.

Keywords: Suspensions; ZrO_2; Fuel cells; Sensors; Dispersants

1. Introduction

The dispersion of ceramic powders in an organic medium to obtain slurries is of considerable importance in the ceramic industry for many processes like screen printing, slip-casting, tape-casting, injection molding and extrusion. Obtaining a stable slurry is a prerequisite for all these processes. Stable dispersions with high solid loadings are also required for the colloidal forming of ceramics which offers a potential way to eliminate structural defects and stress centres in sintered ceramics.[1–3] The stability of the dispersion in such concentrated systems depends on the ability of the dispersant to force the particles to remain separated, and in turn on the sign and magnitude of the total interparticle potential energy, V_T.[4] The general equation for describing V_T incorporates the sum of attractive and repulsive contributions,

$$V_T = V_A + V_R$$

where V_A is the attractive potential energy due to long range van der Waal's forces and V_R encompasses electrostatic, steric, and other repulsive potential energies. Electrostatic repulsion results from the development of an electrical double-layer around each particle when the powder is dispersed into a polar liquid. With steric stabilisation, stability is conferred by long-chain molecules adsorbed onto the particle surface. The stability of the dispersion is achieved when the repulsive forces are high enough to overcome the attractive van der Waal's forces.[5]

The parameters involved in the electrostatic repulsion are well described by the DLVO theory and have been the subject of many reports and reviews.[5–7] The electrostatic repulsion between particles depends on the dielectric constant of the medium, therefore it is less effective in the majority of the non-aqueous media than in water because of the lower ionic concentration and the lower dielectric constant.

Nevertheless, the electrostatic repulsion can not be neglected for explaining the stabilisation of dispersions in media with low dielectric constant.[8–10] In non-aqueous media,

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the charging mechanism involves three steps: (1) adsorption of the dispersants; (2) dissociation of the adsorbed molecule via acid–base reaction with the surface; and (3) a process in which some dissociated dispersant molecules desorb into the solution, leaving charges on the particle surface.[8]

Contrary to electrostatic stabilisation, steric stabilisation is not yet well understood, although a strong effort has been made in the last several years.[1,2,8,11–18]

Pure steric stabilisation is reached only if two requirements are satisfied: (1) strong anchoring of the dispersant molecules to the particle surface; and (2) sufficient extension of the long-chain into solution to prevent the particles from approaching each other at distances shorter than 10–20 nm.[8,12,15] Some small molecules, such as oleic acid or stearic acid, can be effective in stabilising dispersion in organic media despite the fact that they do not have chains long enough to provide pure steric stabilisation. These adsorbed molecules modify the Hamaker constant of the particles and therefore reduce the van der Waal’s attraction between particles.[1,12,18] The combination of steric repulsion and of the reduction of the Hamaker constant has been termed semisteric stabilisation and has been successfully used to produce many ceramic dispersions.[12,18] Even if the steric stabilisation is as effective in non-aqueous media as in water, it is much more common in organic liquids.

Prerequisite for steric and semisteric stabilisation of oxide ceramics is a strong adsorption of the dispersant onto hydroxylic particle surfaces. Four different mechanisms can be postulated for this adsorption. The first is ligand exchange (Mechanism I): The metal ion acts as a Lewis acid which can exchange the coordinating hydroxyl group with the dispersant molecule, resulting in the release of a molecule of water:[19–22]

$$\text{M–OH} + \text{H–L} \rightleftharpoons \text{M–L} + \text{H}_2\text{O} \qquad \text{(I)}$$

This mechanism becomes important in the presence of a dispersant which is able to form a chelate complex with the metal atom where two or more OH-groups are removed by one chelating molecule.

The second adsorption mechanism is ionic interaction (Mechanism II): After an acid–base reaction where the surface of the particle reacts with the dispersant, the charged dispersant molecule remains anchored to the particle surface via an ionic bond:[9,17]

$$\text{H–L} + \text{HO–M} \rightleftharpoons \text{H}_2\text{L}^{\oplus} \cdot {}^{\ominus}\text{O–M} \qquad \text{(II)}$$

The third way a molecule can adsorb on the surface is by hydrogen bonding (Mechanism III) between the hydroxylic group of the particle surface and atoms of the dispersant molecule with non-bonding orbitals:[23]

$$\text{M–OH} + \text{B–R} \rightleftharpoons \text{M–O–H} \cdots |\text{B–R} \qquad \text{(III)}$$

The final mechanism is chem-adsorption (Mechanism IV). The dispersant reacts with an oxygen atom on the surface and forms a covalent bond while releasing a new molecule into solution. Typically, chlorosilanes are used for chem-adsorption, where after the formation of a new Si–O bond there is cleavage of a hydrogen halogenide:[17,24]

$$\text{M–OH} + \text{X–SiR}_3 \rightleftharpoons \text{M–O–SiR}_3 + \text{HX} \qquad \text{(IV)}$$

In non-aqueous media, the effectiveness of the dispersant can be determined by viscosity measurements. The viscosity of a concentrated colloidal dispersion strongly depends on the interactions between the particles, therefore the lower the viscosity the lower are the interactions, and the better is the given dispersant.[25] Thixotropic behaviour and a yield point are usually indicative of a strongly-flocculated dispersion.[2] Shear thinning can also be an indication of a weakly-attractive, but non-touching, particle network, and this has been found to be a very useful property for new shape-forming technologies.[17,18]

The considerations discussed above must be taken into account every time a ceramic material is fabricated from powder via a fluid or plastic forming method. Yttria stabilised zirconia (YSZ) powders, for example, are widely processed in slurry-form for fabricating electrolyte materials for oxygen sensor and fuel cell applications, and here it is important that the resulting microstructures are highly dense and homogeneous without connected porosity. However, a homogeneous product of uniform density can only be obtained if the starting slurry has a high degree of homogeneity and stability.

In this work, 12 dispersants with different structural features were systematically compared for their ability to produce low-viscosity dispersions of yttria stabilised zirconia in five different organic media.

Table 1
Characteristics of the YSZ powders

Name	Manufacturer	BET specific surface area (m^2/g)	Particle size distribution (μm)
FYT13-005 (micron-powder)	Unitec Ceramic Ltd. (UCM Group PLC, Stafford, UK)	4.31	$d_{10} = 0.56$ $d_{50} = 1.07$ $d_{90} = 2.09$
TZ-8YS (submicron-powder)	Tosoh Corporation (Tokyo, Japan)	6.10	$d_{10} = 0.19$ $d_{50} = 0.37$ $d_{90} = 1.34$

2. Experimental procedure

2.1. Materials

Two different yttria-doped zirconia (YSZ) powders, one micron-sized and one submicron, were used in this work. According to the manufacturers' data sheets, both are high-purity zirconia powders doped with 13 wt.% (8 mol%) yttria. Table 1 summarises some powder characteristics. The BET was measured with a Beckman-Coulter SA 3100 (nitrogen adsorption) (Beckman Coulter Inc., UK), the particle size distribution was determined using laser light diffraction (Beckman-Coulter LS 230).

The organic dispersants and solvents were laboratory-reagent-grades used without further purification. The supplier was Fluka AG (Buchs, Switzerland) with the exception of Solsperse3000, a commercially available penta-(12-hydroxystearic acid) (Avecia Additives, Manchester, UK), and kerosene (JET A1 quality; 80 vol.% saturated hydrocarbons, 18 vol.% aromatics and 2 vol.% olefins). According to Moloney et al.,[23] Solsperse3000 consists primarely of a pentamer made up of one stearic acid unit and four units of 12-hydroxystearic acid. Tables 2 and 3 give further details of these dispersants and solvents, respectively.

2.2. Preparation of suspensions

The effectiveness of each dispersant was evaluated by measuring the viscosity of suspensions of the Unitec micron-sized YSZ powder in diethyleneglycol-mono-

Table 2
Molecular structure of the investigated dispersants

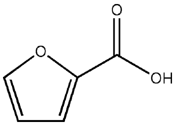
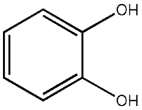
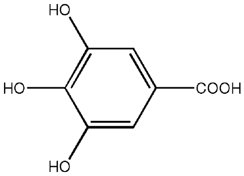
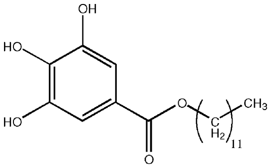
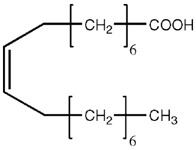
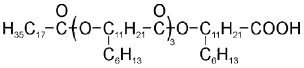
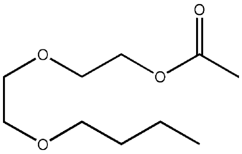
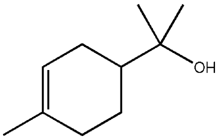
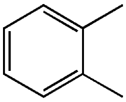
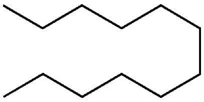
Name	Molecular formula	Structure	Molecular weight (g/mol)	Section
2-Furoic acid (furan-2-carboxylic acid)	$C_5H_4O_3$		112.08	3.1.1
Catechol (1,2-dihydroxybenzene)	$C_6H_6O_2$		110.11	3.1.1
Gallic acid	$C_7H_6O_5$		170.12	3.1.1
Lauryl gallate (dodecyl gallate)	$C_{19}H_{30}O_5$		338.44	3.1.1
1-Hexadecanol	$C_{16}H_{34}O$	$H_3C-[CH_2]_{15}-OH$	242.44	3.1.2
1-Octadecanol	$C_{18}H_{38}O$	$H_3C-[CH_2]_{17}-OH$	270.49	3.1.2
1-Hexadecylamine	$C_{16}H_{35}N$	$H_3C-[CH_2]_{15}-NH_2$	241.46	3.1.2
1-Octadecylamine	$C_{18}H_{39}N$	$H_3C-[CH_2]_{17}-NH_2$	269.51	3.1.2
Palmitic acid	$C_{16}H_{32}O_2$	$H_3C-[CH_2]_{14}-COOH$	256.42	3.1.3
Stearic acid	$C_{18}H_{36}O_2$	$H_3C-[CH_2]_{16}-COOH$	284.48	3.1.3
Oleic acid	$C_{18}H_{34}O_2$		282.46	3.1.3
Solsperse3000	$C_{90}H_{172}O_{10}$	 $H_{35}C_{17}-\overset{O}{C}\{O-\underset{C_6H_{13}}{C_{11}H_{21}}-\overset{O}{C}\}_3O-\underset{C_6H_{13}}{C_{11}H_{21}}-COOH$	1414.35	3.1.3

Table 3
Molecular structure and selected physical data of the employed solvents[31]

Name	Molecular formula	Structure	Boiling point (°C)	Viscosity (mPa·s)	Dielectric constant (ε)
Diethyleneglycol-monobutylether acetate (DEG-MBEA)	$C_{10}H_{20}O_4$		245	8.8 ± 1.7	∼6–8
Terpineol (mixture of isomers)	$C_{10}H_{18}O$		213–218	39.5 ± 1.5	2.8
Kerosene	80 vol.% saturated hydrocarbon, 18 vol.% aromatic, 2 vol.% olefin		155–255	4.5 ± 0.6	∼2
Xylene (mixture of isomers)	C_8H_{10}		137–144	3.7 ± 0.7	2.4
Dodecane	$C_{12}H_{26}$		213–216	4.9 ± 0.6	2.0

butylether acetate (DEG-MBEA) with varying amounts of dispersant. These suspensions were prepared by gradually adding the dry YSZ powder into the DEG-MBEA, in which a given dispersant had been previously dissolved. The powder was then effectively dispersed by a three-step milling procedure using a triple-roller mill (Exakt 80S, Exakt GmbH, Germany) with a minimum gap between the aluminium oxide rollers of about 3 μm. All the evaluations were carried out at a solid content of 40 vol.%. The amount of dispersant added to each suspension varied between 0.05 and 2 wt.% (based on the weight of ceramic powder). All the dispersants exhibited good solubility in DEG-MBEA with the exception of gallic acid, 2-furoic acid and the amines, where the dispersants could be dissolved only by heating the solvent, and of the alcohols, where only suspensions with dispersants concentration below 1% could be prepared.

The different organic media were evaluated in the same way by measuring the viscosity of 40 vol.% YSZ dispersions prepared with varying amounts of Solsperse3000 as standard dispersant. As already described above, Solsperse3000 was dissolved in the organic medium before the YSZ powder was added to the system. Suspensions without dispersant were also prepared for comparison.

2.3. Rheological measurements

The rheological properties of the suspensions were measured with a rotational viscosimeter (Rheolab MC120, Physica Messtechnik GmbH, Germany) using a concentric-cylinder measuring geometry (Z4 measuring systems: sample volumes: 3 cm^3; gap between cylinders: 0.59 mm). During these measurements, the suspension temperature was kept constant at 25 ± 0.5 °C by a thermostat. A range of shear rates was employed (10 points from 1 to 1000 s^{-1}). This range was scanned forwards and then backwards in order to check if a given sample was shear-stable or thixotropic. Measurements were made over a period of 10 s at each shear rate, and, at several defined shear rates (1, 10, 100 and 1000 s^{-1}), six points were collected in order to achieve a steady state. The measuring program was repeated five times for each sample with 10 min between measurements to check reproducibility. Apparent viscosity data at a shear rate of 100 s^{-1} were used as the basis for comparing the different dispersants and solvents.

3. Results and discussion

3.1. Effectiveness of dispersants

Twelve dispersants (see Table 2) were compared for their ability to produce stable dispersions of YSZ (Unitec powder) in DEG-MBEA. This organic medium was chosen as the reference solvent on the basis of the work of Gödickemeier.[26] The selected dispersants can be roughly divided into four categories according to their anchor group: Chelating molecules, which are able to build chelate complexes with metals; long-chained amines; long-chained alcohols; and fatty acids. The effectiveness of these dispersants was determined by rheology measurements. The rheology of the dispersion medium, DEG-MBEA, was also assessed and found to be near-Newtonian (see Table 3). The viscosity of a 40 vol.% YSZ dispersion in DEG-MBEA without any addition of dispersant was also determined for comparison with the stabilised dispersions. The measured apparent viscosity of this dispersion at 100 s^{-1} was

10.2 ± 0.9 Pa·s. All the dispersions containing the following dispersants showed shear thinning behaviour, indicating the presence of a weakly attractive network.

3.1.1. Molecules with a chelating functional group

Catechol, 2-furoic acid, gallic acid and lauryl gallate belong to this category of dispersants. Because of the presence of two (or more) oxygen atoms that can act as donors and build a complex with a central metal atom (Table 2), all these molecules can act as bidentate ligands and build chelate complex with metals. These molecules are, therefore, expected to adsorb strongly on the surface of YSZ through the complexation of the metal atoms (Mechanism I). In Fig. 1, the apparent viscosity (measured at 100 s^{-1}) of the resulting slurries is plotted against the amount of dispersant in wt.% of the ceramic used.

2-Furoic acid, which is known to act as a bidentate ligand for heavy metals,[27] has very little dispersing power, reducing the viscosity relative to dispersant-free dispersion by only 30% (Fig. 1). This can be explained in terms of the dimensions of the molecule, which are far too small to develop effective steric interactions, the inability of the adsorbed molecule to reduce the Hamaker constant (and therefore the attractive van der Waal's forces), and also the lack of electrostatic stabilisation stemming from the fact that the dispersant has no basic atoms able to react with the acidic YSZ surface and to produce the charged molecules needed to build up an electrostatic double-layer.[8]

In contrast, catechol, which is known to bond very strongly with transition metals,[22,28,29] causes a much greater reduction of the viscosity of the slurries, with a minimum viscosity of 4 Pa·s being achieved between 0.15 and 0.25 wt.% of catechol (Fig. 1). The effectiveness of this dispersant can be explained by strong adsorption on, and then modification of the properties of, the surface which results in a strong reduction of the Hamaker constant. However, the catechol molecule is too small to provide steric stabilisation and is a too weak base to react with the acidic surface and therefore cannot generate an electrostatic double-layer.

The lowest viscosity in this class of dispersants was achieved for slurries containing lauryl gallate (Fig. 1), a gallic acid ester with a chain length comparable to that of the fatty acids used later (see Section 3.1.3). In comparison with the dispersant-free dispersion, the viscosity is reduced by a factor of 10. Because of the structural similarities with catechol, this dispersant should also be able to build stable chelate complexes with transition metals. The viscosity drops significantly after the addition of only 0.05 wt.% lauryl gallate, reaches a minimum at around 0.15 wt.%, and then slowly increases with further addition of the dispersant. The increase in the viscosity can be explained by dispersant–dispersant and/or dispersant–solvent interactions due to the free-floating dispersant molecules. The effectiveness of this molecule can be explained by strong adsorption through the building of chelates, and the combination of a reduced Hamaker constant (reduction of V_A) with the presence of steric repulsion due the thickness of the adsorbed layer (∼4 nm). Lauryl gallate can, therefore, be classified as a semisteric dispersant.

More difficult to explain is the behaviour of the dispersions containing gallic acid. Surprisingly, these dispersions exhibit a two-fold increase in viscosity compared to the dispersion without dispersant after the addition of only a small amount of gallic acid (0.15 wt.%). Further addition of gallic acid does not significantly affect the viscosity until a concentration of 2 wt.% gallic acid is reached and the viscosity finally decreases (Fig. 1). Considering its structure (Table 2), gallic acid should also adsorb strongly on the YSZ surface

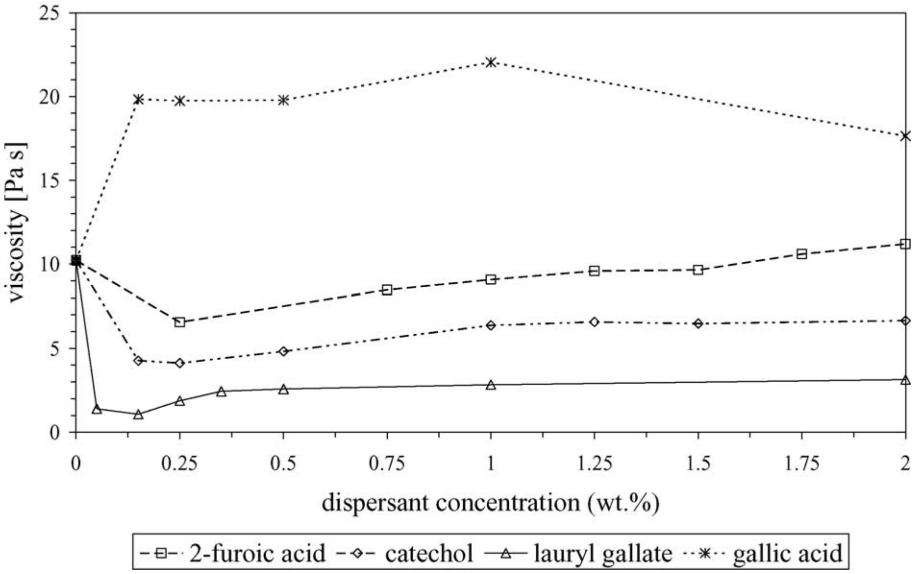


Fig. 1. Viscosity of dispersions prepared with dispersants possessing a chelating anchor group. (□) 2-Furoic acid; (◇) catechol; (△) lauryl gallate; and (✻) gallic acid.

through complexation, therefore the explanation of the increase in the viscosity probably lies in a modification of the surface properties of the particles which leads to an increased van der Waal's attraction. Moreover, the lack of basic atoms and therefore the absence of acid–base reactions with the particle surface prevents gallic acid from providing an electrostatic stabilisation component.

3.1.2. Molecules with hydroxyl and amine functional groups

The following long-chained molecules were compared: hexadecanol, octadecanol, hexadecylamine and octadecylamine (Table 2). These molecules were chosen because they have the same chain dimensions as the well-known dispersants palmitic acid, stearic acid, and oleic acid (see Section 3.1.3) and therefore differences in stabilisation behaviour should mainly be a function of the different properties of the anchor group. The chosen dispersants can adsorb on the YSZ surface through the first three mechanisms described in the introduction, although the alcohols are not expected to react as bases (Mechanism II) with the acidic surface of YSZ.

The viscosity (measured at $100\,s^{-1}$) of the resulting dispersions is shown in Fig. 2. The alkyl-alcohols lead to only a small decrease in the viscosity of the YSZ dispersions compared to the dispersant-free case. The alkyl-alcohols concentration has no apparent influence, with the viscosity of the dispersions remaining constant with increasing dispersant content from 0.25 to 1 wt.%. At concentrations above 0.5 wt.%, the dispersions containing the two amines show poor stabilisation comparable with that of the alkyl-alcohols, but at lower concentrations (0.25 wt.%), the viscosity decreases dramatically by a factor of two (Fig. 2). In both cases, the two additional carbon atoms in the alkyl chains do not improve significantly the effectiveness of the dispersant.

The poor effectiveness of the alkyl-alcohols in stabilising the YSZ dispersions is probably caused by poor adsorption because the only difference between the amines and the alcohols lies in the anchor group. The effectiveness of the amines can be explained by strong adsorption and semisteric stabilisation. According to Fowkes and Pugh,[8] since the amines have a basic anchor group, they are expected to react with the acidic particle surface building an electrostatic double-layer and, therefore, to provide further stabilisation. However, this fact is not consistent with the poor stabilisation reached at dispersant concentrations above 0.5 wt.% (Fig. 2). Here, the increase in dispersant concentration should lead to a higher charge on the powder surface through the exchange of adsorbed charged molecules with non-dissociated dispersant molecules, and as a result the viscosity should be lowered. In fact, it seems that the interactions between the free-floating amines overcome all the other factors and lead to an increase of the viscosity.

3.1.3. Molecules with carboxyl functional group

In this section, the following long-chained carboxylic acids are examined: palmitic acid, stearic acid, oleic acid and Solsperse3000 (Table 2). These dispersants are also able to build chelate complexes with the surface and therefore should adsorb strongly to the powder particles.[22] The viscosity curves of the resulting dispersions are shown in Fig. 3.

The dispersions with palmitic acid and stearic acid exhibit nearly identical viscosity curves. Interestingly, the viscosity exhibits a sharp minimum at 0.15 wt.%, increases significantly up to 0.5 wt.%, and then remains almost unaffected by the further addition of dispersant. As already seen above,

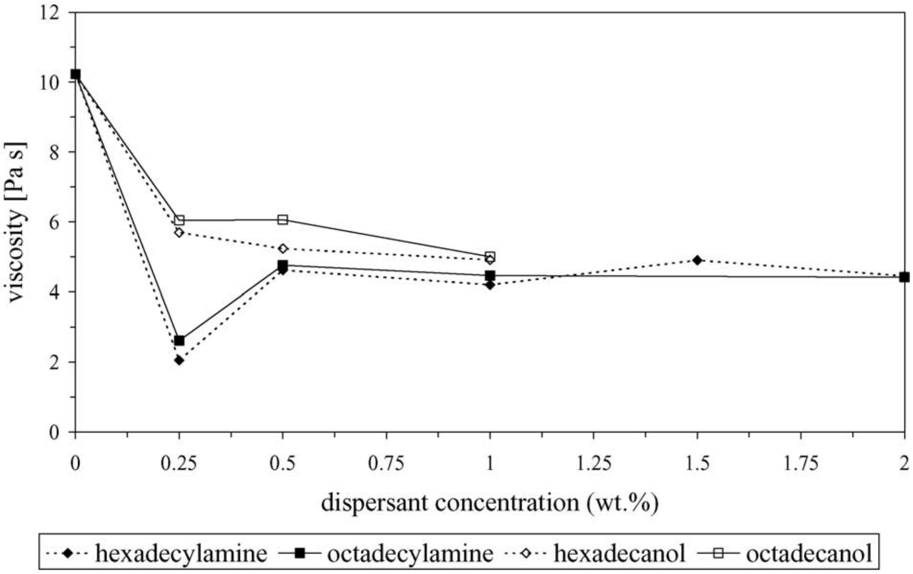


Fig. 2. Viscosity of dispersions prepared with dispersants possessing amine or alcohol anchor groups. (◆) Hexadecylamine; (■) octadecylamine; (◇) hexadecanol; and (□) octadecanol.

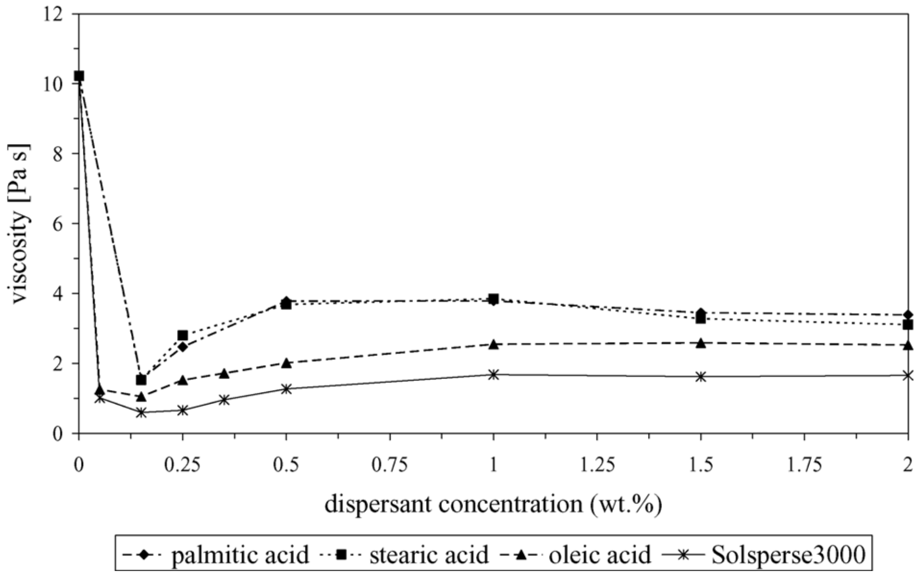


Fig. 3. Viscosity of dispersions prepared with dispersants possessing a carboxylic anchor group. (◆) Palmitic acid; (■) stearic acid; (▲) oleic acid; and (⋇) Solsperse3000.

increasing the chain length by two carbon atoms does not influence the efficiency of the dispersant. In general, the viscosity of these dispersions is lower than those of dispersions prepared with the alkyl-amines.

Dispersions with oleic acid show lower viscosity compared to those with the other two fatty acids discussed above. The viscosity exhibits a minimum at about 0.15 wt.% and then slowly increases with increasing oleic acid up to 2 wt.%. This difference, despite the similarity in the chain length, is likely due to the presence of the double bond in the oleic acid chain, which increases the polarisability of the molecule and leads to a larger reduction of the Hamaker constant. The better dispersant properties of oleic acid compared to stearic acid and palmitic acid has already been reported elsewhere.[12,23]

All three molecules above are semisteric dispersants and act by combining a reduction of the attractive forces with a steric barrier. The steric barrier alone would be insufficient to provide stabilisation since, according to a review of the Koelmans-Overbeek analysis by Johnson and Morrison,[12] these molecules provide an adsorbed layer that keeps particles 4 nm apart, whereas a separation of greater than 10 nm is required for true steric stabilisation of micrometer-sized particles.[8,9,12,15]

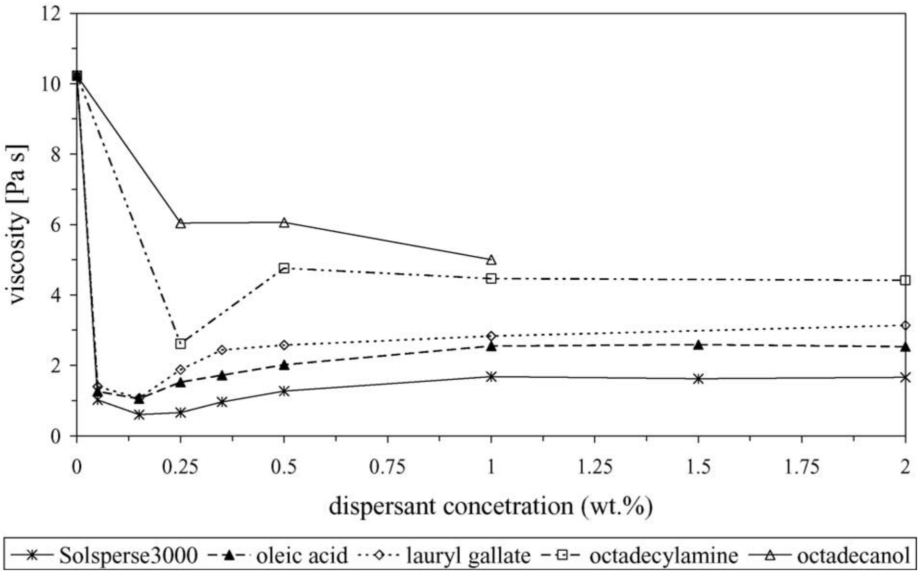


Fig. 4. Summary of the viscosity of dispersions prepared using the four classes of dispersants. (⋇) Solsperse3000; (▲) oleic acid; (◇) lauryl gallate; (■) octadecylamine; and (△) octadecanol.

The best stabilisation is obtained in dispersions containing the commercial dispersant Solsperse3000. These slurries exhibit a minimum viscosity between 0.15 and 0.25 wt.% dispersant and, as already observed before, the viscosity then increases smoothly with further dispersant additions because of interactions between the free-floating dispersant molecules.

The good performance of this dispersant is achieved due to the combination of the good adsorption properties of the carboxylic acid group with a long C66 chain which extends about 10 nm into the solvent.[23] While this adsorbed layer should already provide a sufficiently high steric barrier for good stabilisation, an additional stabilisation contribution is expected due to the modification of the Hamaker constant that results in a reduction of the van der Waal's attractions, as observed above with the other three fatty acids.

3.1.4. Comparison of dispersant effectiveness

In Fig. 4, the viscosity curves obtained with octadecanol, octadecylamine, lauryl gallate, oleic acid, and Solsperse3000 (i.e. representatives of the four different types of dispersants) are summarised for comparison. Since the first four dispersants are all of about the same size (C18 chain length) and have the same alkyl chain, the differences lie only in the adsorption strength and in the modification of the surface properties of the ceramic powder. The –OH anchor group is apparently the least effective surface-active group since the dispersions show only a small decrease in the viscosity compared to dispersant-free dispersions. It is likely that this molecule can adsorb only through hydrogen bonding (Mechanism III) which is a relatively weak interaction. A greater effect is obtained using the dispersants with a $–NH_2$ anchor group. These molecules, after an acid–base reaction, can bind to the surface via ionic bonds (Mechanism II) which are stronger than hydrogen bonds. The best results for the semisteric dispersants are obtained with the molecules which are able to form chelate complexes with metals. This is particularly true with oleic acid and lauryl gallate. These two molecules combine the steric barrier with a larger polarisability due to the presence of double bonds in their structures. This leads to a reduction of the attractive force (V_{A}) between the particles through the modification of the Hamaker constant of the surface.

As expected, the lowest viscosity is reached for the dispersions containing Solsperse3000. This can be explained in terms of the chain length of this molecule since all other parameters, anchor group and tail structure, are approximately the same. The increase in the chain length from 18 C atoms for the fatty acids (∼4 nm) to 66 C atoms (>10 nm) in the case of Solsperse3000 leads to a much higher repulsive force V_{R}.

3.2. Influence of solvents on dispersion properties

The effectiveness of Solsperse3000 was subsequently tested with different solvents ranging from strong apolar organic media like dodecane, kerosene (JET A1) and xylene, to more polar media like DEG-MBEA and terpineol. Some selected physical and chemical data of these solvents are given in Table 3. The rheology of these pure solvents were assessed and found to be near-Newtonian in all cases.

40 vol.% YSZ suspensions with a dispersant concentration ranging from 0 to 2.0 wt.% could be prepared in DEG-MBEA and terpineol. The viscosity of the dispersions without Solsperse3000 measured at $100\,\mathrm{s}^{-1}$ was 10.2 ± 0.9 Pa·s for DEG-MBEA and 7.1 ± 0.3 Pa·s for terpineol. In the case of the strong apolar solvents, the preparation of dispersions with less than 0.5 wt.% Solsperse3000 turned

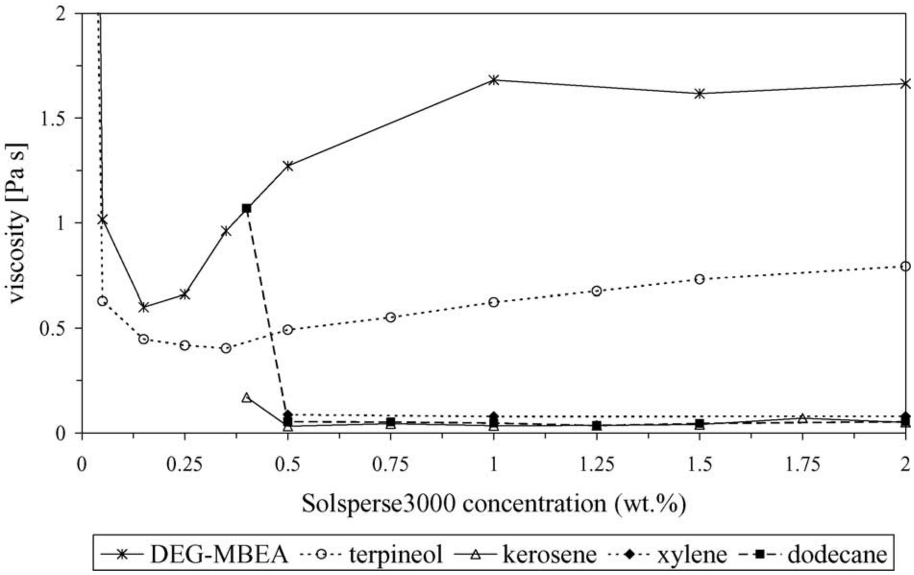


Fig. 5. Viscosity of the dispersions prepared with different organic media. (✶) DEG-MBEA; (○) terpineol; (△) kerosene; (◆) xylene; and (■) dodecane.

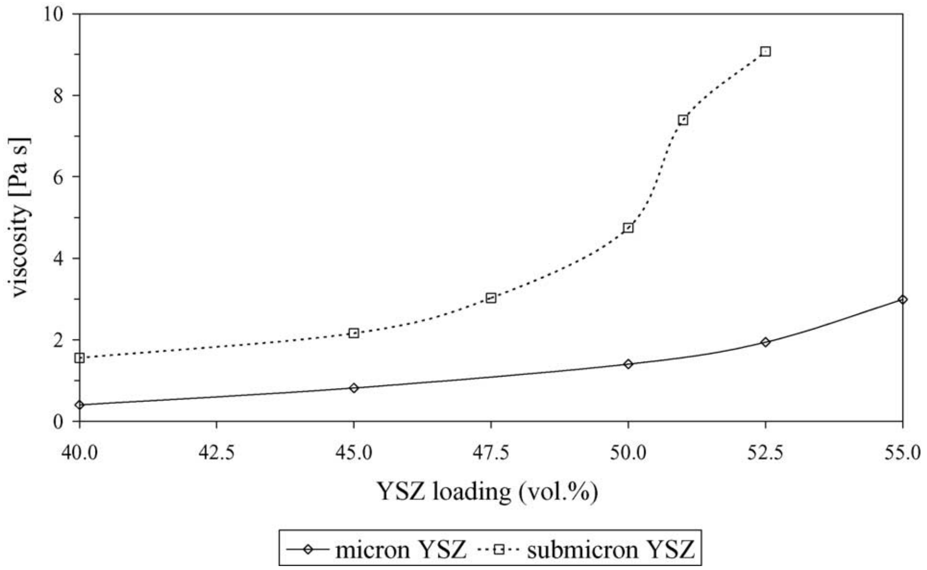


Fig. 6. Viscosity of the terpineol-Solsperse3000 dispersions as a function of powder size and solids loadings. (◇) Micron YSZ; and (☐) submicron YSZ.

out to be very difficult, with the viscosity increasing suddenly and preventing the preparation of these dispersions. While terpineol and DEG-MBEA contain polar groups in their molecular structures, the apolar solvents contain no such groups and consequently particles agglomerate when mixed in these liquids. The minimum concentration of dispersant necessary to obtain free-flowing dispersions in these cases was 0.4 wt.% for kerosene and dodecane, and 0.5 wt.% for xylene.

Fig. 5 summarises the results obtained with the various solvents. It is obvious that the less polar the solvent is, the lower is the viscosity of the dispersion prepared with it. Compared to the dispersions in DEG-MBEA, those prepared in terpineol, have significantly lower viscosity. Above 0.5 wt.% Solsperse3000, the viscosity in terpineol is smaller by a factor of three and the minimum viscosity is smaller by a factor of 1/3. In the more apolar solvents the viscosity decreases by a further factor of 10. The lowest viscosity was obtained in dodecane and kerosene (JET A1), whereas dispersions in xylene show slightly higher viscosity.

For all the solvents, the viscosity increases by varying degrees after passing through a minimum. This increase is likely due to dispersant–dispersant and/or dispersant–solvent interactions due to the free dispersant molecules in solution. Interestingly, the Solsperse3000 concentration necessary to obtain the minimum viscosity varies from solvent to solvent. For DEG-MBEA the minimum lies at around 0.15–0.25 wt.%, corresponding to surface

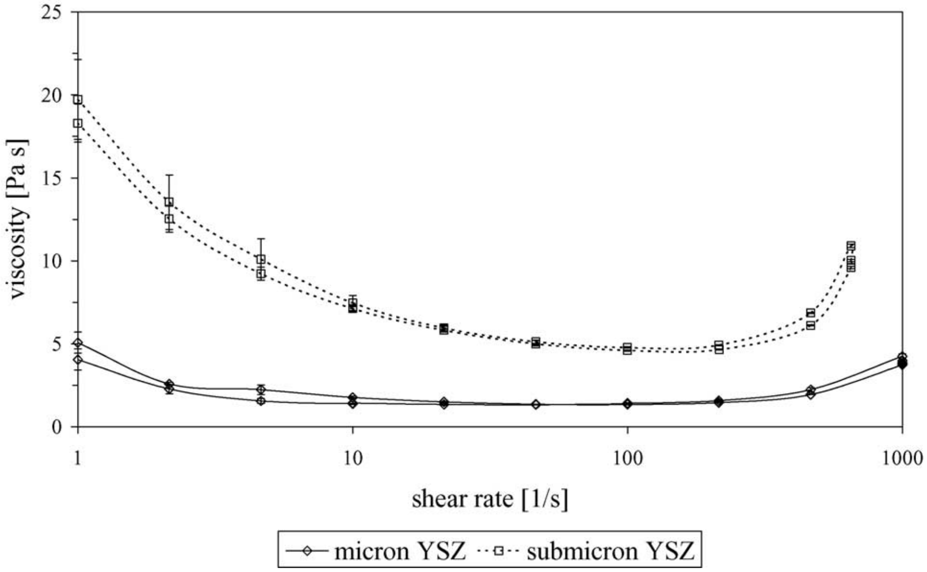


Fig. 7. Viscosity as a function of shear rate of 50 vol.% YSZ dispersions in terpineol. (◇) Micron YSZ; and (☐) submicron YSZ.

concentration of 0.35–0.6 mg/m^2 (assuming 100% adsorption). In the case of terpineol, the minimum was found at about 0.35 wt.% of Solsperse3000, corresponding to 0.8 mg/m^2. For kerosene, dodecane, and xylene the minima in the viscosity were reached at about 1 wt.%, corresponding to ~2.3 mg/m^2. These effects emphasise the importance of the dispersant–solvent interactions.

The lower viscosity of the dispersions with the apolar solvents can be explained by better solvation of the dispersant tail and better matching of the Hamaker constants of the solvent and the powder particles covered with adsorbed dispersant.

3.3. Dispersions with different powder particle size and powder concentration

The relatively high viscosity of the terpineol dispersions prevented the YSZ particles from sedimenting too quickly, making terpineol a very attractive solvent for ceramic dispersions. The dispersions with Solsperse3000 showed long time stability for over three months. To analyse this behaviour further, the rheology of dispersions with different solid loadings and two different YSZ powder grades was investigated. The dispersions with the finer submicron powder (Tosoh TZ8-YS) were prepared by attrition milling (Netzsch PE 075, Netzsch Feinmahltechnik GmbH, Germany) during 3 h with 3 mm YSZ milling beads.

Fig. 6 shows the viscosity with respect to the powder concentration for dispersions of the two powders. The viscosity increases with increasing volume fraction of ceramic powder and with decreasing particle size. Volume fraction and particle size impact the rheological behaviour in two ways, affecting both the density of interparticle links and the microstructure of the suspension.[12,16,18,30] The dispersion containing 55 vol.% of the coarser micron powder (FYT13-005) has about the same viscosity (3.0 ± 0.1 Pa·s) as the 47.5 vol.% submicron YSZ dispersion. In the case of the micron powder, dispersions with solid loadings up to 55 vol.% (88.7 wt.%) could be prepared, while for the submicron YSZ powder the maximum achievable loading was 52.5 vol.% (87.7 wt.%). The dispersions with solid loadings greater than 50 vol.% showed strong shear thickening behaviour above 100 s^{-1}, as shown in Fig. 7. In such highly-concentrated dispersions, shear thickening behaviour is common because the increase in shear stress requires increased ordering of the particles in the dispersion, leading to a higher viscosity.

4. Conclusion

The effects of dispersant molecular structure and solvent type on the dispersion of YSZ particles in organic media were studied during this work. The following conclusions can be drawn: (1) –OH is not a good anchoring group for dispersants; (2) $-NH_2$ is a better anchoring group but also not very effective, although, as a base group, it is expected to provide a degree of electrostatic stabilisation; (3) chelating anchoring groups like –COOH and *ortho*-dihydroxybenzene (catechol) moieties bind very effectively to the YSZ surface; (4) a difference in length of two carbon atoms in the chain of semisteric dispersants does not influence the dispersing properties of these molecules; (5) the presence of double bonds within the chain structure leads to better stabilisation of the particles due to the larger polarisability of the dispersant molecules and the resulting reduction in the Hamaker constant of the dispersed particles; and (6) the combination of a strongly-adsorbing anchor group with a chain length longer than 10 nm leads to the best results as observed for the commercial dispersant Solsperse3000 in this work. These remarks can in future be taken in account for the design of a new dispersant: It should have an *ortho*-dihydroxybenzene moiety as an anchoring group and should include some double bonds in a “tail” which is at least 10 nm long.

With Solsperse3000, dispersions with very low viscosity in strong apolar solvents like dodecane can be produced. On the other hand, dispersions of YSZ with Solsperse3000 in terpineol are stable over long periods, making this combination suitable for many ceramic processing applications. Even in the case of submicron YSZ powder, free-flowing dispersions with up to 52.5 vol.% (87.7 wt.%) solid loading can be produced.

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