# Effect of aminosilane adsorption on rheology of silica powders in nonaqueous media

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An aminosilane, *N*-(3-acryloxy-2-hydroxyl propyl)-3-amino-propyltriethoxysilane (AHAS), was used to disperse and stabilize Stober silica suspensions via steric stabilization in non-aqueous media. The effect of variables, such as the calcination temperature of the silica, the water content of the solvents, the physicochemical properties of solvent media, the particle size distributions of the silica, and the proportions of mixed solvent were studied. Viscosity measurements were conducted to assess the dispersion behaviour of the silica suspensions. Fourier transform-infrared analysis was used to deduce the mechanism of AHAS adsorption on the silica surface. The effect of the water content in the silica suspension was found to be highly dependent upon the degree of silica surface hydration before AHAS addition and also upon the kind of solvent medium used. It was observed that electrostatic contribution to the silica stabilization was appreciably greater than anticipated and was found to be a function of the relative acid-base nature of the organic solvent. Analyses of rheological data and infrared spectra were used to explain the behaviour of the silica suspensions.

## 1. Introduction

Recent developments in complicated and precise ceramic products require greater control over the powder processing techniques. Understanding of the particle/liquid/dispersant interactions, such as wetting and dispersion phenomena, to control rheological properties is essential in optimizing the properties of the processed materials [1]. Well-dispersed systems, in which particles are well separated in the liquid medium, are desirable in ceramic powder-forming processes such as tape casting and injection moulding. Higher solid loadings can be obtained from welldispersed systems while retaining acceptable viscosity values for processing. It is well known that a key to high green density and homogeneous microstructure is in the dispersibility of the starting powder materials. [2].

Pure silica glass is an expensive material largely because of the difficulties in the manufacturing process. Silica has a high melting point, high viscosity, volatility, and a propensity for dissolving its container [3]. These difficulties may be avoided if a plastic forming process, such as slip casting, tape casting, or injection moulding, can be used followed by sintering to the full density at low temperature (< 1000 °C) without melting [4]. Good dispersion and high solids loading in the suspension are keys to the processing conditions.

Non-aqueous solvents are sometimes preferred to work with when the presence of water in the ceramic powder suspension causes deleterious effects (e.g. development of oxide surfaces) and where a complicated ceramic-forming process is required. The presence of water in the silica suspension may or may not play an important role in the stabilization of the silica particles in non-aqueous solvents. It is dependent upon the degree of silica surface hydration and the kind of solvent medium used. The interactions between particles with the added organic dispersant highly depend on the nature of the particle surface and the solvent medium [5–7].

Limited resources are available to understand the stabilization of ceramic powders in non-aqueous solvents. Steric stabilization has been thought to be the main mechanism of dispersion of fine particles in non-aqueous solvents [8, 9]. Steric stabilization can be achieved by constructing a physical barrier around the ceramic particles with an adsorbed layer of polymers [9, 10]. The thicker the layer, the greater is the separation of the particles, and hence the more stable the dispersion. However, ceramic powders dispersed in non-aqueous solvents can produce larger electrostatic potentials than those dispersed in water [11].

Ion formation in silica suspensions prepared with non-aqueous solvents is dependent upon an interfacial process between the particles and the organic medium by which hydrogen ions are transferred to the ceramic particles [11]. When the silica surface is positively charged, the particles should be deposited on the cathode and vice versa in an electrophoresis. These electrostatic repulsive forces on the silica surface reduce interparticle van der Waals interactions and thus

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cause the viscosity values to decrease. This should contribute to high green density and homogeneous microstructure of the green body [12].

It should be possible then that the best stabilized dispersion be obtained from an optimal combination of steric and electrostatic stabilization. It was the objective of this study to investigate the effects of such variables as the calcination temperature of the silica, water content of the solvent, the physico-chemical properties of the organic solvent medium, and the amount of solids loading on the rheology of silica suspensions.

## 2. Experimental procedure

The overall flow diagram showing the experimental procedure is given in Fig. 1.

## 2.1. Materials

High-purity submicrometre monosized  $(0.45 \ \mu m)$  spherical silica particles were produced by hydrolysis/precipitation method of Stober et al. [13]. The as-synthesized Stober silica was calcined at 90 °C for 24 h in air to remove adsorbed ammonia and alcohol. It was then washed with deionized water to remove soluble impurities. To investigate the effects of the silica surface hydroxyl groups on the stabilization of silica suspensions in organic media, silica powders were calcined in an alumina crucible at 200, 500 and 750 °C for 6 h in air. Scanning electron microscopy showed that the particle size was unaffected by the calcination treatments. X-ray diffraction revealed that the silica powder was amorphous. All of the organic solvents used were HPLC grade and used without



Figure 1 Experimental flow diagram.

Silica		Organic solvent			
Calcination ten	pperature (°C)	Acid	Solvent	Lewis acid/base	Dielectric constant
Silica calcined	200	strong acid	Chloroform	Acid	4.79
	500	t	Ethyl Alcohol	Weaker acid	24.55
	750	weak acid	Acetone	Weaker base	20.7
			Tetrahydrofuran	base	7.58

TABLE I Materials characteristics (SiO<sub>2</sub>, organic solvent)

further purification. The organic solvents studied were chloroform  $(CHCl_3)$ , ethyl alcohol (EtOH), acetone, and tetrahydrofuran (THF). Relevant physical and chemical properties of these are listed in Table I along with other materials used. *N*-(3-acryloxy-2-hydroxyl propyl)-3-amino-propyltriethoxysilane (AHAS) which has polar anchoring groups and a long extended nonpolar group, was used as a dispersant and cross-linker binder. The structural formula for AHAS is given in Fig. 2. Deionized water was added in incremental amounts to the organic solvents to investigate the effect of water on the rheology of the silica suspensions.

#### 2.2. Viscosity measurements

A Brookfield digital viscometer (model LVT DV-II, Brookfield Engineering Laboratory, Stoughton, MA) was employed to examine the rheological behaviour of the silica suspensions prepared in the non-aqueous media. The model LVT DV-II is an automatic digital viscometer with continuous sensing designed for lowviscosity fluids. The viscometer was fitted with a small-sample adaptor and spindle number 31. The small-sample adaptor allowed the viscometer to operate on coaxial cylinders, thus providing accurate values even at low shear rates. All of the silica suspensions examined were prepared at a 35 vol % solids loading unless otherwise stated, and with 5 wt % AHAS loading. The amount of HPLC grade organic solvents for each suspension was 7 ml. To study the effect of water in the silica suspensions, various amounts of deionized water were added to the organic solvents.When this was done, the total amount of water and organic solvents was still 7 ml so as not to change the volume fraction of the solids loading. The suspensions were ultrasonicated under an air-tight cover for 15 min prior to measuring the viscosity.

#### 2.3. Electrophoretic deposition study

After the viscosity measurements, the silica suspensions were placed in a high d.c. voltage supply (Spellman, Model RHR 30PN30) with copper plate electrodes. This was to examine the electrokinetics of the silica particles in organic media. If silica particle

$$\begin{array}{cccc} 0 & OH & H \\ \parallel & & 1 \\ H C = CH - C - O - CH CH - CH & - N - (CH)_{3} Si(OEt)_{3} \end{array}$$

Figure 2 Chemical structure formula of AHAS: N-(3-acryloxy-2-hydroxylpropyl)-3-amino-propyltriethoxysilane.

surfaces are positively charged, they will move to the cathode and be deposited on the electrode. Similarly, silica particles will move to the anode if they are negatively charged. The amounts of silica deposited on the electrode in a given time is the indication of electrokinetics and the charge on the Stern layer of the silica surface.

### 2.4. Ultraviolet spectrophotometry

Ultraviolet absorption was used to determine the amount of AHAS adsorbed on the silica surface. The silica suspensions were centrifuged at 2500 r.p.m. for 60 min to separate the silica particles from the suspension. The supernatant was carefully withdrawn and quantitatively analysed by ultraviolet absorption at  $\lambda = 340$  nm for AHAS in acetone and at  $\lambda = 250$  nm for AHAS in ethyl alcohol.

#### 2.5. Fourier transform-infrared (FT-IR) spectrophotometry

Infrared spectra were taken to check AHAS adsorption on the silica surfaces and to possibly determine which functional group of AHAS was used to anchor on the silica surfaces. A diffuse reflectance stage in a Perkin-Elmer FT-IR 1600 spectrophotometer was used with a wave number range 4000-400 cm<sup>-1</sup>. After centrifugation of the silica suspension, the sedimented silica was washed with the same solvent to remove the excess AHAS on silica surfaces and then dried in a vacuum oven at 90 °C for 12 h to remove the organic solvents. The sediment was then subjected to infrared runs. The AHAS adsorption isotherms on the wellcharacterized silica surface were obtained as a function of silica calcination temperatures in acetone and ethyl alcohol. These two media were selected for their relative basicity and acidity to the silica surface, respectively, and their high miscibility with water.

#### 3. Results and discussion

Fig. 3 shows the effect of AHAS adsorption on the rheology of silica suspended in four different non-aqueous media. A mild shear thinning behaviour is shown at the low shear rates for all of the media. This was expected for such crowded silica particles of colloidal size. The suspension prepared with acetone and AHAS produced well-dispersed suspensions with the lowest viscosity value of 4 mPa s at 60 r.p.m. shear rate. Acetone must be the best solvent for the AHAS system and EtOH the worst. These results can be



Figure 3 Plot of viscosity versus shear rate for 30 vol % silica suspensions prepared with silica calcined at 750 °C in four different solvents with AHAS. ( $\square$ ) Chloroform, ( $\blacklozenge$ ) ethyl alcohol, ( $\blacksquare$ ) acetone, ( $\diamondsuit$ ) tetrahydrofuran.

understood by analysis of electrostatic and steric stabilizations which contribute to silica stabilization in the non-aqueous solvents. Tables II–IV show the results of electrophoretic deposition experiments. A silica surface was charged positively when it was dispersed in acidic solvents such as chloroform, whereas basic solvents such as acetone and THF caused negative charge, which stabilized the silica suspensions by electrostatic repulsive forces between the charged particles. Tetrahydrofuran (THF) and chloroform

TABLE II Solvent effect on electrokinetic behaviour of silica particles

Solid	Solvent	Charge of silica <sup>a</sup>
Silica	Chloroform	More positive
	Ethyl alcohol	None
	Acetone	Negative
	Tetrahydrofuran	More negative

<sup>a</sup> Assessed by particle deposition kinetics

TABLE III Silica calcination effect on electrokinetic behaviour of silica particles in acetone

Calcination temp. (°C)	Solvent	Change of silica <sup>a</sup>	
200	Acetone	More negative	
500	Acetone	Negative	
750	Acetone	Less negative	

<sup>a</sup> Assessed by particle deposition kinetics.

TABLE IV Water and AHAS effects on electrokinetic behaviour of silica particles

Solid	Organic media	Charge of silica <sup>a</sup>
Silica	Acetone	More negative
	Acetone + AHAS	Negative
	Acetone + Water	None
	THF	More negative
	THF + AHAS	Negative
	THF + water	None
	Water $(pH = 2.5)$	None
	Water $(pH = 5)$	Less negative

<sup>a</sup> Assessed by particle deposition kinetics.

(CHCl<sub>3</sub>) generated the largest electrostatic potentials which should contribute to the greater dispersibility of the silica particles. An acidic silica surface in a basic medium becomes negatively charged by donating protons to the medium. Similarly, the silica powders in a stronger acidic medium, i.e. chloroform, become positively charged. However, THF, which is more basic than acetone, competes with AHAS for the acidic silanol groups on the silica surfaces. Chloroform is apparently more acidic than the silica surface because it caused the silica particles to move to the cathode and became stabilized by electrostatic repulsive forces between positively charged particles. Addition of AHAS reduced the surface charge of the silica, as a result of the base action of AHAS. However, chloroform tends to solvate and neutralize the basic groups of the AHAS and should curtail AHAS adsorption (if the solvent is more acidic than the surface sites of the acidic silica) [14]. This would reduce the steric stabilization effect. Silica suspensions prepared with AHAS and acetone in this study showed the most welldispersed suspensions. This must be a combination of two factors: steric and electrostatic stabilization, suggesting that an optimal combination of steric and electrostatic stabilization had been reached. From these considerations the best well-dispersed silica suspension prepared in non-aqueous media is obtained by electrosteric (electrostatic and steric) stabilization.

The effect of particle modality on the silica rheological behaviour is shown in Fig. 4. For monodispersed systems the volume fraction of the spherical powder packing in a liquid is limited to 68 vol %. In order to obtain higher powder packing density, multidispersed systems may be utilized. In bimodal distributions of spherical ceramic powder suspensions, particles having diameter d (small particle size) and D(large particle size) should be controlled by calculating the interstitial sizes and the volume fraction. When additional smaller particles larger than the interstitial sizes, or an excess amount of additional smaller particles are added in monodispersed systems, powder packing density is not improved [15]. Fig: 4 shows that the use of trimodal silica particles is an effective



*Figure 4* The effect of silica particle size distribution on the silica suspensions prepared with silica calcined at 750 °C. ( $\Box$ ) 0.452 µm, ( $\blacklozenge$ ) 0.52 µm, ( $\blacksquare$ ) 0.595 µm, ( $\diamondsuit$ ) 0.452 µm, 0.52 µm ( $\blacksquare$ ) 0.452, 0.52 and 0.595 µm.

way to lower the viscosity of silica suspensions prepared with acetone and AHAS at a given solids fraction. As particle sizes decrease, it becomes difficult to maintain the low viscosity of the silica suspensions. At a given solids loading, multidispersed powder gives lower viscosity. An optimum particle size distribution, e.g. multidispersed powders, should be utilized to obtain higher powder packing density in a ceramic powder suspensions [16]. In order to obtain high green density and homogeneous microstructure, the green bodies should be prepared with well-dispersed ceramic particles. The suspension must have high solids loading within the acceptable viscosity range, which depends on the particular forming process. However, the packing uniformity requirements are less critical for monodispersed powders than multidispersed ones. Good sinterability could be obtained with the multidispersed powders if homogeneity in the spatial distribution of powder packing is carefully controlled [17]. Therefore, the limitation of ceramic particle size distributions should be well controlled to obtain the highest packing density. We are now studying the relationship between particle size and polymer chain length. Such small ceramic particles are easily flocculated because one polymer molecule may extend through many bridges.

Figs 5 and 6 show the effects of water in both acetone and ethyl alcohol on the silica suspensions prepared with 200 and 500  $^{\circ}$ C calcined silica. The rheology of the silica suspension is less sensitive to water in EtOH medium than in acetone for silica



Figure 5 The effect of water in (a) acetone and AHAS and (b) EtOH and AHAS suspension prepared with silica calcined at 200 °C. ( $\Box$ ) 0.0 ml, ( $\blacklozenge$ ) 0.5 ml, ( $\blacksquare$ ) 1.0 ml, ( $\diamondsuit$ ) 2.0 ml.



Figure 6 The effect of water in (a) acetone and AHAS and (b) EtOH and AHAS on silica suspension prepared with silica calcined at 500 °C. ( $\Box$ ) 0.0 ml, ( $\blacklozenge$ ) 0.5 ml, ( $\blacksquare$ ) 1.0 ml, ( $\diamondsuit$ ) 2.0 ml.

calcined at 200 and 500 °C. This may be due to the greater dielectric constant of EtOH than that of acetone (Table I). It is also true that water is more like EtOH with respect to Lewis acidity-basicity. The increases in viscosity, which were the result of the increase in water contents in the silica suspension prepared with acetone and EtOH, are explained by the fact that water reduced the electrostatic potentials of the silica particles (Table IV). Table V shows that the water in acetone produces little change in the AHAS adsorption isotherms at room temperature on the silica surface. However, water in EtOH increased

TABLE V Amount of AHAS adsorption on silica particles

Calcination temperature (°C)	Organic solvent with AHAS and amount (ml)	Water in solvent (ml)	AHAS <sup>a</sup> adsorption amount (g/g silica)
200	Acetone (10)	0.0	0.020
500	Acetone (10)	0.0	0.015
750	Acetone (10)	0.0	0.011
200	Acetone (8.5)	1.5	0.021
500	Acetone (8.5)	1.5	0.016
750	Acetone (8.5)	1.5	0.013
200	EtOH (10)	0.0	0.015
500	EtOH (10)	0.0	0.009
750	EtOH (10)	0.0	0.005
200	EtOH (8.5)	1.5	0.021
500	EtOH (8.5)	1.5	0.015
750	EtOH (8.5)	1.5	0.012

<sup>a</sup> At room temperature

the AHAS adsorption. Water reduced the solubility of AHAS in EtOH and reduced the EtOH/AHAS interaction by lowering the acidity of the EtOH. This increased the amount of AHAS adsorption on the silica surfaces, which agrees with the results of Stromberg *et al.* [18]. They also observed increases in the amount of polyester adsorption on alumina as the solubility of the polymer was decreased by changing the non-aqueous solvent. However, water in EtOH decreased the electrical double layer on the silica surfaces and caused aggregation of silica particles thus raising the viscosity of the silica suspension. This is supported by the work of Micale *et al.* [19] who used heptanol and a trace of water for titanium dioxide particles.

Fig. 7a shows the greater dependency of water content on the rheology of 750 °C calcined silica suspensions in acétone than that for silica calcined at 200 and 500 °C. This is because the silica calcined at 750 °C is less hydrated and less acidic than silica calcined at 200 and 500 °C. This makes the added water interact more with the basic AHAS and less with the silica surfaces. This decreased the surface charge of the silica (Table IV) especially for 750 °C silica. Fig. 7b shows that water amounts less than 2 ml (29 vol %) in silica suspensions prepared with AHAS in EtOH have little effect on dispersion rheology. This suggests a strong adsorption of AHAS on the silica surface. Water can easily form a hydrogen bond with EtOH through the OH groups and reduce the relative acidity of EtOH (see Tables II-IV). This should reduce the AHAS/ EtOH interaction and increase the amount of AHAS adsorption on the silica surface, causing greater steric contribution to the silica stabilization. It has generally been shown that the effect of water in EtOH on silica suspensions was less than that in acetone. In EtOH, increased adsorption of AHAS on silica surfaces occurred with water addition (Table V). This is in disagreement with the two requirements for effective steric stabilization, i.e. strong adsorption of the dispersant molecules on the solid surface and high solubility of the long tail of the molecules extending into the medium. The latter is best satisfied by  $\theta$ -solvent. Addition of water must reduce the solubility of the AHAS dispersant molecules which should lower the steric contribution to the suspension stabilization. It was shown that the charge was little affected by the added water, as indicated by the viscosity increase in Figs 5-7. Much more work is needed to understand the effect of water in non-aqueous solvents on the rheological behaviour of silica suspensions.

Fig. 8a shows that increasing calcination temperatures increased the viscosity of the silica suspensions. This happened because the stabilization of silica suspensions prepared with acetone were greatly affected by electrostatic forces developed from the transfer of hydrogen ions to the silica particles, as given in Tables II-IV. The stabilization of silica particles in acetone solvent is sensitive to the hydroxyl groups on the silica surface and the presence of water in the



Figure 7 The effect of water in (a) acctone and AHAS and (b) EtOH and AHAS on silica suspension prepared with silica calcined at  $750 \,^{\circ}\text{C.}$  ( $\Box$ ) 0.0 ml, ( $\blacklozenge$ ) 0.5 ml, ( $\blacksquare$ ) 1.0 ml, ( $\diamondsuit$ ) 2.0 ml.



Figure 8 The effect of silica calcination temperature on silica suspension prepared with (a) acetone and AHAS, and (b) EtOH and AHAS. ( $\Box$ ) 200 °C, ( $\blacklozenge$ ) 500 °C, ( $\blacksquare$ ) 700 °C.

solvent medium. For ceramic-powder stabilization in aqueous media, the number of surface hydroxyl groups often has an influence on the adsorption of dispersant molecules [20]. There is no reason for polymer adsorption on silica in non-aqueous media to be insensitive to surface hydration of the adsorbent silica. This adsorption depends on the kind of adsorbing functional group on the silica surface and the electrostatic behaviour of the silica suspension. Fig. 8b shows a smaller change in the viscosity of the silica suspensions in EtOH than in acetone as the calcination temperature was increased. The same reasons given for previous figures should apply here. EtOH is considered to be a relatively neutral or weakly acidic solvent compared with the other organic solvents used in this study. Silica particles are partly stabilized by AHAS adsorption on the silica surfaces and partly stabilized by the surface charge. The greater the degree of calcination, the lower is the surface charge on the silica in an aqueous medium [21]. This is also shown to be true in a non-aqueous medium (Table III). Table V shows less adsorption of AHAS for greater degrees of calcination. These two effects, reduced charge and reduced adsorption, must have caused the increase in the viscosity as the calcination temperature increased.

Fig. 9 shows the effect of mixed solvents on the silica rheology. The solvent quality for AHAS was studied for various ratios of acetone and chloroform by observing the rheological and electrokinetic behaviour of the silica suspensions. Because acetone is a basic solvent and chloroform is an acidic solvent, mixing the two solvents would modify the acid/base nature of the solvent and the solvent parameters. This, in turn, may alter the interaction between the solid-solvent, solvent-dispersant, and solid-dispersant. As the basicity of the solvent increased, polymer adsorption (Table V) and electrostatic potentials on the silica particles increased (Table II) producing more stable suspensions (Figs 3 and 9). The results in Fig. 9 indicate that 0% CHCl<sub>3</sub> in acetone for 200 °C calcined silica, the volume ratio of 1:1 CHCl<sub>3</sub>/acetone for 500 °C calcined silica, and 6:1



Figure 9 Plot of viscosity versus various chloroform/acetone ratios for silica suspensions prepared with AHAS.(  $\Box$  ) 200 °C, ( $\blacklozenge$ ) 500 °C, ( $\blacksquare$ ) 750 °C.

CHCl<sub>3</sub>/acetone for 750 °C calcined silica are the best solvent mixture ratios for the silica suspensions. Because silica suspensions are stabilized by two factors, electrostatic and steric stabilization, the best solvent mixture to produce electrostatic repulsive forces on the silica particles and steric hindrance by adsorbing AHAS on the silica surface is changed depending on the silica surface chemistry. Because silica calcined at  $200 \,^{\circ}\text{C}$  is more acidic than that calcined at  $750 \,^{\circ}\text{C}$ , the more basic solvent mixture, i.e. more acetone, gave a greater effect for 200 °C calcined silica, to develop electrostatic charges on the silica particle surfaces. However, 750 °C calcined silica dispersed in the acidic medium CHCl<sub>3</sub> developed greater electrostatic charges on the silica surfaces than for 200 °C calcined silica in the same medium. This is because the surface became less acidic, i.e. more basic, which made CHCl<sub>3</sub> relatively more acidic.

Fig. 10 shows the effective solids loadings with the acceptable limit of the viscosity value for processing. The silica suspension prepared with acetone and AHAS for 50 vol % solids loading still produced viscosity values below 1000 mPas which is acceptable for a processing operation such as slip casting. These experimental results show that AHAS is an effective dispersant for the stabilization of the colloidal silica prepared with acetone.

Fig. 11 shows the infrared spectra for AHAS adsorbate on the silica surface. The results are consistent with the ultraviolet absorption data. The AHAS band observed in the range  $1640-1630 \text{ cm}^{-1}$  in these materials is associated with N–H bending vibrations. When the silica calcination temperature is increased, the infrared spectra in the range  $1640-1630 \text{ cm}^{-1}$  are decreased. This indicates that the amount of AHAS adsorbed on the silica surfaces decreased with increasing calcination temperatures.

Chemisorption of AHAS on silica surface should cause a shift in the infrared peaks to higher wave number. Because AHAS has several possible adsorption sites, the peak shifts may give information about the adsorption mechanism. The peak shifts of Si–O and N–H functional groups due to adsorption of



Figure 10 Plot of viscosity versus shear rate for silica suspensions prepared with silica calcined at 200 °C in acetone with 5 wt % AHAS for different solids loadings:  $(\Box)$  30 vol % without AHAS,  $(\bullet)$  20 vol %,  $(\Box)$  30 vol % ( $\diamondsuit$ ) 40 vol %,  $(\blacksquare)$  50 vol %.



Figure 11 Diffuse reflectance FTIR spectra of AHAS adsorbate on the silica particle surfaces prepared with different calcination temperatures of silica suspended in (a) acetone and AHAS and (b) EtOH and AHAS: (1) 200 °C; (2) 500 °C; (3) 750 °C.

AHAS are tabulated from Fig. 11 and given in Table VI. In the acetone system,  $\overline{v}_{si-O}$  shifted downwards as the calcination temperature increased. This suggests that AHAS adsorption on the silica surface is favoured for a more hydrated surface, i.e. less AHAS adsorption via Si-O as the calcination temperature increased. However, the AHAS adsorption increased via the N-H functional group. The N-H group on AHAS can adsorb on silica via the hydrogen bond.

Thus it appears that AHAS adsorption via the N–H functional group is favoured as the silica surface becomes more and more dehydroxylated. In ethanol, this is partially reversed. The intermediate calcination temperature, 500 °C shows the most adsorption of AHAS via the Si–O group. At 500 °C, the surface is partially hydrated. The most adsorption via the N–H group is shown for 200 and 500 °C. At 750 °C, the silica surface is less acidic and the basic group N–H in

TABLE VI Infrared peak shifts of  $\bar{v}_{Si-O}$  and  $\bar{v}_{N-H}$  as a function of calcination temperature

Solid/organic media	Calcination temperature (°C)	$\bar{v}_{si \rightarrow 0}$ (cm <sup>-1</sup> )	$\overline{\nu}_{N \rightarrow H}$ (cm <sup>-1</sup> )
Acetone + AHAS	200	1105	1626
	500	1100	1635
	750	1090	1645
EtOH + AHAS	200	1088	1635
	500	1095	1632
	750	1094	1625

AHAS would interact less with the solid surface, hence giving less adsorption. It appears that the influence of the solvent media and silica surface chemistry on the adsorption mechanism is significant. A more systematic study is required to confirm these effects.

## 4. Conclusions

1. AHAS is an effective dispersant for silica stabilization in non-aqueous media.

2. Silica suspensions prepared with acetone and AHAS give the best stabilized system due to the best combination of steric and electrostatic stabilization.

3. The effect of water content in silica suspensions is highly dependent on the degree of silica hydration before the AHAS addition and the kind of solvent medium.

4. Analysis of ultraviolet absorption results and electrophoretic deposition results developed a better understanding of silica stabilization in non-aqueous media.

5. The mechanism and the amount of AHAS adsorption on the silica surface could be detected by analysis of the shift in infrared peaks and the increase of the AHAS peak areas. The solvent media are important in determining the adsorption sites of AHAS on silica surface.

6. It is evident that there are many interactions in the silica suspension system. A more systematic study is needed to identify the effect of each contributing interaction.

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