



# Intrinsically stable dispersions of silicon nanoparticles

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## ABSTRACT

Stable suspensions of silicon nanoparticles (SiNP) were fabricated by dispersion in 1-butanol as well as ethanol without the application of an additive. In order to achieve an in-depth insight into the stabilizing mechanism, the particle–particle interactions need to be considered. In this respect the total interaction energy of the silicon nanoparticles in 1-butanol and ethanol was calculated for three model systems according to the DLVO theory: (1) two solid silicon spheres, (2) two spheres with a silicon core and an amorphous silicon dioxide shell, and (3) two spheres with a silicon core, an amorphous silicon dioxide shell and a monolayer of adsorbed solvent molecules. The results of the calculations are evaluated and discussed with regard to experimental data obtained by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), high resolution transmission electron microscopy (HRTEM), and zeta potential measurements.

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## 1. Introduction

Nanoparticles are of growing interest in many areas of the chemical, pharmaceutical, ceramic, and microelectronic industry from the scientific as well as the technological point of view. Applications range from pigments, nanocomposites, drug delivery and ceramic materials to the fabrication of thin semi-conductive films based on various printing technologies. Therefore a high industrial demand exists on stable suspensions (with regard to aggregation) of nanoparticles in aqueous as well as non-aqueous media. Besides the direct synthesis by chemical methods, wet grinding and dispersing are suitable methods for the production of nanoparticulate systems, since a high specific energy input is accomplished [1]. However, the stability of the dispersions is strongly influenced by particle–particle interactions. Particles in the order of 1  $\mu\text{m}$  and below feature a high mobility due to Brownian diffusion, which leads to a high collision frequency between the particles. Non-stabilized nanoparticles usually tend to aggregate easily, especially when dispersed in an organic medium. Therefore the particle–particle interactions need to be understood in detail in order to tailor the properties of the nanoparticulate system according to specific needs.

In this case stable suspensions of silicon nanoparticles (SiNP) in an organic solvent are required for the manufacture of electronic/optoelectronic devices using printing technologies. As reported recently [2,3], intrinsically stable suspensions of SiNP in 1-butanol were obtained by dispersing in a stirred media mill

without the application of an additive. This work focuses on determining the particle–particle interactions of SiNP in 1-butanol and ethanol to achieve an in-depth insight into the stabilizing mechanism of the particulate system. In this regard the total interaction energy of the SiNP was calculated via DLVO theory for different models including core–shell approaches. The approach of describing colloidal stability with core–shell models has been reported in literature before [4–6]. The results of the calculations of this work are evaluated and discussed with regard to experimental data obtained by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), high resolution transmission electron microscopy (HRTEM) and zeta potential measurements.

In literature a suspension is typically considered as stable [7,8], if the total interaction energy develops an energy barrier larger than  $15kT$ . However, this approach explains the observed stability of the SiNP only for a limited range of particle sizes. The present work shows that one has to consider not only the height of the energy barrier but also the depth of the primary minimum of the total interaction energy, to achieve a detailed understanding of the particle interactions and the associated suspension stability.

## 2. Experimental

### 2.1. Materials

Ethanol (absolute) and 1-butanol (p.a.) purchased from Aldrich and used as received. Silicon nanoparticles (SiNP) with a primary particle size of approximately 100 nm were obtained from Evonik Degussa GmbH (Evonik). Suspensions of 20 wt% SiNP in 1-butanol and in ethanol (volume fraction 0.080 and 0.078, respectively)

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were dispersed for 6 h using a stirred media mill. A detailed description of the dispersing procedure is reported elsewhere [2,3].

## 2.2. Transmission electron microscopy (TEM)

A suspension of SiNP was placed on an ultra thin carbon film on a 400 mesh Cu-grid and then dried in air. The HRTEM images were obtained using a Philips CM 300 UltraTwin microscope at an acceleration voltage of 300 kV in the bright-field mode.

## 2.3. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

The DRIFT spectra of the SiNP were recorded on a Varian FTS 3100 FTIR spectrometer equipped with a Pike Technologies EasiDiff accessory.

## 2.4. Zeta potential measurements

The zeta potentials were determined on a Malvern Zetasizer 3000 DTS 5300 by laser Doppler electrophoresis.

# 3. Results and discussion

## 3.1. Theoretical approach

As mentioned before stable suspensions (with regard to aggregation) of SiNP in 1-butanol and ethanol were obtained by dispersing in a stirred media mill [2,3] without the use of any additives. The high stability of SiNP in 1-butanol and ethanol has been predicted theoretically and confirmed experimentally by Bleier [9]. However, only attractive forces were considered thereby and the calculated Hamaker constants differ noticeably from other literature values. In order to achieve a more detailed understanding of the stability of SiNP in 1-butanol and ethanol the total interaction energy of the SiNP was estimated according to the DLVO theory [7,10] in this work. The total interaction energy  $E_T$  results from summation of the van der Waals interaction  $E_{vdW}$ , electrostatic repulsion  $E_{El}$ , and the Born repulsion  $E_B$

$$E_T = E_{vdW} + E_{El} + E_B. \quad (1)$$

For calculations, which explain the stability of the SiNP with regard to the height of the formed energy barrier of the total interaction energy, the Born repulsion can be neglected. For consideration of the primary minimum of the total interaction energy the Born repulsion, approximated by a hard sphere potential at the minimal contact distance of 0.165 nm [11], was included in the calculations. The non-retarded van der Waals interaction  $E_{vdW}$  of two solid spherical particles of radii  $R_1$  and  $R_2$  at a distance  $H$  apart is given by [12]

$$E_{vdW} = -\frac{A}{6} \left\{ \frac{2R_1R_2}{2(R_1+R_2)H+H^2} + \frac{2R_1R_2}{4R_1R_2+2(R_1+R_2)H+H^2} + \ln \left[ \frac{2(R_1+R_2)H+H^2}{4R_1R_2+2(R_1+R_2)H+H^2} \right] \right\}, \quad (2)$$

where  $A$  is the Hamaker constant. For the “symmetric case” of two identical phases 1 interacting across vacuum, one can infer the Hamaker constant  $A_{11}$  via [11]

$$A_{11} = \frac{3}{4}kT \left( \frac{\varepsilon_1 - 1}{\varepsilon_1 + 1} \right)^2 + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_1^2 - 1)^2}{(n_1^2 + 1)^{3/2}}, \quad (3)$$

where  $k$  is the Boltzmann constant,  $\varepsilon$  is the static dielectric constant [13],  $h$  is the Planck constant,  $\nu_e$  is the main electronic absorption frequency in the UV typically around  $3 \times 10^{15} \text{ s}^{-1}$  [11]

**Table 1**  
Applied Hamaker constants

Material	$A_{11} (J \times 10^{-20})$	$A_{11} (kT)$ at 293.2 K
Ethanol	4.24	10.46
Butanol	4.99	12.33
Silicon	20.60	50.89
Amorphous SiO <sub>2</sub>	6.28	15.51

and  $n$  is the refractive index [13]. Equation [3] usually applies to what are normally referred to as dielectric or non-conducting materials [11] and was therefore used for calculating  $A_{11}$  of 1-butanol and ethanol. The calculations of  $A_{11}$  of silicon and amorphous silicon dioxide were based on the dielectric functions for a large energy range instead of the relative dielectric constants for more accurate approximation [14]. The calculated Hamaker constants for all involved materials are listed in Table 1.

An expression for the Hamaker constant  $A_{131}$ , i.e., for the situation of two particles suspended in a liquid, is derived by assuming that the interaction constant between the two different materials equals approximately the geometric mean of the interaction constants of the individual materials [11]. Therefore  $A_{131}$  is given by [11]

$$A_{13} \approx \sqrt{A_{11}A_{33}}, \quad (4)$$

followed by

$$A_{131} \approx A_{11} + A_{33} - 2A_{13}. \quad (5)$$

For media 1 and 2 interacting across medium 3 the Hamaker constant  $A_{132}$  can be written as [11]

$$A_{132} \approx (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}). \quad (6)$$

The electrostatic repulsion  $E_{El}$  between two spherical particles can be estimated by using [8]

$$E_{El} = \frac{a}{\nu^2} \frac{32\pi\varepsilon\varepsilon_0(RT)^2}{F^2} \gamma^2 e^{-\kappa H}, \quad (7)$$

with  $\gamma = (e^{z/2} - 1)/(e^{z/2} + 1)$  and  $z = \nu F\psi_0/RT$ , where  $\nu$  is the valency,  $R$  is the gas constant,  $F$  is the Faraday constant, and  $\psi_0$  is the surface potential [8]. The surface potential  $\psi_0$  was substituted by the zeta-potential  $\zeta$  determined by the means of electrophoresis, i.e.,  $-46.6$  mV for SiNP in 1-butanol and  $-40.0$  mV for SiNP in ethanol.  $\kappa$  is the Debye–Hückel parameter expressed [8]

$$\kappa^2 = \frac{2F^2}{\varepsilon\varepsilon_0RT} I, \quad (8)$$

where  $I$  is the ionic strength. The Debye–Hückel parameter  $\kappa$  has the dimension of a reciprocal length. The quantity  $1/\kappa$  is related to the thickness of the diffuse layer surrounding the particles. Applying the formulas above the total interaction energy  $E_T$  was calculated for three model systems depicted in Fig. 1: (a) two solid silicon spheres (solid sphere model), (b) two spheres with a silicon core and an amorphous silicon dioxide shell (core-shell model), and (c) two spheres with a silicon core, an amorphous silicon dioxide shell and a monolayer of adsorbed solvent molecules (core-shell adsorbate model). For the calculations an overall sphere diameter  $x$  of 100 nm was assumed, which is roughly the primary particle diameter of the SiNP used for the dispersing experiments. The thickness of the shell of amorphous silicon dioxide  $d$  was estimated being 4 nm, whereas the thickness of the adsorbate layer  $\sigma$  was estimated being equal to the Lennard–Jones diameter of one molecule of 1-butanol/ethanol, i.e., 0.527 and 0.437 nm [15,16], respectively.

The van der Waals interaction with regard to the solid sphere model was determined for two silicon spheres (radius =  $x/2$ ) by a

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