Sedimentation behaviour and colloidal properties of porous, chemically modified silicas in non-aqueous solvents

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Abstract

The sedimentation behaviour and colloidal properties of porous, chemically modified silicas dispersed in non-aqueous solvents have been studied. The free settling behaviour of non-aggregated silica suspensions could effectively be described with a modified Stokes equation that takes into account the possible inclusion of gas in the pores of the particles. The effects of hindered settling and of the dimensions of the sedimentation vessel on the rate of sedimentation were investigated too. The colloidal properties of the silica particles were compared with predictions by the DLVO theory. The Hamaker and Lifshitz theories were utilized to describe the attraction forces between the chemically modified silica particles. The electrophoretic mobilities of the particles in the non-aqueous liquids were determined in order to quantify the electrostatic repulsion forces. The electrostatic repulsion appears to generate a large barrier against coagulation with all investigated porous silicas. However, the way in which the particle suspensions are prepared determines whether the particles remain in the primary minimum or are colloiddally stable. The level of gas entrainment provides information on the homogeneity of the particle coating. © 1997 Elsevier Science B.V.

Keywords: Suspension stability; Electrostatic stabilization; Settling velocity; Gas entrainment; Van der Waals interaction; Coating inhomogeneity

1. Introduction

Hydrophobic silicas are widely used in various fields of chemical technology. Examples of application are as fillers in polymer materials and pharmaceutical products, as thickeners in varnishes and paints and as stabilizers or additives in detergents [1,2]. Future applications may be the use of silica sols — which can be applied in non-aqueous systems — in making magnetic colloids and recording media, high technology ceramic composites and catalytic supports [3]. Silica organosols may also be used as low temperature binder, as adhesion promoter or as silica source for magnesia refractories [3]. Thus silica-containing suspensions are studied in detail with regards to their rheological behaviour and adsorption, immersion and optical properties [1,4–8]. A very important scientific application of chemically modified silicas is as stationary phases in high performance liquid
chromatography and supercritical fluid chromatography [9,10]. The performance of a packed chromatographic column may vary considerably when comparing similar silicas from different manufacturers. The colloidal stability of the slurries employed in the column preparation is of critical importance in achieving stable chromatographic column beds using slurry-packing techniques [11]. Colloidal stability may also play a role in the often not adequate mechanical stability of the column (shrinkage of the packed bed) over its lifetime: bed shrinkage can lead to a reduced resolution.

In the present study we examine the colloidal characteristics of porous silicas with chemically modified surfaces in non-aqueous solvents, that are applied as stationary phases. The colloidal stabilities of the suspensions were studied by sedimentation experiments. The experimentally determined settling rates are compared with theoretical predictions for single particles in a suspension, as based on a modified Stokes relation. To this end the particles had also to be characterized by size, porosity and amount of air entrapped in the pores.

2. Theory

2.1. Sedimentation

The colloidal stability of porous silicas can be studied by sedimentation experiments because aggregated silica particles will show increased rate of sedimentation and volume of the final sediment. Taking into account the full two-body hydrodynamic interactions, it has been derived that the sedimentation velocity \( u \) of a colloidally stable suspension can be written as [12]

\[
\frac{u}{u_{\text{Stokes}}} = 1 + K_2 \phi + O(\phi^2)
\]

With hard sphere dispersion \( K_2 = -6.55 \). Interparticle attractions reduce the linear coefficient \( K_2 \); long-range repulsions tend to increase it. In practice this coefficient is often found to be at its hard sphere value or somewhat lower.

The sedimentation velocity at higher \( \phi \) (outside the “Einstein” and “Batchelor” regimes, for which linear and quadratic dependences on \( \phi \) hold) is less straightforward. It has been found that a fairly good fit to experimental data at both low and high \( \phi \) can be obtained (in the case of low Reynolds numbers) using the equation proposed by Richardson and Zaki [13]:

\[
\frac{u}{u_{\text{Stokes}}} = (1 - \phi)^{-K_2}
\]

A complication with the particles under investigation is that they have pores which are only partially filled with liquid. This can be taken into account by calculating the effective mass of the particles. Thus the sedimentation velocity of the particles applied in this study can be written as

\[
\frac{u}{u_{\text{Stokes}}} = (1 - \phi)^{-K_2} \left[ \rho_{\text{kel}} (1 - e_i) + \rho (e_f - 1) \right] g
\]

\[
18 \eta
\]

where \( d_p \) is the hydrodynamic diameter of the particles, \( \rho_{\text{kel}} \) is the skeleton density of the particles, \( \rho \) and \( \eta \) are the density and viscosity of the suspension liquid, \( g \) is the gravitational constant, \( e_i \) is the particle porosity and \( e_f \) is the fraction of the total hydrodynamic particle volume (particle plus pores) that is filled with suspension liquid. The permeability through the particles during sedimentation is assumed to be negligible.

For the sedimentation of doublets of particles analytical solutions are available. A doublet of equal spheres has a settling velocity of \( 1.381 u_{\text{Stokes}} \) if the line connecting the centres of the spheres is horizontal [12]. If this line is oriented vertically, the velocity becomes \( 1.550 u_{\text{Stokes}} \). With larger aggregates analytical solutions for the settling velocity appear to be too complicated. Numerical approaches taking into account multibody interactions are more successful [14,15]. With collooidally unstable suspensions one can qualitatively say that larger aggregates settle faster. For a given aggregate this speed is slightly faster if the aggregate is more compact.

2.2. Colloidal stability and interparticle interaction

Thermodynamically two charge-stabilized particles in a quiescent liquid mutually exert a van der Waals attractive and an electrostatic repulsive
force. The sum of these effects is called the “total interaction” [16]. Aggregation may proceed if the secondary minimum (“flocculation”) is sufficiently pronounced or if the repulsive barrier to the primary minimum is sufficiently shallow (“coagulation”). In order to assess the secondary minimum and the barrier, the equations used in this paper for assessing the van der Waals and electrostatic forces are briefly discussed.

2.3. Van der Waals attraction

The principles of van der Waals forces have been treated elsewhere [16]. However, the problem of heterogeneous particles — as stationary phase particles are — has not been dealt with yet. In a separate paper the van der Waals interaction between composite particles in a medium is discussed along the lines of both the classical Hamaker theory and the Lifshitz approach [17]. Here we only refer to the main results.

In the Hamaker approach the basic assumption is that the long-range, attractive forces between molecules are additive. Based on this, an expression for the Hamaker constant \( A_t \) of composite particles in a medium was derived [17]:

\[
A_t = A_{00} - 2 \sum_{i=1}^{n} \phi_i A_{0i} + \sum_{i=1}^{n} \sum_{j=1}^{i-1} \phi_i \phi_j A_{ij}
\]

where \( A_{ij} \) is the Hamaker constant of interaction between two particles of media \( i \) and \( j \) respectively. The index 0 refers to the medium and the indices 1, ... \( n \) refer to the components in the composed particle. These components with volume fractions \( \phi_i \) are supposed to be distributed over the whole particles uniformly in such a way that the granularity of the mixing is not noticeable in the interparticle interaction. Within the framework of the Lifshitz theory the composite character of the particles can be taken into account by calculating the absorption spectrum of a composite from adding their respective spectra with the volume fraction as the weighing factor. This again requires the granularity of the particle to be small enough to not giving rise to light scattering. The Lifshitz theory has two major advantages. First of all, the retardation is dealt with automatically. Secondly, the evaluation of \( A_{ij} \) is better than when using the Hamaker theory.

2.4. Electrostatic interactions

For assessing the electrostatic repulsion \( V_r \), the following equation was used:

\[
V_r = 2\pi \varepsilon_0 \varepsilon_r a \psi_0^2 \ln(1 + e^{-kh})
\]

where \( \psi_0 \) is the surface potential, \( h \) is the inter-particle distance, \( \varepsilon_0 \) is the permittivity of vacuum and \( \varepsilon_r \) is the relative dielectric constant of the liquid medium [12,16]. Here it is assumed that the constant-potential approach holds for the moderate polarity slurry liquids investigated: complete dissociation of the ionic groups on the surface of the particles is unlikely. Additionally, the surface potentials will be approximated by \( \zeta \) potentials. This is justified as the potential gradient near a surface in a liquid of moderate polarity is relatively small.

3. Experimental details

3.1. Chemicals

Acetone, carbon tetrachloride (CCl\textsubscript{4}), methanol and isopropanol were purchased from Merck (Darmstadt, Germany). Acetonitrile (CH\textsubscript{3}CN) was from Janssen Chemica (Beerse, Belgium) and tetrahydrofuran from Biosolve (Barneveld, Netherlands). All chemicals were of p.a. grade. Water was purified and demineralized with a Milli-Q water purification system (Waters-Millipore, Milford, MA, USA) prior to use.

The Zorbax ODS and Zorbax SB-C18 ODS modified silicas were obtained from Rockland Technologies (New Port, DE, USA). Nucleosil 100-5 C18 was from Macherey-Nagel (Düren, Germany), Bio-Sil C18 HL 90-5 S from Bio-Rad (Nazareth, Belgium) and Spherisorb ODS-1 from Phase Separations (Deerfield, UK). All silicas were spherically shaped and were used as received, having been chemically modified by using octade-cysilanes. The functionality of the silica varies from one to three. In the case of monofunctionality the silicon atom had been either dimethyl or diisobutyl substituted. The available information for the various types of silica particles is given in Table 1.
3.2. Particle characterization

The particle sizes and particle size distributions of the silicas were measured with a Malvern 2600 particle sizer (Malvern Instruments, Worcestershire, UK). The light-scattering pattern of an He–Ne 5 mW laser was converted into a particle size distribution by means of home-made software dedicated for porous materials. The median $d_{50}$ was taken as the average particle diameter $d_p$. Particle porosities were determined using the relationship [18]

$$\varepsilon_i = \frac{V_{\text{pore}}}{V_{\text{particles}}} = \frac{V_{\text{pore}}}{V_{\text{pore}} + 1/\rho_{\text{skeleton}}}$$

where $V_{\text{pore}}$ is the pore volume per mass of the particles, $V_{\text{particles}}$ is the total hydrodynamic volume per mass of the particles and $\rho_{\text{skeleton}}$ is the skeleton density. This indirect method for assessing $\varepsilon_i$ was used since direct methods are destructive and require large amounts of material. Skeleton densities of the materials were determined with a gas pycnometer (Stereopycnometer, Quantachrome, Greenvale, NY, USA). Pore volumes were assessed with a BET apparatus (Sorptomatic 1900, Carlo Erba Instruments, Milan, Italy). All particle characteristics are summarized in Table 1.

The ratio of mass and volume of the particles (solid plus entrapped gas) as dispersed in a liquid medium was determined with a 10 ml capped liquid pycnometer after sonication for 10 min and thermostating at 20°C in a water bath for 15 min. The fraction of the pores that is filled with liquid equals $\varepsilon_i/\varepsilon_i$. For the various combinations of particles and liquids these data are summarized in Table 2. From Table 2 it can be seen that Zorbax ODS and Zorbax SB-C18 particles enclose large amounts of gas in acetone and CH$_3$CN. Generally it can be concluded that the amount of gas entrapped in the pores of the hydrophobic silicas is larger for the Zorbax materials. This is most likely caused by the wettability of the various materials in the non-aqueous solvents [5,6].

### Table 1

Characteristics of chemically modified silicas investigated

<table>
<thead>
<tr>
<th>Hydrophobic silica</th>
<th>$d_p$ (μm)</th>
<th>Span$^a$</th>
<th>$V_{\text{pore}}$ ($10^{-6}$ m$^3$ kg$^{-1}$)</th>
<th>$\rho_{\text{skel}}$ (kg m$^{-3}$)</th>
<th>$\rho_{\text{app}}$ (kg m$^{-3}$)</th>
<th>Specific surface ($10^3$ m$^2$ kg$^{-1}$)</th>
<th>Carbon content (%)</th>
<th>Functionality of silane</th>
<th>End capped</th>
<th>$\varepsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-Sil C18 HL 90-5</td>
<td>5.70</td>
<td>0.67</td>
<td>357</td>
<td>2104</td>
<td>560</td>
<td>200</td>
<td>16</td>
<td>Di or tri</td>
<td>Yes</td>
<td>0.429</td>
</tr>
<tr>
<td>Nucleosil 100-5 C18</td>
<td>5.10</td>
<td>0.54</td>
<td>809</td>
<td>2106</td>
<td>360</td>
<td>340</td>
<td>15</td>
<td>—</td>
<td>Yes</td>
<td>0.630</td>
</tr>
<tr>
<td>Spherisorb ODS-1</td>
<td>4.84</td>
<td>0.60</td>
<td>430</td>
<td>2166</td>
<td>620</td>
<td>220</td>
<td>7</td>
<td>Tri</td>
<td>Yes</td>
<td>0.482</td>
</tr>
<tr>
<td>Zorbax ODS</td>
<td>4.40</td>
<td>0.74</td>
<td>358</td>
<td>1987</td>
<td>700</td>
<td>300</td>
<td>17</td>
<td>Mono$^d$</td>
<td>—</td>
<td>0.413</td>
</tr>
<tr>
<td>Zorbax SB-C18</td>
<td>5.24</td>
<td>0.60</td>
<td>318</td>
<td>2194</td>
<td>810</td>
<td>180</td>
<td>10</td>
<td>Mono$^d$</td>
<td>No</td>
<td>0.411</td>
</tr>
</tbody>
</table>

$^a$ Span, $(d_{90}-d_{10})/d_{50}$. $^b$ After chemical modification. $^c$ $\rho_{\text{app}}$, apparent density (packed dry density). $^d$ Two methyl side-groups. $^e$ Two isobutyl side-groups.

### Table 2

Density of hydrophobic silica particles as measured by immersion (ratio of mass and volume of solids and entrapped gas) and, in parentheses, fraction $\varepsilon_i/\varepsilon_i$ of pores that is filled with liquid.

<table>
<thead>
<tr>
<th>Hydrophobic silica</th>
<th>$\rho_{\text{particle}}$ (kg m$^{-3}$)</th>
<th>$\varepsilon_i/\varepsilon_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(CH$_3$CN)</td>
<td>CCl$_4$</td>
</tr>
<tr>
<td>Bio-Sil C18 HL 90-5</td>
<td>1607 (0.594)</td>
<td>1463 (0.420)</td>
</tr>
<tr>
<td>Nucleosil 100-5 C18</td>
<td>1605 (0.817)</td>
<td>1504 (0.765)</td>
</tr>
<tr>
<td>Spherisorb ODS-1</td>
<td>1802 (0.782)</td>
<td>1730 (0.730)</td>
</tr>
<tr>
<td>Zorbax ODS</td>
<td>1494 (0.528)</td>
<td>1494 (0.530)</td>
</tr>
<tr>
<td>Zorbax SB-C18</td>
<td>1706 (0.591)</td>
<td>1683 (0.564)</td>
</tr>
</tbody>
</table>
CCl₄ seem to have the best wetting properties for these kinds of hydrophobic silicas.

3.3. Particle-settling device

A particle-settling device was constructed from a glass tube with an inner diameter of 7 mm and a length of 130 mm. The silica slurries were transferred into the tube by means of a pipette. The tube was shut by means of a rubber stopper to prevent solvent evaporation and held in a vertical position. The distance travelled by the upper boundary of the slurry was measured at 5 min intervals until the final height of the sediment was reached. All experiments were conducted twice. It was found that with 7 mm tubes the effect of the wall on the sedimentation rate was negligible.

3.4. Zeta potential measurements

The ζ potentials of the hydrophobic silicas in the various liquids were measured with a Malvern Zeta-sizer 3 (Malvern Instruments) equipped with an AZ4 cell and using the Helmholtz-Schmoluchowski equation [16]. Low conductivity ζ potential experiments were conducted with an AZ26 cell. Electrophoretic mobility measurements on the hydrophobic silica particles in liquids with a relatively high dielectric constant (ε > 10) were conducted at a voltage drop over the measuring cell of approximately 100 V. In the case of liquids with ε < 10 this voltage drop was kept at 50 V.

3.5. Conductivity measurements

Conductivity measurements were made with a CDM 83 conductivity meter (Radiometer, Copenhagen, Denmark) equipped with a CDC 134 conductivity cell. All measurements were performed at ambient temperature.

4. Results and discussion

4.1. Sedimentation

Sedimentation of slurries of all combinations of particles and solvents was investigated at levels of φ of approximately 0.05, 0.10 and 0.15. As a typical example of a stable hydrophobic silica suspension, the result with Spherisorb in CH₃CN is depicted in Fig. 1(a), where the experimentally determined height Sₑ of the clear, particle-free, top layer is plotted as function of the settling time. The distance travelled by the interface between suspension and top layer increases linearly for times up to approximately 2500 s for all the concentrations investigated. After 2500 s the whole slurry becomes influenced by the presence of the sediment and settling starts to become retarded. Thus for the first 2500 s the settling velocities are time independent, which indicates that the particles do not aggregate during sedimentation. The full lines in Fig. 1(a) represent the theoretical progress of sedimentation Sₜ for hard non-aggregated spheres according to Eq. (3) when using a value of K₂ equal to -5.4. Theoretical and empirical settling rates show good agreement, confirming the assumption that the silica suspensions are stable. The results in Fig. 1(a) also show that the settling rate is strongly dependent on the hydrophobic silica particle concentration.

The distance travelled by the suspension as a function of time for the colloidally unstable suspension Spherisorb in CCl₄ is presented in Fig. 1(b). The experimentally determined sedimentation curves Sₑ indicate much faster settling of the particles than the theoretical curves of Sₜ with K₂ = -5.4, indicating that the particles are aggregated. Remarkable is the fact that with these aggregated suspensions the higher volume fraction suspensions settle slower than those with lower volume fractions. This indicates that the more concentrated suspensions are either aggregated less compactly [19], form smaller aggregates [20] or that the effective volume fraction becomes so high that excessive hindering of the sedimentation occurs.

The optimal coefficient K₂ for colloidally stable suspensions in most cases is -5.4. Only for two suspensions that are not definitely unstable did the optimal value of K₂ deviate significantly: for Spherisorb in isopropanol (K₂ ≈ -4.0) and for Nucleosil in CH₂CN (K₂ ≈ -4.6). However, their sedimentation speeds (to be discussed later on) are slightly higher than the theoretical value, indicating
that some agglomeration had occurred in these cases. How $K_2$ was evaluated can be seen in Fig. 2 for the colloidally stable suspensions of Nucleosil in acetone at $\phi = 0.05$, 0.10 and 0.15. In this figure the experimental sedimentation distances $S_0$ of the sediment during settling are given as a function of the theoretical values of $S_i$ for three different values of $K_2$. Both axes have been non-dimension- alized by the filling height of the tube, $h_0$. Note that the variations in $S_i$ at fixed $S_0$, being due to variations in $K_2$, are larger for higher $\phi$, as can be understood from inspection of Eq. (2).

Aggregated suspensions can be characterized also by the height of the sediment after complete
Fig. 2. Experimental vs. theoretical values of normalized sedimentation distance for Nucleosil 100-5 C18 in acetone with $K_z$ equal to (O) -4.7, (+) -5.4 and (●) -6.6.

Fig. 3. Normalized final height $h_{\text{final}}/h_0$ of sediment vs. volume fraction $\phi$ for Zorbax SB-C18 in (●) acetone, (○) CH$_3$CN, (+) CCl$_4$, (⊗) isopropanol, (▲) methanol and (■) tetrahydrofuran.

sedimentation. Fig. 3 shows the normalized final height $h_{\text{final}}/h_0$ of the sediment of Zorbax SB-C18 as a function of the initial volume fraction of the particles in the suspension. All liquids except for CCl$_4$ show a linear relationship between the normalized height of the settled slurry and the volume fraction. Based on these results, only CCl$_4$ and, to a lesser extent, methanol are definitely aggregating liquids for Zorbax SB-C18. The theoretical rate of sedimentation yields absolute information on the extent to which the particles are aggregated, whereas the height of the sediment provides only
relative information. To describe to what extent the particles are aggregated, the "instability ratio" is introduced, which is defined as the ratio of the experimental sedimentation rate of a suspension and the theoretical sedimentation rate for that suspension in the absence of any colloidal interaction between the particles. A summary of the instability ratios of all the systems investigated is given in Table 3.

4.2. Zeta potential measurements

The Helmholtz–Schmoluchowski equation was employed to convert mobilities into \( \zeta \) potentials. Strictly speaking, this equation is only applicable at low potentials and with values of \( \kappa a > 100 \). With low potentials and \( \kappa a < 1 \) this equation would underestimate the \( \zeta \) potential by a factor \( \frac{2}{3} \) [16]. It is evident from the values of \( \kappa \) and the \( \zeta \) potentials that the Helmholtz–Schmoluchowski equation is not exactly applicable. However, it will be used in view of the fact that (i) the nature and amount of the dissolved electrolyte are not accurately known, thus leading to uncertainties in applying more sophisticated theories, and (ii) the exact values of the high \( \zeta \) potentials found seem not to be critical for the conclusions (coagulation should not occur anyhow). \( \kappa \) was derived from conductivity measurements of the pure liquids in order to assess \( \kappa a \), assuming a 1:1 electrolyte with an ionic radius of \( 10^{-10} \) m [21]. The conductivity of the pure liquids and the calculated value of \( \kappa \) are given in Table 4.

The calculated \( \zeta \) potentials for the various systems are summarized in Table 4. In all cases the \( \zeta \) potential of the chemically modified particles is negative, in line with what would be expected for native silica particles. In a number of cases the particles were severely aggregated and settled quicker than they could be measured. In addition, no \( \zeta \) potentials of particles in CCl₄ could be recorded. This is due to the fact that these suspensions are almost transparent. Whereas their sedimentation behaviour could be recorded, the laser Doppler detector in the \( \zeta \) potential equipment used could not detect the electrophoretic movements.

4.3. Colloidal stability and DLVO theory

In Fig. 4 the electrostatic repulsion, the van der Waals attraction and the total interaction energy of two Zorbax ODS particles in methanol are shown. This result is typical for all suspensions investigated. The van der Waals attraction and, especially, the electrostatic repulsive energy are large at small distances owing to the fact that both are proportional to the radius of the particles (which is very large, about 2.5 \( \mu \)m). The van der Waals interaction at small distances drops with the inverse of the interparticle distance. At larger distances this drop is even more severe owing to

### Table 3

<table>
<thead>
<tr>
<th>Hydrophobic silica</th>
<th>Instability ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>CH₃CN</td>
</tr>
<tr>
<td>Bio-Sil C18 HL 90-5</td>
<td>1.02</td>
</tr>
<tr>
<td>Nucleosil 100-5 C18</td>
<td>1.05</td>
</tr>
<tr>
<td>Spherisorb ODS-1</td>
<td>0.96</td>
</tr>
<tr>
<td>Zorbax ODS</td>
<td>1.14</td>
</tr>
<tr>
<td>Zorbax SB-C18</td>
<td>0.96</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Conductivity ( (10^{-5} \Omega^{-1} \text{m}^{-1}) )</th>
<th>( \kappa ) ( (10^9 \text{m}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>1.27</td>
<td>3.19</td>
</tr>
<tr>
<td>CH₃CN</td>
<td>0.04</td>
<td>0.43</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>0.27</td>
<td>4.31</td>
</tr>
<tr>
<td>Methanol</td>
<td>7.09</td>
<td>8.26</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>0.08</td>
<td>7.75</td>
</tr>
</tbody>
</table>
the retardation effect. However, the electrostatic interaction is large and almost constant until the distance rises beyond the double-layer thickness $\kappa^{-1}$, which in these cases typically is 0.1–1 $\mu$m. The result is that a large barrier exists that should be adequate in avoiding coagulation in the "primary minimum". The curve also indicates that the "secondary minimum" is negligible. On increasing the distance to the point where the repulsion has dropped to $1kT$, the attraction has always been reduced to less than $10^{-2}kT$. This excludes flocculation in the secondary minimum as the mechanism for aggregation: aggregation should be interpreted as being coagulation in the primary minimum. Note that calculations indicate that with these systems for $\zeta$ potentials larger than a few millivolts an effective barrier against coagulation exists.

In order to gain insight into the role played by attractive and repulsive forces in the stability, the instability ratios as summarized in Table 3 are plotted in Fig. 5 as a function of the attractive and repulsive potentials at a fixed, very short interparticle distance of $10^{-10}$ m. For completeness the suspensions for which no $\zeta$ potential was available have also been plotted at $V_{rep}=0$. The results in Fig. 5 indicate that it should be possible to obtain stable suspensions over the whole range of repulsive and attractive potentials investigated. No criterion for instability as found in practice can be deduced from these data. However, in the case of
severe coagulation (most of the data plotted at $V_{\text{rep}}=0$), larger attraction seems to promote practical instability. Note that the effect of entrapped gas on the Hamaker constant of composite particles in a medium largely depends on the medium employed. Using the Lifshitz theory, as an example, values of $1.0 \times 10^{-21}$ and $0.91 \times 10^{-21}$ J were found for Zorbax ODS particles in methanol and CCl$_4$ respectively. The same calculations with the assumption of no entrapped gas would have led to $1.60 \times 10^{-21}$ and $0.07 \times 10^{-21}$ J respectively.

4.4. Colloidal stability and processing

The question remains as to why some slurries are colloidal stable and others are not, while on the other hand they should all be stable for theoretical reasons. A possible answer may be that particles in the systems that contain aggregates in reality have been in contact with each other from the start of the preparation of the suspension and have never been separated from each other while being stirred or vibrated ultrasonically. Two types of experiments were conducted to check whether it is possible to change the degree of aggregation by changing the method of preparation of the suspension. In the first type of experiments a slurry of 100 mg Bio-Sil in 1 ml acetone was prepared. As expected, it was colloidal stable. The liquid was gradually replaced by CH$_3$CN. The final slurry and all the intermediates were completely stable, while according to Table 3 the final slurry should be unstable. Apparently the processing dominates over the thermodynamic arguments. Once two particles have been separated, on gradually replacing the liquid, the $\zeta$ potential presumably remains large enough to keep a sufficient barrier against coagulation. Note that this explains why replacement of liquid does not induce coagulation. However, it does not explain why acetone disperses dry Bio-Sil particles better than CH$_3$CN does.

In the second type of experiments the influence of the way of mixing the dry particles with the liquid was investigated. Two experiments were performed (in all cases 500 mg particles in 5 ml liquid).

(i) Instead of adding the liquid to the dry silica particles, the particles were slowly strewn on top of the liquid until the top of the liquid was covered with a very thin layer of these poorly wetting particles, whereafter the mixture was shaken in order to disperse the added particles. This procedure was repeated until all particles had been added. In that way the final height of the sediment of Spheresorb particles in CCl$_4$ reduced significantly with respect to the adding-liquid-to-particles process, suggesting a reduction of the degree of aggregation. The final height of the sediment was,
Table 6
Influence of processing conditions on colloidal stability

<table>
<thead>
<tr>
<th>Test</th>
<th>Addition Method</th>
<th>Time</th>
<th>Instability ratio (from settling rate)</th>
<th>Reduced final height of sediment ($h_{final}/h_0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Liquid poured on top of particles</td>
<td>1 s</td>
<td>31</td>
<td>0.166</td>
</tr>
<tr>
<td>B</td>
<td>Particles slowly strewn by hand on top of liquid (liquid shaken a number of times)</td>
<td>5 min</td>
<td>23</td>
<td>0.179</td>
</tr>
<tr>
<td>C</td>
<td>Particles slowly strewn by hand on top of liquid (ultrasonic vibration of liquid)</td>
<td>5 min</td>
<td>31</td>
<td>0.177</td>
</tr>
<tr>
<td>D</td>
<td>Particles slowly strewn on top of liquid by vibration chute (ultrasonic vibration of liquid)</td>
<td>5 min</td>
<td>21</td>
<td>0.145</td>
</tr>
</tbody>
</table>

however, higher than that of stable suspensions, indicating that the particles are still aggregated to some extent.

(ii) Suspensions of Spherisorb in CCl$_4$ were prepared in a number of ways as described in Table 6. In all cases after the addition step the suspension was vibrated in an ultrasonic bath for 10 min. The sedimentation patterns for the first 90 min are shown in Fig. 6. From these curves the initial sedimentation rates were evaluated. The corresponding colloidal instability ratios (to be compared with the data in Table 3) were calculated and are shown in Table 6 together with the final heights of the settled suspensions. Note that the individual data points in Fig. 6 scatter slightly around the smoothed curve because it is difficult to observe the slurry boundaries in the almost transparent suspensions in CCl$_4$. It is clear that samples A and C settle down faster, indicating larger aggregates. The fact that sample A has a relatively low final sediment volume suggests that its aggregates are more compact. Samples B and D are definitely less agglomerated although they are colloidal still quite unstable.

The fact that typically 25% of the pores of these particles was filled with gas after prolonged immersion in any of the liquids used indicates that the coverage by the octadecyl coating is rather inhomogeneous. The reason is that if the coverage would have been homogeneous, either a 0% or a 100% entrapment of gas could be expected, given the small sizes of the pores. In this respect Nucleosil and Spherisorb can be considered as having the best homogeneity in coverage by the octadecyl chains. As the better wetting areas in a particle presumably do not form a continuous, totally interconnected area, wetting will at least partly proceed by gas diffusion. This is a much slower process than when liquid is simply sucked in by capillary forces. Because wettability of particles will be related to the liquid content of a particle, the wettability itself during mixing can be expected to rise slowly up to its equilibrium level. This is confirmed by the observation of initially very poor and finally adequate wettability (after prolonged immersion the particles did not stick to the surface any more). It is reasonable to expect that poor initial wettability may keep together any
particles that initially touch each other. Initially a gas bridge between the particles may assist in keeping the particles together [22]. However, the fact that the severely agglomerated dispersions in CCl₄ were almost perfectly transparent suggests that gas bubbles bridges between the particles are absent in the final suspensions. Once the particles are kept together, they will have a larger chance to be kept together in the primary minimum. Thus adding single particles sequentially on to a liquid will avoid this sticking mechanism and improve their colloidal stability. This is confirmed by the results with process D in Table 6.

5. Conclusions

The degree of aggregation of chemically modified silica particles in non-aqueous liquids can be determined by means of sedimentation experiments. The ratio of the experimentally observed rate of sedimentation of a suspension and the theoretically calculated rate of sedimentation of a non-aggregated silica particle suspension proved to be a very accurate and sensitive method for the determination of the colloidal stability of chemically modified silica suspensions. The colloidal stability of the suspension is controlled by processing rather than thermodynamical arguments. An important aspect in the application of this method is that the amount of entrapped gas in the particles pores and the effect of hindered settling have to be taken into account. The surfaces of the particles are not chemically modified homogeneously. The ϵ potential was found to be negative in all cases and was relatively large, i.e. $-\zeta > 40 \text{ mV}$. All chemically modified silica suspensions investigated should be colloidal stable according to the van der Waals interaction theories. However, slurry processing is found to be very important in achieving colloidal stability in practice.

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References