Suspension Stability; Why Particle Size, Zeta Potential and Rheology are Important

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ABSTRACT

This paper presents the combined technologies, rheology, zeta potential and particle size measurements, that are important to characterize particle suspensions. We will use a system that sediments at room temperature and explain why different techniques are needed to characterize the system to show its potential stability

INTRODUCTION

Suspensions or dispersions of particles or droplets in a liquid medium are encountered in a variety of industries and find use in a diverse range of applications. These include liquid abrasives, ceramics, medicines, foodstuffs and inks to name a few. One key criterion which is important across this range of applications is suspension stability. For a suspension to be functional it must be capable of suspending the dispersed phase for the lifetime of the product and/or be easily dispersed should sedimentation occur. A number of factors contribute to dispersed phase stability and these may be thermodynamic or kinetic in origin. Examples of the former include steric and electrostatic stabilization which induce stability through particle repulsion, while kinetic stability can be induced by increasing the viscosity of the suspending medium thus slowing down particle aggregation and sedimentation.

For sub-micron suspensions Brownian motion is usually significant to maintain the particles in a dispersed phase, however, for larger particles the effect of gravity becomes significant if there is a sizeable difference in density between dispersed and continuous phases. In this case the likelihood for sedimentation can be predicted from the ratio of gravitational to Brownian forces using Eq. 1[1].

$$a^4 \Delta \rho g / k_B T \qquad (1)$$

where a is the particle radius, $\Delta\rho$ is the density difference between the dispersed and continuous phases, g is acceleration due to gravity, k_B is the Boltzmann constant and T is the temperature. If this ratio is greater than unity some degree of sedimentation can be expected while a ratio less than unity is likely to indicate a stable system. This equation, however, does not take into account potential interactions between particles. Due to Brownian motion, particles will be continually colliding with each other and consequently particles may become aggregated due to Van der Waals attractive forces. This can lead to formation of secondary particles (flocs) of much larger size and therefore a larger gravitational contribution to Eq. 1, with consequent settling.
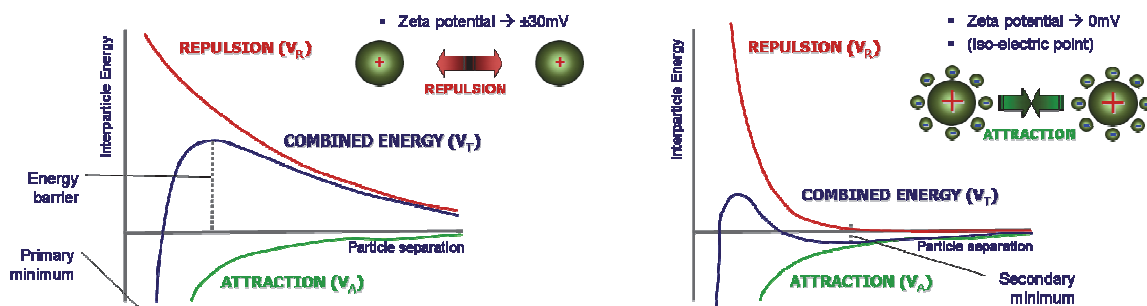
Figure 1. Schematic diagram showing the variation of free energy with particle separation for a suspension with (a) a high zeta potential (b) low zeta potential.

To prevent particles becoming aggregated it is necessary to provide some barrier. This can be achieved through steric or electrostatic means by adsorbing polymers or introducing a charge onto the particle surface by, for example, modifying the pH. If the repulsive force exceeds the attractive force then a stable system should result. For an electrically charged suspension such a force balance can be described by DLVO theory where the combined/total energy (V_T) is the sum of attractive (V_A) and repulsive ((V_R) contributions as shown in Fig. 1a. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together unless the particles have sufficient thermal energy to overcome this barrier. The size of this potential barrier can be indicated by the magnitude of the zeta potential which is the potential at the slipping plane between the particle and associated double layer with the surrounding solvent[4,5]. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there will be no tendency for the particles to come together. However, if the particles have low zeta potential values then there will be insufficient repulsion to prevent the particles coming together and flocculating. The general dividing line between stable and unstable suspensions is generally taken as +30 or -30mV with particles having zeta potentials outside of these limits normally considered stable[6,7]. Such an assumption, however, is very much dependent on particle properties[1,4]. In this paper we consider the importance of particle size, zeta potential and rheology on sedimentation behaviour and demonstrate how these properties can be manipulated to induce stability.

EXPERIMENTAL
The sample used in this study was a microcrystalline silicon dioxide with a density of 2.6g/cm^3 and a Dv(50) of 3.7μm as measured on a Malvern Mastersizer 2000 with Hydro S dispersion unit. These samples were evaluated using zeta potential measurements and steady shear rheological measurements to assess stability as a function of pH. For zeta potential measurements, a dilute dispersion of the material was made up in deionised water ready for analysis using a Malvern Zetasizer Nano ZS in conjunction with an MPT2 autotitrator. The titrator was set up with 0.25M and 0.025M HCl to titrate from the start/sample pH to an end pH of 1.0 and record 3 repeat zeta potential measurements at 10 equally spaced pH intervals across the range. All tests were performed at 25ºC
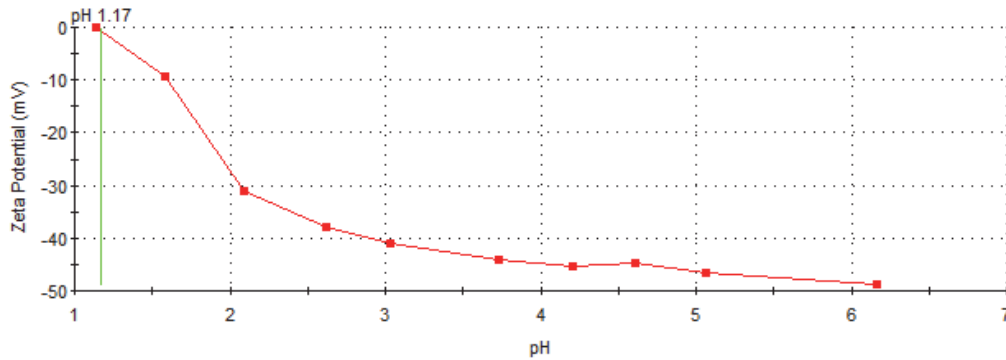
Figure 2. Zeta potential and isoelectric titration data for a standard silica sample.

Rheological measurements were performed on concentrated dispersions (75% w/w) of the silica sample in deionised water. Samples were adjusted with HCl to give pH values equivalent to those used in the zeta potential study. Rheological tests were performed on a Kinexus Pro and Gemini 2 rheometer using serrated parallel plates and a working gap of 0.5 mm. Two types of test were performed on the samples including an equilibrium step shear rate test and a shear stress ramp test. The first test involved increasing the shear rate stepwise between 0.1 and $100s^{-1}$ to generate a flow curve (shear viscosity vs. shear rate). The second test involved ramping up the shear stress linearly from 0 to 100Pa in a 60s period to determine the yield stress. All tests were performed at 25 ºC.

RESULTS AND DISCUSSION

Fig. 2 shows the effect of pH on a suspension of silica particles dispersed in deionised water with an average particle size of 3.7μm as determined using a Mastersizer 2000. Despite having a negative zeta potential in excess of 30mV this suspension has been shown to be unstable, forming a compact sedimented layer upon standing. If the associated particle/fluid parameters are inputted in to Eq. 1, the ratio of gravitational to Brownian forces comes out in excess of 45. This suggests that gravitational forces are highly dominant and therefore zeta potential would not be expected to significantly influence sedimentation stability. The same equation suggests that Brownian forces are only dominant for particles less than approx. 1.5μm in diameter. When gravitational forces driven by particle size and density dominate the system, the electrostatic interactions are no longer sufficient to provide stability and another means of stabilisation is therefore required.

One way of doing this is to increase the kinetic stability of the suspension by slowing down the rate of sedimentation. This can be achieved by increasing the viscosity of the continuous phase. The rate of sedimentation can then be estimated from Stokes' law (Eq. 2) assuming a dilute suspension of spherical particles[2].

$$V = \frac{2\Delta\rho g a^2}{9\eta} \qquad (2)$$

where V represents the sedimentation velocity and η the shear viscosity of the continuous phase. Therefore, doubling the viscosity will reduce the rate of sedimentation by the same factor, while halving the particle size will reduce the sedimentation rate by a factor of 4. This expression, however, is only applicable for dilute suspensions where particle interactions are minimal. Settling of
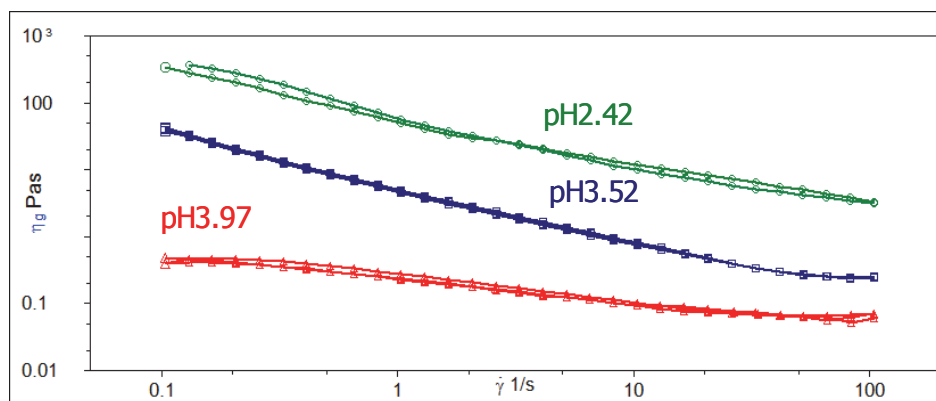
Figure 3. Equilibrium flow curves for silica samples prepared at different pH values.

concentrated suspensions is more complex due to interactions between neighbouring particles and the fact that the high particle loading leads to an increase in overall density and viscosity. There are a number of equations for predicting sedimentation velocity in concentrated dispersions, one of which (Eq. 3) is a modification of the Stokes equation where φ represents the volume fraction and the exponent varies depending on particle size, having a value of approx. 5.25 for particles larger than 1μm and 4.75 for sub-micron particles[2].

$$V = \frac{2\Delta\rho g a^2}{9\eta}(1-\phi)^{5\pm0.25} \qquad (3)$$

The charge on the particle can also play a significant role in slowing down sedimentation since the associated electrostatic layer will have a finite thickness which will increase the effective phase volume of the dispersed phase. This effect will be more pronounced with smaller particles[1, 2].

Another way of inducing stability in suspensions where gravitational forces dominate is by introducing a network structure and hence a yield stress into the system. One way to achieve this is by gelling the continuous phase through use of suitable additives. Another approach, which may seem counter intuitive, is to reduce the repulsion between particles and actually promote flocculation in the system as shown in Fig. 1b. This latter approach will be considered in more detail.

From Fig. 2 it can be seen that reducing the pH reduces the zeta potential with the isoelectric point occurring at a pH of 1.17. The impact of such a change on the rheology can be demonstrated in Fig. 3 which shows shear viscosity as a function of shear rate for the various samples. At pH 3.9 the viscosity is fairly low and there is a slight decrease in viscosity with increasing shear rate indicative of non-Newtonian or shear thinning behaviour. The slightly higher plateau in viscosity at lower shear rates is termed the zero shear viscosity plateau and arises due to both the random orientation of particles at low shear rates and the increase in effective phase volume due to the charge on the particles. At higher shear rates, hydrodynamic factors become dominant with a consequent ordering of the dispersed phase and a resultant decrease in viscosity[1].

As the pH is further decreased the viscosity increases and this low shear viscosity plateau is no longer visible. This indicates that the material is showing solid-like behaviour inferred from the absence of this low shear plateau; although lower shear rate measurements would be needed to confirm this. Repeating the same test on the pre-sheared samples gives almost identical
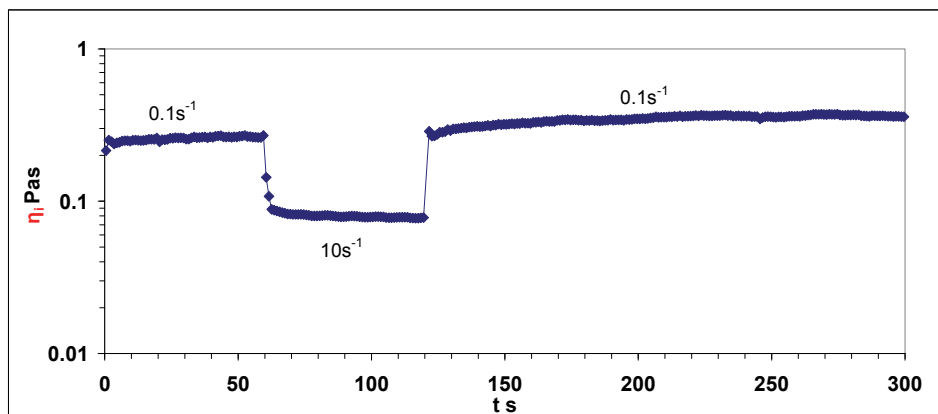
Figure 4. Results of step shear rate test for sample prepared at pH 4.

flow curves in all cases indicating that samples are not permanently flocculated but form a temporary network structure which rapidly reforms following perturbation. This has been confirmed from a three step shear rate test which determines the viscosity at a low shear rate and then measures the time it takes to recover this viscosity after being sheared at a high shear rate for a period of time. Such a test is shown in Fif. 4 for the sample at pH 4 using a start/end shear rate of $0.1s^{-1}$ and an intermediate shear rate of $10s^{-1}$. This shows that the sample recovers its viscosity almost instantaneously although it has a slightly higher viscosity than observed initially which is probably due to a reorganisation of the microstructure.

This reversible flocculation can be explained using DLVO theory. By reducing the surface charge on the particles, the repulsive contribution to the total interaction potential is reduced. This leads to the emergence of a secondary minimum in the potential energy curve as shown in Fig. 1b which permits a much weaker and reversible adhesion between particles. These interactions are strong enough to resist the effects of Brownian motion but sufficiently weak to be broken down under the application of shear. The depth of this secondary minimum plays a critical role in determining the floc structure and consequently the potential for network formation. When this secondary minimum is relatively deep i.e. 10 to 20kT, colliding particles will adhere strongly forming an open structure with greater phase volume which is favourable for network formation. In contrast, weakly flocculated systems are able to rearrange themselves on a local scale forming denser flocs which are more likely to sediment[1,2].

The strength of this network structure can be reflected in the yield stress which is the stress required to overcome these attractive forces and initiate flow. There are a number of experimental tests for determining yield stress on a rheometer. One of the quickest and easiest methods is to perform a shear stress sweep and determine the stress at which a peak in viscosity is observed. The observed increase in viscosity prior to this peak is the result of elastic deformation (strain hardening); therefore the peak value represents the point at which this elastic structure yields.

From Fig. 5 it can be seen that the two low pH samples show a peak in viscosity indicative of a yield stress. Also the stress at which this peak occurs is much higher for the low pH sample indicating that structural strength increases as zeta potential decreases. For the high pH sample there is no peak in viscosity indicating that this material does not have a yield stress and hence no network structure.
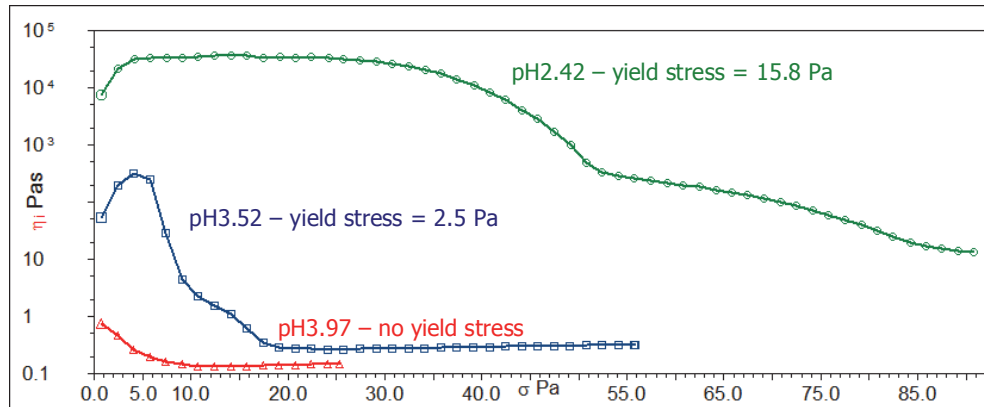
Figure 5. Yield stress measurements for samples prepared at different pH values.

In this latter case sedimentation rate can be estimated from Eq. 3 while in the case of a particulate gel thermodynamic stability results only if the stress imposed on the structure is below the yield stress. An estimate of the stress imposed by a particle on its surroundings can be given from Eq. 4, where ρ_D is the density of the dispersed phase and ρ_C is the density of the continuous phase.

$$\sigma = \frac{(\rho_D - \rho_C)rg}{3} \qquad (4)$$

For the silica suspension used in this study, the calculated value is approximately 0.01Pa for the largest particle which is approximately 10μm in diameter. Consequently these low pH systems should be stable to sedimentation under quiescent conditions, although stresses resulting from external perturbation such as those encountered during transportation for example need consideration also.

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