Stability for dispersions

For certain coatings applications, it is important to maintain the stability of fine particles in aqueous suspension. The theoretical effects of pH on the suspension stability of china clay in water were evaluated, and practical (centrifuge) tests were used to determine the effects of adding different molecular weights of the polymer polyvinylpyrrolidone (PVP) at constant pH.

Determining the effects of PVP upon sedimentation of clay suspensions
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The preparation of particle suspensions, which are widely used in different applications (such as paints, pharmaceuticals etc.) is known to be very difficult. Studies on the influences which are responsible for the stability of these particle dispersions are limited in number. But the stability and characterisation of nanoparticle systems is a central research issue, because knowledge about the stability of dispersions is important for their practical application.

Pigments and their properties play an important role in the stability of paints. Properties of pigments such as particle charge, particle size and size distribution all influence the stability of dispersions. The pigments in a paint must be well dispersed in order to perform successfully. If the pigment agglomerates, then the paint will appear to have larger pigment particles and the colour quality may be degraded. The rate of agglomeration depends on many factors, including particle concentration, size distribution, velocity gradients, ionic strength, pH, the presence of polymers and what is termed the zeta potential - the potential difference between the dispersion medium and the layer of fluid effectively attached to particles dispersed in it.

In the work reported below, the stability of clay particles in aqueous dispersion and in the presence of the water-soluble polymer poly(vinylpyrrolidone) or PVP has been investigated. Various methods for particle characterisation such as zeta potential and particle charge determination, laser diffraction and separation analysis in a centrifugal field were used.

The results will show how the particle size, particle size distribution and also the surface charge of particles and the stability of dispersions are influenced by the conditions of suspension preparation such as time of ultrasonication and the addition of PVP as a stabiliser.

The significance of clay and its suspension stability
Most naturally occurring particles in water are clay minerals, which have a negative surface charge over a broad pH range. Clay minerals of the kaolin type have a wide range of applications in papers, paints, ceramics, plastics, medicine, construction materials etc. Due to the importance of its applications, the interaction of clay with polyelectrolytes has been investigated in great detail by different researchers, but in most cases with respect to its flocculation [1-7]. However, as stated above, the stabilisation of kaolin dispersions is also important. But detailed studies about the influences of polymers on the stability of dispersions are limited in number. For instance, Schaller [8] investigated the particle stabilisation properties of modified copolymers with titanium dioxide.

In the experiments reported here, kaolin with very fine particles, also known as china clay, was used. The shape of the kaolin particles was studied by Scanning Electron Microscopy (SEM). Clay minerals are characterised by occurring in two-dimensional sheets. In Figure 1 a broad distribution of large and small kaolin plates can be seen.

How zeta potential and charge affect stability
Particles in aqueous solution become charged. The charge, measurable by the zeta potential, is an important parameter in determining the stability of a dispersion. The magnitude of the zeta potential gives an indication of the potential stability of a colloidal system.

If the particles have a large zeta potential they will repel each other, and the dispersion is stable. If they have low zeta potential values, then there is no force to prevent the particles from coming together. The dispersion is unstable and particles aggregate.

It is well known that kaolin has positively charged edge faces and negatively charged basal faces. With increasing pH the dissociation of the silanol groups presented on the basa plane of kaolin particles increases and so they are effective in the aqueous dispersion. The net charge is negative, as shown in Figure 2. This figure shows the zeta potential as a function of the pH of kaolin, measured as the electrophoretic mobility of the dispersion using a "ZetaSizer 3000". The black curve shows a negative zeta potential in the pH range from 2 to 10. The isoelectric point (the point where the value of the zeta potential is zero) is about pH 2. Dispersions with a pH near the isoelectric point are unstable.

If the charge is high enough, the particles will remain separate, dispersed and in suspension. The charge and the stability should also be highest in the basic range because the zeta potential in this range is also high. All measurements in the tests below were carried out at pH 6 with a negative zeta potential of -37 mV and at room temperature.

The surface charge density \( q \) in relation to pH was measured by polyelectrolyte titration with a Particle Charge Detector (PCD, Mütek GmbH, Germany). These results are also shown in Figure 2. The charge density at certain pH values gives an initial indication of the stability.

The best dispersion stability, independent of the sign of the charge, is to be expected for samples with high values of charge density. In the basic range the kaolin dispersion has a higher stability than at lower pH values. At pH 6 the surface charge density is -1.9 C/g.
How ultrasonication affects particle size distribution

Dispersions of particles in "Millipore" high-purity water (of pH approximately 6) were prepared by dispersing 10 g of powder into 1 l of water or PVP (ie. 1 % solids content) with a "UP200s" high intensity ultrasonic processor, operating at 24 kHz and up to 200 W. The particle characterisation methods are used to determine specific properties of a dispersion quantitatively as well as to measure, control or optimise changes in dispersion states. The volume particle size distribution of the particles in aqueous dispersion was determined by laser diffraction using a Malvern "MasterSizer". The samples were stirred at 2000 rpm during measurements. Figure 3 shows how the particle size distribution for aqueous kaolin dispersions is affected by ultrasonication. A constant specific energy dispersion with ultrasonication is more effective than homogenisation with a magnetic stirrer (red curve). All curves show a bimodal distribution. The average sizes for the kaolin dispersion prepared with the magnetic stirrer are 3.5 µm and 7.5 µm. Dispersion times greater than five minutes have a minor influence on the particle size. However, small particles were obtained almost independently of time for 10, 20, and 30 min. They are in the range of 300 nm, and in addition a fraction of around 2 µm was observed. Since the effect of particle size distribution is largely independent of ultrasonication time, a time of 10 minutes was selected for further studies.

PVP modifies electrophoretic mobility of kaolin

The charge on the particles can be controlled by modifying the suspending liquid, changing the pH or the ionic strength in solution. Another, more effective, technique is to use polymers such as polyvinylpyrrolidone (PVP) which are directly adsorbed on the surface of the particle and change its surface properties. The adsorption of polymers onto different surfaces can be investigated by zeta potential measurements [9].

PVP was obtained as "Luvitec" brand material from BASF with different molar masses and used as a stabiliser for the kaolin dispersions. The results are related to molar masses (Mw) in the range from 45 000 up to 2 million g/mol. According to the producer, the relative viscosity for 1% solutions in water ranges from 1.2 up to 6.2. mPas. A stock solution of 10% PVP was prepared in "Millipore" water. In Figure 4 the zeta potential versus pH profiles for kaolin dispersions in the presence of PVP grades "K30" (PVP with low molar mass, Mw = 50 000) and "K90" (PVP with high molar mass) are shown. As the concentration of PVP increases, the value of the zeta potential decreases. The effect is stronger for polymers with higher molar mass (mw), with approximately 1-2 M g/mol. The influence of the polymer concentration was investigated in a broad range from 0.1 up to 9 %. The results presented in the following figures show the large influence of polymer concentration on stability. The stability increases with polymer concentration as well as with increasing molecular weight. Therfore the polymer content is calculated as a percentage of the water and the clay concentration in the later experiments is 1 %.

Steric stabilisation and the effects of molar mass

Some polymers are known to reduce the zeta potential in dispersion because loops and tails are formed which extend into the solution. This leads to a shift of the shear plane. If the loops or tails are longer because of the higher molar mass of the polymers, the zeta potential is further decreased. These loops and tails prevent particles from aggregating. Surfaces covered with polymer show a decrease of the zeta potential and charge. In spite of this, their dispersions are stable because of these loops and tails. This mechanism, known as steric stabilisation, can explain the ability of certain polymers to inhibit aggregation of dispersions. Those polymers with long chains are believed to cover the system in such a way that long loops and tails extend out into the solution. Systems that are sterically stabilised tend to remain well dispersed even at high salt concentrations or under conditions where the zeta potentials of the surfaces are reduced to near zero.

The effectiveness of steric stabilisers has been attributed to the thermodynamic penalty when one tries to confine polymeric chains to smaller volumes. Another explanation is that such chains are water-loving (hydrophilic), and they will preferentially associate with water, rather than interact with any other surface (apart from the fact that they are attached at one end to a surface).

The curve shapes and implications of Figure 5 are similar to those of Figure 4. Zeta potential, measured by electrophoresis, and streaming potential, measured by PCD and shown in Figure 5 give essentially the same results. Loops and tails extend into the solution and reduce the potential, especially in the case of the polymer with the highest molecular weight. So the dispersions are then stabilised by a mechanical barrier.

Effects of PVP on stability studied in more detail

Suspension stability typically increases with the polymer concentration. The dispersion stability has been analysed in relation to the addition of different stabilisers very precisely and rapidly using the "Lumitec" analytical centrifuge, which permits analysis by centrifugal separation. This centrifugal sedimentation method allows stability parameters such as sedimentation velocity and shelf life prediction to be directly calculated. This microprocessor-controlled centrifuge is adapted for rapid classification of stability and separation of even concentrated dispersions of up to 40 % solids content [10]. It records the kinetics of transmission changes for 12 samples simultaneously, like a time lapse motion picture, up to 25 000 times faster than tests under gravity assessed by the naked eye. It characterises any demixing phenomena and calculates the particle size distribution.

The principle of this device is based on the following steps: the light source sends out parallel NIR-light with l = 880 nm which is passed through the sample cells lying on the rotor. The distribution of local transmission is recorded over the entire sample length by the CCD-line detector. Finally, space and time resolved transmission profiles are obtained, and the integrated value of this indicates the progress of sedimentation over time. Figure 6 shows different transmission profiles of clay dispersions obtained by this technique. The first line in each of the figures is the initial transmission profile, followed by the second (10 s later) and so on. For example, the transmission for the pure clay dispersion, without polymer (Figure 6a) is 87 % at position 112 after the measuring time. With increasing PVP concentration the stability increases. At the same position (112) the transmission is only 29 % in the presence of 9 % PVP with low mw (Figure 6b). A high transmission of...
100% indicates air or clear supernatant. Figure 7 shows the integrated transmission curves from the same experiment as Figure 6. The slope of the integrated transmission curves, which represent the stability of dispersion, is lower in the presence of PVP than in water. The transmission profiles recorded during sample centrifugation (1000 rpm) show that the lower the integral transmission, the less sedimentation can be observed. Thus, the slope of the curves in Figure 7 indicates that the sedimentation velocity has its maximum for the pure kaolin dispersion (without polymer). The highest stability is achieved by the highest polymer concentration (9% PVP). The stabilising effect is significantly higher with increasing molar mass. The most stable dispersion is thus the dispersion with 9% PVP with high mw. But increasing the PVP concentration as well as increasing the molecular weight also leads to an increase of the viscosity, which has not yet been investigated in these studies. The study of dependence on viscosity is important for industrial applications.

**Effectiveness of stabilisation is broadly predictable**

In the work reported here, suspended clay particles have been characterised by different methods in the presence of PVP of different molar masses. The characterisation of particle systems in terms of charge, size, shape and polymer content is fundamental for the improvement of such processes as stabilisation. All systems investigated showed increased stability in the presence of PVP. These results showed that polymers such as PVP, especially in forms with high molar mass, can be very effective for stabilising aqueous kaolin dispersions.

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**Results at a glance**

For many coatings applications, it is important to maintain the stability of fine particles in aqueous suspension. Tests were carried out to evaluate the theoretical effects of variations in pH on the suspension stability of china clay in water, and practical tests were used to determine the effects of adding the polymer polyvinylpyrrolidone (PVP) at constant pH. The zeta potential and surface charge (q) of kaolin suspensions both move to larger (negative) values as the pH increases from the isoelectric point at about pH 2, indicating that stability will be greater at high pH than at acid pH. Tests with PVP showed that increasing either the addition rate or the molecular mass of the polymer increased stability. This was confirmed by sedimentation tests in a centrifuge equipped with optical detection.

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Figure 1: SEM picture of china clay reveals plates of widely varying size
Figure 2: Zeta potential and surface charge density (q) of kaolin as a function of pH
Figure 3: Effect of ultrasonication time on the particle size distribution of kaolin dispersion
Figure 4: Zeta potential-pH profiles, effect of polymer type and concentrations
Figure 5: Streaming potential (U)-pH profiles of kaolin dispersions in the presence of PVP at different polymer concentrations; the solids content is 1 %.
Figure 6: Transmission profiles of a) pure kaolin dispersion and b) in the presence of 9 % PVP with low mw; solids content is 1 %
Figure 7: Integrated transmission of kaolin dispersions in presence of PVP with low and high mw