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COLLOIDAL STABILITY OF ALKYL KETENE DIMER (AKD) DISPERSIONS. INFLUENCE OF SHEAR, ELECTROLYTE CONCENTRATION, POLYELECTROLYTES AND SURFACTANTS

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ABSTRACT

The influence of shear, electrolytes, polyelectrolytes (anionic trash), and surfactants on the colloidal stability of differently formulated AKD dispersions was investigated. The stability was tested under shear in a Britt Dynamic Drainage Jar by measuring particle size distributions and microelectrophoretic mobilities. Three cationic dispersions were used, stabilised with (1) starch with low charge density, (2) starch with medium charge density and a polyaluminum salt, (3) synthetic polymer with high charge density.

All dispersions showed good to excellent stability to high levels of shear and electrolytes.

All tested dispersions were influenced by carboxymethylcellulose, CMC, and flocculation was induced at a CMC addition giving a z-potential around zero. Dispersions with a higher charge density formed larger flocs and the floc size was a function of the ratio dispersion/CMC. The presence of xylan and sodium oleate only affected the dispersions with high charge density.

Experimental results and theoretical calculations of the rate of AKD flocculation are in good agreement. The theoretical calculations are based on Smoluchowski's equation for collisions between spherical particles in an uniform shear with a correction for hydrodynamic and van der Waals forces between the particles. Calculations indicate that AKD flocculation can compete with deposition on fines and fibres under papermaking conditions.

INTRODUCTION

Alkylketene dimer, AKD, is one of the most frequently used chemicals in the paper industry to produce sized papers, papers with a hydrophobic character. A hydrophobic paper has a good resistance towards water penetration and the hydrophobicity is also important for good printability.

The AKD wax is dispersed in water most commonly with cationic polymers. The AKD wax exists in the dispersion as small spheres covered with a charged polymer layer which prevents flocculation through electrostatic and steric stabilisation. The AKD dispersion is usually added to the thick stock furnish and the AKD particles are assumed to be retained through heterocoagulation with the fibre material [1].

Sizing of paper is a combination of several subprocesses. It is believed that important factors for sizing efficiency are retention, distribution of the AKD particles on the fibres, spreading and the extent of reaction with the cellulose [2–4].

The retention of AKD can be affected by an increased level of dissolved and colloidal substances from the pulp and non retained additives [1,5]. Dissolved and colloidal substances are often referred to as *anionic trash* [6], and consist of e.g. hemicellulose, lignin, extractives and dispersants. These substances can, at high levels, eliminate and even reverse the surface charge of dispersed AKD particles and prevent attachment to the fibres. This would lead to an increased level of AKD circulating in the white water system.

If AKD circulates in the system for a considerable time, the particles can start to agglomerate. Agglomeration will most probably influence the distribution on the fibres. A high temperature and a high pH favour the hydrolysis of AKD which has also been claimed to induce agglomeration [7–9]. An inhomogeneous distribution could lead to an inefficient sizing if AKD does not spread efficiently during drying. Recent results [10] indicate that spreading of AKD is not as complete as stated earlier [11].

Spreading of AKD can be affected by extractives. Lindström et al. [12] reported that sodium oleate can be detrimental to AKD sizing. It was proposed that sodium oleate on the fibre surfaces prevents AKD to spread and react with cellulose. The question of how AKD spreads is important because if AKD can spread rapidly to a monolayer, some flocculation of AKD particles could even be preferable since the flocs are easier to retain.

Due to environmental concerns, paper producers tend to minimise their fresh water consumption. A higher degree of closure leads to elevated temperatures and also increased levels of electrolytes, dissolved and colloidal substances and non retained additives in the white water. To improve the AKD sizing efficiency in more demanding white water systems and at higher machine speeds, dispersions have been designed in different ways [13,14]. A common procedure is to change the surface charge of the particles by using different polyelectrolytes. An increased surface charge is aimed at improving the tolerance towards high electrolyte concentrations, dissolved and colloidal substances and also to increase size retention.

The aim of this study was to investigate how different conditions in the wet end affect the colloidal stability of differently stabilised AKD dispersions. The stability was studied as a function of shear, conductivity, presence of xylan and carboxymethylcellulose, CMC. Influence of sodium oleate in absence and presence of air bubbles was studied as well. The kinetics of AKD flocculation was studied experimentally and theoretically and also compared to theoretical calculations of particle deposition on fines and fibres.

Of the factors studied it was found that CMC, xylan and oleate could seriously influence the colloidal stability, while shear and electrolyte concentration played a smaller role.

EXPERIMENTAL

Materials

Dispersions

Three different dispersions were used in this study, see Table 1.

All the dispersions were prepared from the same AKD wax with a melting point of 52–53°C. The pH of the dispersions was 3–4. The dispersion B with

Table 1 Properties of the AKD dispersions.

Dispersion	Stabilising polymer	Charge density of polymer	Solids content %	AKD content %
A	Cationic starch	Low	10	7.7
B with PA	Cationic starch	Medium	13.3	10
C	Polyamideamine	High	10	8.9

PA, was delivered with a polyaluminium salt (PA) included, primarily to prevent flocculation during storage.

The dispersions were prepared by Eka Chemicals Ltd., Worle, UK. They were stored at 4.0 ± 2.0°C and were used within 3 months after preparation.

In this paper, the dispersion concentration is given as solids content.

Buffers

The pH7 and pH8 buffer solutions were prepared from KH_2PO_4 and NaOH and the pH4 buffer was prepared from potassium hydrogen phthalate and HCl according to [15]. The chemicals were primary standards and analytical concentrates from J.T. Baker, The Netherlands.

Polyelectrolyte standards

1000 μeq/l of poly-diallyldimethylammonium chloride, poly-DADMAC (M_w (weight average) ≈ 300,000, Mütek Analytical, Germany).

Polyelectrolytes

Potassium polyvinylsulfate, KPVS, (esterification degree 97.7%, M_w ≈ 240,000, Wako, Japan) was dissolved in Milli-Q water. The charge density (6.12 meq/g) was determined by titration with poly-DADMAC.

Carboxymethylcellulose, CMC, (M_w ≈ 250,000, Sigma-Aldrich Chemie, Germany) was dissolved in Milli-Q water. The charge density (3.65 meq/g) was determined by titration with poly-DADMAC.

A solution of xylan from birchwood (Sigma-Aldrich Chemie, Germany) was prepared by adding 2.50 g xylan to 50.0 ml of 0.30 M NaOH. The solution was stirred for two days. It was then diluted to 500 ml with Milli-Q water and separated into different fractions by filtering through 0.45 μm, 300,000 D and 10,000 D filters (Sartorius, Germany). Chemical oxygen demand, COD (LCK 214, Dr. Bruno Lange, GmbH, Germany), was used to determine the xylan content in the fractions.

Sodium Oleate

Sodium oleate (iodine number of free acid 85–95, J.T. Baker, The Netherlands) was dissolved in Milli-Q water.

Water quality

The Milli-Q water used in the experiments had a resistance of ≥18 MΩ and was filtered through a 0.22 µm filter.

Methods

Polyelectrolyte titration

Polyelectrolyte titrations were made by using streaming current measurements for end point detection (Mütek PCD 03 pH, Mütek Analytical, Germany). The isoelectric point was set as the end point.

Charge measurements of xylan solutions were made by polyelectrolyte titration with a photometric detection of the end point (Phototitrator 94, BASF, Germany) using *o*-Toluidine Blue (Merck, Germany) as an indicator.

Particle size distribution

A Malvern Mastersizer Microplus (Malvern Instruments Ltd., UK) with a small volume cell top was used. The relative particle refractive index for AKD particles was set to 1.15, the imaginary refractive index was set to 0.1 and the refractive index for the dispersing medium (water) was set to 1.33. The data were analysed according to a polydisperse model, 5OHD, supplied with the instrument.

The particle size distribution was presented as PSD D(v. 0.5) and PSD D(v. 0.9), representing a volume weighted particle size for which 50% and 90% respectively of the sample is below the value given.

The instrument was aligned and the background was measured with Milli-Q water between each measurement.

Measurement of z-potential

The z-potential was determined by microelectrophoresis detected with photon correlation spectroscopy. The instrument, Zetasizer 2000 (Malvern

Instruments Ltd., UK), was calibrated daily with a standard dispersion of polystyrene latex supplied with the instrument.

Stability tests in Britt Dynamic Drainage Jar

The colloidal stability tests were performed in a Britt Dynamic Drainage Jar, BDDJ [16], (Paper Research Materials Inc., USA). The BDDJ was equipped with three baffles and the propeller of the stirrer was placed 3 mm from the wire. The particle size distribution was measured within 2–3 minutes after the sample was taken from the BDDJ. The samples were taken by emptying through the BDDJ bottom tube. The first 100 ml was discarded.

The BDDJ was cleaned with Milli-Q water containing a small amount of acetone and finally rinsed with Milli-Q water between the runs. In all tests the total sample volume was 500 ml and the dispersion concentration 75 mg/l, unless otherwise stated.

Influence of shear

The dispersions were diluted in phosphate buffer (pH7, 2000 µS/cm) and stirred at 2000 rpm during 45 minutes.

Influence of electrolytes

The electrolyte concentrations, obtained by diluting phosphate buffer pH7 with Milli-Q water, varied between 0.020–10.2 mS/cm (ionic strength 0.16–90 mM). The samples were stirred at 1000 rpm for 60 seconds.

Influence of CMC and xylan

The dispersions were added to CMC solutions in phosphate buffers (0–61 µeq/l CMC, pH7, conductivity range 600–2000 µS/cm at 22°C) and stirred at 1000 rpm for 60 seconds. For sample B with PA, the concentration was 95 mg/l.

To study the influence of xylan the dispersions were added to a high molecular fraction of xylan < 0.45 µm (0–76 mg/l xylan, phosphate buffer pH7, 600 µS/cm) and stirred at 1000 rpm for 60 seconds. Dispersion C was also tested in xylan solutions of low molecular weight $< 10{,}000$ D (0–30 mg/l xylan, pH7, 600 µS/cm), stirring speed 1000 rpm for 60 seconds.

A test sequence was also performed to estimate the flocculation rate. Three levels of CMC, 7.5–22 µeq/l were added to dispersion C (phosphate buffer pH7, 600 µS/cm). The dispersions were stirred at 1000 rpm and samples taken between 12–120 seconds.

Influence of sodium oleate

The dispersions were added to sodium oleate solutions (0–0.40 mM) in phosphate buffer pH7 and stirred at 1000 rpm for 60 seconds.

The stirring in BDDJ generates air bubbles. These experiments thus give information on the interactions between a surface active compound and AKD particles in presence of air bubbles.

Stability tests in a cylinder with a screen plate

To study the interaction between AKD particles and a surfactant in absence of air bubbles, stability tests were carried out in a 150 ml graduated Plexiglass cylinder with a screen plate (Figure 1). The holes in the screen plate were 3.0 mm in diameter. AKD dispersions were added to sodium oleate solutions 0–0.40 mM in phosphate buffer pH7 and pH8.

All liquids were degassed by vacuum in ultrasonic bath until no gas bubbles were visible. The samples were stirred by moving the screen plate vertically

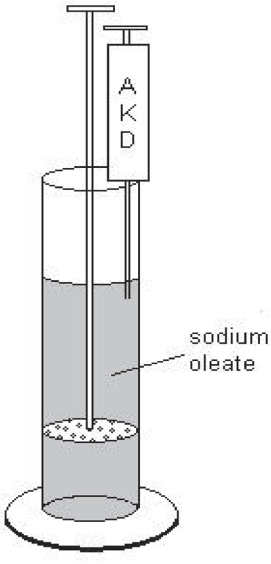

Figure 1 Equipment for stability tests in absence of air bubbles. The top of the cylinder was plugged during the tests. To stir the samples the screen plate was moved vertically without breaking the liquid surface.

without breaking the liquid surface. The equipment was cleaned in the same way as BDDJ.

RESULTS AND DISCUSSION

Dispersion properties

Since the focus of this work was to study the colloidal stability of different AKD dispersions, the first step was to select dispersions with a commercially relevant variation in charge density. The selected dispersions have different stabilising systems, but they were emulsified from the same AKD wax and have approximately the same particle size, 0.5–0.8 µm in diameter. Table 2 shows the charge density and the z-potential of the dispersions at different pH.

Table 2 Charge density and z-potential of the AKD dispersions. The figures in the table are the mean values with 95% confidence intervals.

Dispersion	Polyelectrolyte titration pH3–4 µeq/g	z-potential pH3–4 mV	Polyelectroyte titration pH7 µeq/g	z-potential pH7 mV
A	16	12 ± 0.7	26	3.6 ± 0.4
B with PA	270 ± 10	20 ± 0.7	120 ± 3	14 ± 1
C	640 ± 6	67 ± 2	580 ± 20	33 ± 1

Dispersion A has a low, B with PA a medium and C a high charge density.

It is also shown in Table 2 that the charge density of B with PA was significantly lower at pH7 than at 3–4, most probably because of conversion of positively charged aluminium species to aluminum hydroxide.

Dispersion A did not show a normal titration behaviour. The streaming potential decreased at an almost constant rate with the addition of anionic polymer. The charge density of A could thus not be accurately determined by polyelectrolyte titration and the results only give an estimate.

Shear

Could high shear forces alone affect the colloidal stability and is there any difference in shear tolerance between the stabilising systems? One hypothesis is that the stabilising layer could be sheared off and the waxy surfaces interact during collisions and induce flocculation.

In modern papermaking high shear levels can not be avoided. In fact high shear is deliberately generated in headboxes to break up flocs in the pulp suspension. Also the hydrodynamic forces are very important to the performance of retention aids since high shear increases the collision frequency between particles, polymers and fibres [17].

BDDJ has been estimated to give shear stresses similar to those existing on a paper machine. Tam Doo et al. showed that a stirring speed of 1000 rpm in BDDJ corresponded to maximum fluid shear rate of 6000 s^{-1} [18].

The results in Table 3 show that the dispersions are quite tolerant to shear. There is however some difference between the stabilising systems. Dispersion C emulsified with synthetic polymer was slightly affected after 15 minutes in high shear, while dispersion A was unaffected. B with PA withstood high shear up to 30 minutes.

Table 3 Particle size distributions of AKD dispersions at different shear times.

Time of stirring at 2000 rpm BDDJ (min)	A D(v.0.5)/ D(v. 0.9) µm	B with PA D(v.0.5)/ D(v. 0.9) µm	C D(v. 0.5)/ D(v. 0.09) µm
0	0.6/1.1	0.6/1.4	0.6/1.7
15	0.5/1.0	0.6/1.3	0.8/2.2
30	0.5/1.0	0.6/1.5	0.8/3.7
45	0.5/1.0	0.9/7.8	1.0/4.8

Electrolyte concentration

The influence of electrolyte concentration was studied in the conductivity range 0.020–10.2 mS/cm (ionic strength 0.16–90 mM). The results in Figure 2 show that dispersion C was slightly affected at an ionic strength above 15 mM (~2 mS/cm). D(v. 0.9) for dispersion C indicates that some aggregates have been formed while most of the particles remain stable. Steric stabilisation by the cationic starch probably explains why A and B with PA were unaffected at ionic strengths as high as 65 mM (~8 mS/cm).

A normal range for a papermachine is 3–15 mM (10 m^3 fresh water per air dried metric ton pulp), i.e. the lower range studied in this work.

In Figure 3 it is shown that flocculation of AKD particles induced by CMC (to be discussed in detail below) occurred over a much broader range of CMC concentrations at high electrolyte concentrations. An increased electrolyte concentration decreases the thickness of the electrostatic double layer surrounding the particles and the particles can move closer together without

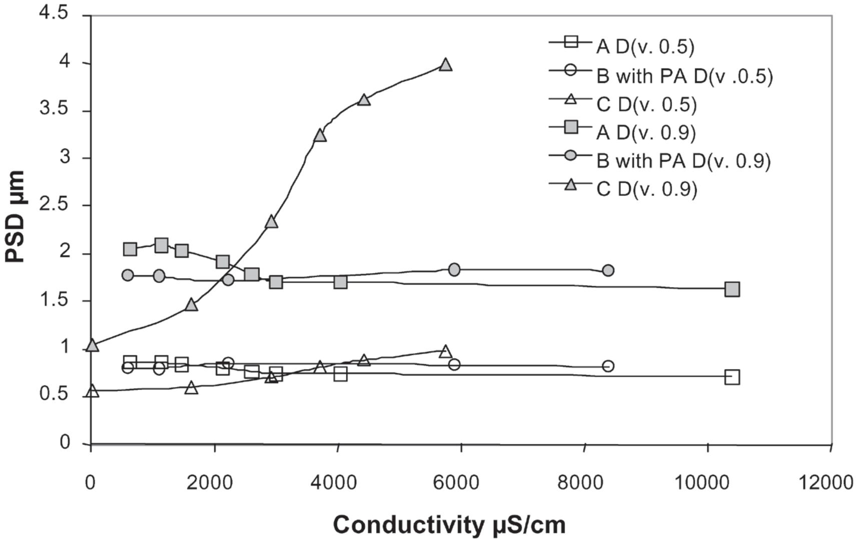

Figure 2 Colloidal stability tests of AKD dispersions at different conductivities. The experiments were performed in a BDDJ at pH7, 1000 rpm for 60 seconds.

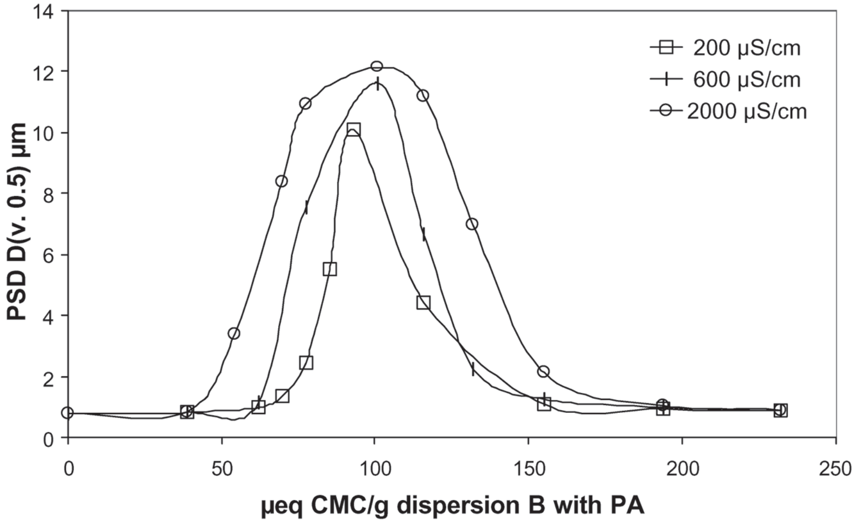

Figure 3 Colloidal stability tests of dispersion B with PA in presence of CMC at different electrolyte levels. The experiments were carried out at 200, 600 and 2000 µS/cm. The samples were stirred at pH7, 1000 rpm for 60 seconds in BDDJ.

repelling each other. This gives the possibility for van der Waals forces to induce flocculation and also for CMC to form bridges between particles.

Anionic trash – CMC and xylan

It is not possible to find one anionic polymer that can serve as a model for anionic trash. Instead two polyelectrolytes were used, CMC and xylan from birchwood. CMC often exists in significant concentrations in white water systems using coated broke. The purpose of using these polymers was to investigate the influence of high versus low charge density polymers on the colloidal stability. The charge density of CMC was 3.6 meq/g and the average Mw ≈ 250,000. Xylan had a charge density of 0.50 meq/g and 65% of the xylan had a molecular weight less than 300,000 and 20% less than 10,000.

Figure 4 shows the results from the experiments with CMC. The dispersions became unstable at a CMC addition bringing the z-potential close to zero. Additions above the isoelectric point gave electrostatically stable systems. The AKD dispersions stabilised with cationic starch thus, as expected, flocculated at lower levels of highly charged anionic polymers than AKD emulsified with high charge polymers.

The results also show that the maximum floc size is a function of the charge density of the dispersions. The particles in dispersion A do not have the same

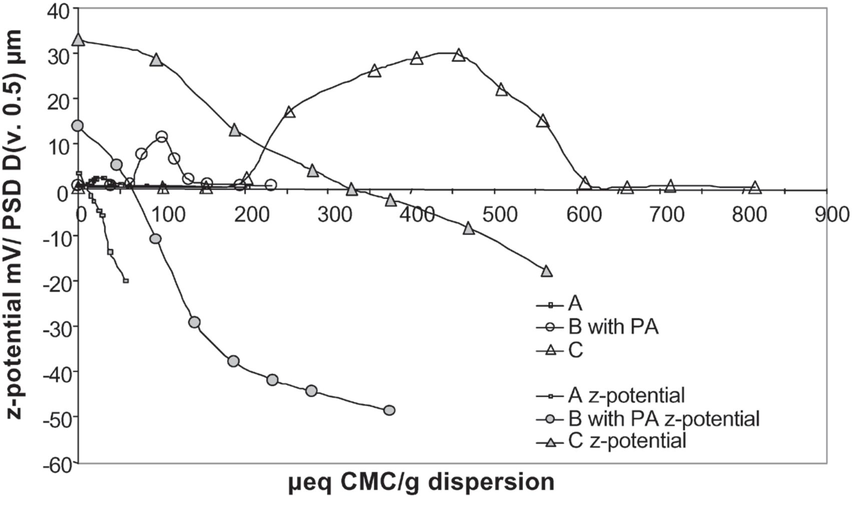

Figure 4 Influence of CMC on the colloidal stability of AKD. The experiments were carried out in BDDJ at pH7, 1000 rpm for 60 seconds.

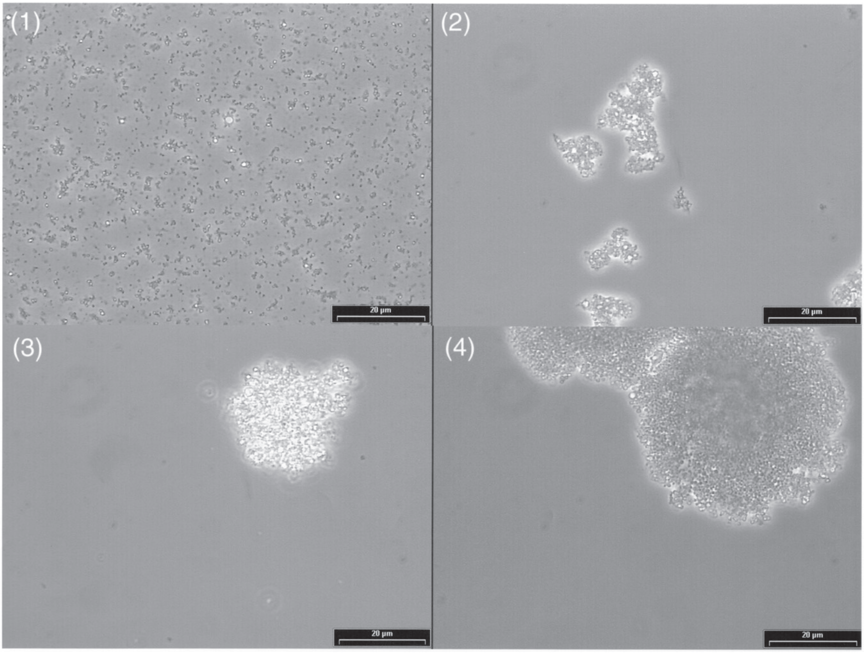

Figure 5 Optical microphotographs of (1) dispersion A unflocculated, (2) dispersion A flocculated with CMC, (3) dispersion B with PA flocculated with CMC and (4) dispersion C flocculated with CMC. The bar is 20 µm.

capability to build a large network of AKD particles and CMC, as particles in B with PA and C with a higher surface charge, see Figure 5.

Xylan did not affect the colloidal stability as efficiently as CMC did. The results in Figure 6 show that emulsion A was unaffected, while B with PA and C started to flocculate at a xylan level of 200 mg xylan/g dispersion.

A reason why A was colloidally stable might be that the starch around the particles has too low charge density to interact with xylan. The more highly charged polymers in B with PA and C carry enough charge to coagulate with the higher molecular weight fraction of xylan. Xylan fragments less than 10,000 D did not seem to affect the colloidal stability even for dispersion C, see insert in Figure 6.

It is interesting to note that a dispersion with a high charge density can be more sensitive to flocculation than a low charge density dispersion in a white water containing low charge density anionic trash.

The concentration of 200 mg/g dispersion corresponds to a xylan level of

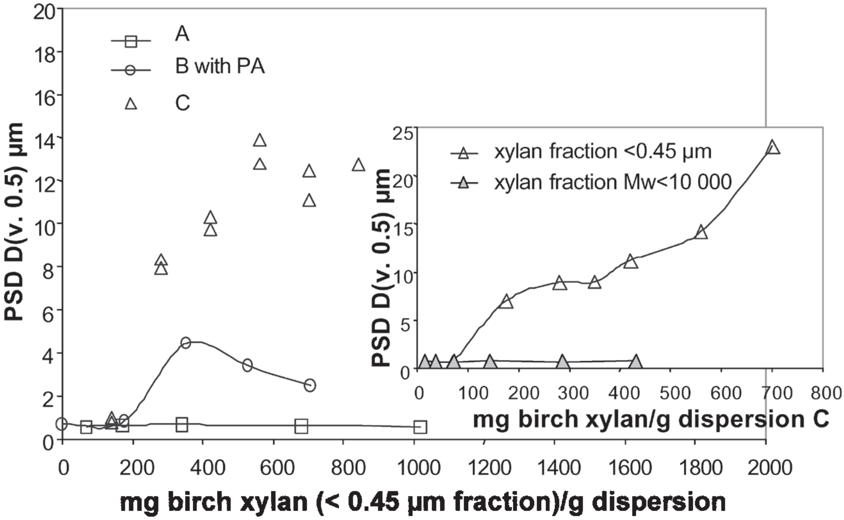

Figure 6 Influence of birch xylan on the colloidal stability of AKD. Two different molecular weight fractions of xylan (< 0.45 µm and Mw < 10,000) were used. Tests were performed in BDDJ, at pH7, 1000 rpm for 60 seconds.

2 mg/l at 2 kg AKD per metric ton pulp and 0.5% consistency. A level of xylan in the range of 50–100 mg/l in the white water of a papermachine using 10 m^3 fresh water per metric ton air dried pulp is not unusual.

Surfactants – sodium oleate

Sodium oleate was chosen as a model substance for surfactants partly because fatty acids exist to a considerable extent in wood extractives. Surface active compounds are also occasionally added in the wet end of a papermachine to overcome problems with foaming.

In this study, the effect of sodium oleate in the absence and presence of air bubbles was studied. Since residual air in stock furnishes can not be avoided, the results from the experiments with air bubbles in the system are more relevant for practical situations. Comparison of the results could indicate the role of air bubbles for flocculation.

First we discuss the results from the study when air bubbles were absent. The z-potential measurements presented in Figure 7 show that oleate adsorbs on the AKD particles in all dispersions. Dispersion A does not flocculate even at z-potentials close to zero. There is obviously a steric stabilisation by the starch.

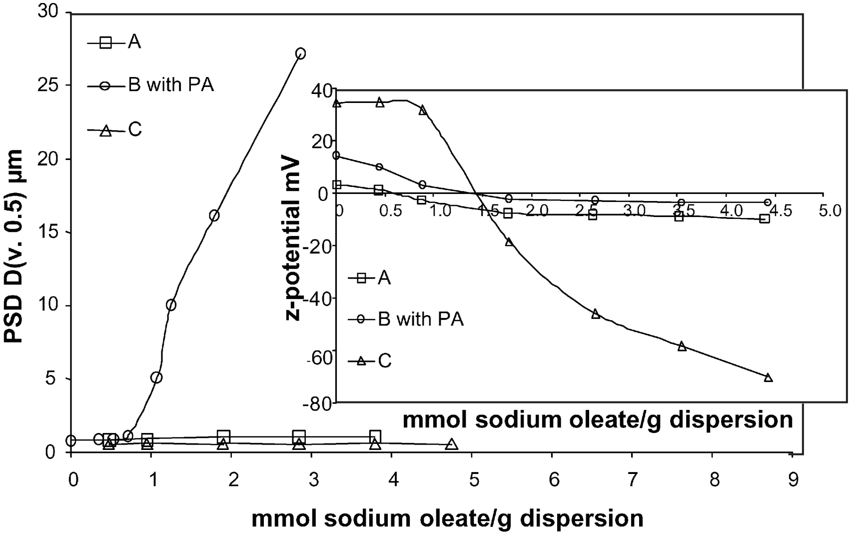

Figure 7 Influence of sodium oleate on colloidal stability of AKD in the absence of air bubbles at pH7. The experiments were carried out in a graduated cylinder with a circular screen plate. The samples were stirred for 60 seconds.

For B with PA a flocculation occurs. A reasonable explanation is that enough oleate molecules have adsorbed to promote flocculation due to hydrophobic interactions. For dispersion C no flocculation is observed. The z-potential for dispersion C changes very rapidly around zero, which might be the reason that we do not observe flocculation.

The results from the more practically relevant experiments with air bubbles present are given in Figure 8. Dispersion A and B with PA have the same behaviour as with no air bubbles present. For C there is, in contrast to the case with no air bubbles, a strong flocculation. There are at least two possible explanations for the instability. The presence of an air/water interface might promote the interaction of the heavily oleate covered AKD particles such that the electrostatic repulsion is overcome. Another possibility is that oleate replaces the emulsifier used as a bridge between the hydrophobic wax and the stabilising polymer. This would lead to a weaker bond between the wax and the polymer that could be broken during the high shear. The shear was not of the same magnitude during the tests with no air bubbles present. Experiments were also made for dispersion C at pH4. The dispersion was completely

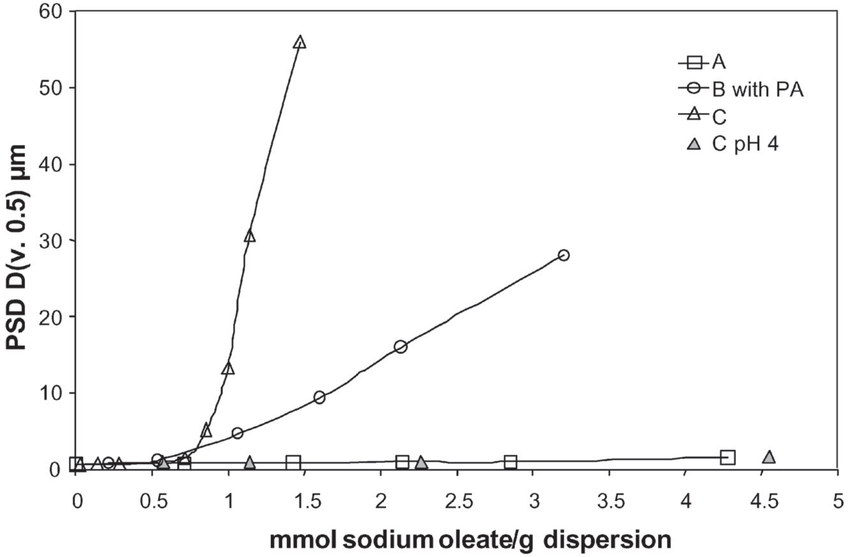

Figure 8 Influence of sodium oleate and air bubbles on colloidal stability of AKD at pH7 and pH4. The experiments were carried out in BDDJ, 1000 rpm for 60 seconds.

stable. This is expected since there are at this pH no oleate ions present, which can adsorb on the particle surface.

Some further experiments with surfactants show how sensitive the stabilising system can be to changes in white water conditions, e.g. pH. Dispersion B with PA lost its colloidal stability at pH7, see Figure 7. When the same dispersion was tested at pH8 there was no flocculation, Figure 9. The z-potential measurements show that the system at pH8 reached much lower values, which most likely is the reason for the colloidal stability.

The dispersions B with PA and C were visibly aggregated at concentrations above 0.7–1 mmol sodium oleate/g dispersion in presence of air bubbles, see Figure 8. This concentration corresponds to a level of 3–4 mg/l sodium oleate (2 kg AKD per metric ton at 0.5% consistency). A fatty acid concentration in this range is not unlikely in a papermachine white water system.

Kinetics of AKD flocculation

An interesting and important question is how fast the flocculation between the AKD particles induced by anionic trash occurs. This flocculation

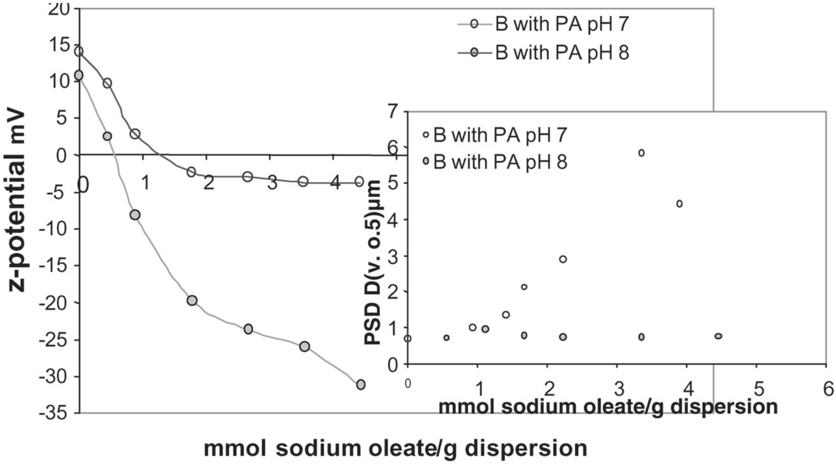

Figure 9 The z-potential and particle size distribution at different levels of sodium oleate in absence of air at pH7 and 8. The experiments were carried out in a graduated cylinder with a circular screen plate used for moderately stirring the sample without breaking the liquid surface. The liquids were degassed by vacuum before the experiments.

rate should be compared with the deposition rate of AKD on fibres and fines.

The flocculation rate was estimated for normal hydrodynamic conditions (1000 rpm in BDDJ) by determining the particle size distribution in dispersion C at different additions of CMC and stirring times. The result from this study showed that the particles started to show appreciable aggregation (D(v. 0.5) > 2.5 µm) after 25 seconds if the CMC concentration was high enough to induce flocculation, Figure 10. The floc size reached a maximum of about 30 µm. Larger flocs did not seem to survive the shear applied in the experiment.

Figure 10 also includes a theoretical calculation of the particle growth with time. In the calculations floc break-up is not considered.

The prediction was calculated according to a model for orthokinetic collision in uniform shear, with a correction for the collision efficiency [17,19]

$$-ln(N/N_0) = K\, N_0 a_{Sh} t \tag{1}$$

The theoretical prediction is based on a very elementary view of binary collisions between spherical particles in a fluid shear. N_0, the initial number of particles, was calculated by division of the total volume of AKD, V*tot*, with the volume of a single AKD particle with a radius of 0.4 µm. V*tot* was calculated by dividing the AKD concentration, 0.075 kg/m^3, with the AKD density, 910 kg/m^3. N is the actual number of particles at time t, K is the rate constant for collisions and α_{Sh} is the collision efficiency constant in fluid shear. The rate constant K is calculated from the expression

$$K = 4/3\ \mathrm{G}(a_1 + a_2)^3 \tag{2}$$

where G stands for the uniform shear rate, and a_1 and a_2 are the radii of spheres involved in the collision.

The collision efficiency factor, α_{Sh}, is calculated according to Han et al. [19], and takes into account hydrodynamic repulsion and van der Waals attraction. The hydrodynamic repulsion exists since the water between the particles has to be moved out of the way before a collision can occur. It is especially unlikely for particles differing widely in size to collide with each other, since a very small particle will follow the streamlines around a large particle. The collision efficiency factor can be as small as 10^{-5} for collisions between particles differing very much in size and having low attraction forces between each other. In the calculations presented in Figure 10 $\alpha_{Sh} = 0.1$ was used [19].

In figure 10 the particle growth is expressed as diameter. The medium diameter, d, was calculated from the expression

$$d = 2(3\ Vtot/4\ \pi\ N)^{1/3} \tag{3}$$

The results in Figure 10 clearly show that the calculations give a very reasonable estimate of the observed flocculation rate.

To try to answer the question if flocculation of AKD can occur before AKD is deposited on the fines and fibres in a pulp suspension, we must calculate the flocculation rate and the deposition rate for AKD at typical white water conditions. The results presented in Figure 10 give us the confidence that such calculations should be at least qualitatively correct.

The calculations were made assuming an AKD dosage of 2 kg/metric ton air dried pulp to a 5 kg/m^3 pulp suspension with a fines content of 5%. A concentration of 4.75 kg/m^3 and a hydrodynamic radius of 30 µm were used for fibres [17]. For fines the concentration was 0.25 kg/m^3 and two different fines radii, 1 and 2 µm were used in the calculations. The AKD dispersion was 0.01 kg/m^3 and the radius was 0.40 µm. The AKD flocculation time and deposition time to the fibre materials were estimated at two levels of shear, 100 and 6000 s^{-1}. The time, $t^{1/2}$, is the time at which half of the AKD particles have either formed doublets or been deposited to fines or fibres.

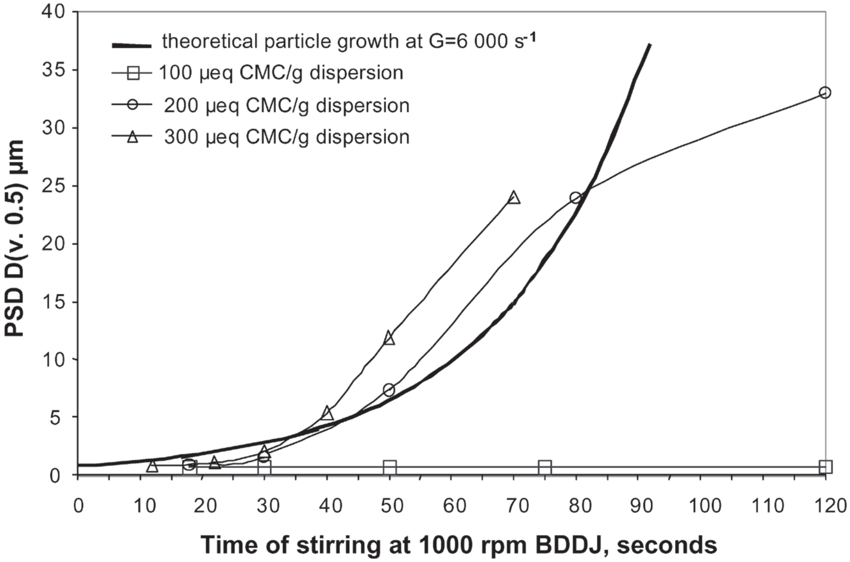

Figure 10 Mean particle size of single particles/aggregates of AKD particles (dispersion C) at different concentrations of CMC and stirring times (1000 rpm). The theoretical particle growth with time was calculated assuming an uniform shear of 6000 s^{-1}.

Table 4 Theoretical estimates of flocculation and deposition times.

	Size ratio	$t^{1/2}$ G = 100 s^{-1}	$t^{1/2}$ G = 6000 s^{-1}
AKD/AKD	1	800	30
AKD/FINES (1 µm)	0.4	100	10
AKD/FINES (2 µm)	0.2	2000	200
AKD/FIBRES (30 µm)	0.01	50,000	900

There are numbers of simplifying assumptions in the calculations e.g. the fibres and the fines are assumed to be smooth with no protruding fibrils. The results from the calculation in Table 4 show that AKD flocculation is likely to occur at least on the same time scale as deposition to the fines and fibres. Although the calculated time for AKD deposition to the fibres is probably overestimated, the results indicate that the deposition to the fibres is slower compared to fines. Fines obviously play an important role in the retention of AKD.

SUMMARY AND CONCLUDING REMARKS

The colloidal stability of AKD dispersions at typical white water conditions has been studied. The following was concluded:

- CMC influenced the colloidal stability of all dispersions tested. Xylan and oleate influenced the colloidal stability of AKD dispersions of medium and high charge density. Shear and electrolyte concentration had a smaller influence.
- Experimental studies and theoretical calculations of AKD flocculation showed good agreement. Theoretical calculations indicate that AKD flocculation occurs on the same time scale as deposition on fines and fibres.

The methods used in this study, a combination of BDDJ and particle size measurements and microelectrophoretic mobilities, are easy to use and can give valuable information about the properties of AKD dispersions that have to be fulfilled to suite a specific wet end system.

It should perhaps be pointed out that in this paper we have not addressed the questions of AKD retention, spreading and the reaction with cellulose.

Investigations of the colloidal stability of AKD in white water samples are in progress, as are experiments at different temperatures with AKD dispersions made from waxes with different melting points.

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Transcription of Discussion

COLLOIDAL STABILITY OF ALKYL KETENE DIMER (AKD) DISPERSIONS. INFLUENCE OF SHEAR, ELECTROLYTE CONCENTRATION, POLYELECTROLYTES AND SURFACTANTS

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Mirjam Sterner AssiDomän

Do you think that this agglomeration actually occurs in real white water?

Rosa Mattsson

Yes, I think so. First of all you must approximately hit the iso-electric point it agglomeration should occur in real white water. Looking at the results it seems that AKD stabilized with a high charge density polymer are the easiest to flocculate with polyelectrolytes with a low charge density; which exist in the real white waters, so I think so.

Lars Wågberg Mid-Sweden University

What would an optimum stabilizer look like? A higher charge density would give a better deposition adsorbtion on the fibre, but a higher charge density would also give a larger sensitivity towards ammonic polymers in solutions? If you were to choose how would you decide on an optimum stabilizer?

Rosa Mattsson

If I would like to have a stable AKD which is not aggregated in the white water I would choose AKD dispersions stabilized with a cationic starch with a quite low charge density because they seem to be more stable in this system because the charge is reversed at high levels of polyelectrolytes.

Lars Wågberg

Yes, but on the other hand you would get a less efficient deposition on the fibres wouldn't you?

Rosa Mattsson

Yes, I would but I might escape problems with scaling and impurities in the paper and as far as I know the AKD retention is quite low if you look at the real situation, around 30–40%. It really would be good to increase that retention and I don't have an idea how you should improve that, just looking at the stabilizing polymer systems that we have today.

John Roberts Department of Paper Science, UMIST

Which of these two mechanisms, AKD flocculation or fibre flocculation do you think would lead to higher levels of retention?

Rosa Mattsson

We have been looking at that quite recently and I don't want to answer that today. I will be giving a presentation at the PIRT meeting in Prague so I will present that there

John Roberts

Following on from that, in terms of the sizing efficiency, would you expect that to be better if you had fibre-AKD flocculation rather than flocculation of the AKD particles themselves?

Rosa Mattsson

You can guess that by yourself I think, can't you?

John Roberts

Well . . . you can always be surprised.

Simon Champ BASF

In the experiments that you did you used the Britt Dynamic Drainage Jar and then studied particle sizing with the Malvern particle analyser. How did you connect those two? Because you're shearing and then removing a sample, then diluting and measuring the particle size. It could be that if flocculation is irreversible there is no problem, effectively you are removing shear and then are diluting, I don't know if you have studied this effect in your results.

Rosa Mattsson

I used fairly low concentrations of AKD so I didn't have to dilute them to measure them in the Malvern and you are right, there could be some secondary flocculation because I took the samples from the Brit Jar to measure the particle size in the Malvern, and so there is a time in between where this flocculation could occur but I really don't think so. If you look at the results for CMC you can see that you have a really nice distribution of aggregate sizes which would not occur if secondary flocculation was important.

Simon Champ

In the paper you have one shear rate, but did you study different shear rates? Obviously if you have different shear rates and your results are different, then that infers that it is the shear rate which is governing the flocculation rather than anything that you do subsequently.

Rosa Mattsson

No, I didn't look at different shear levels when I looked at the flocculation. The shear level of 1000 *rpm* in the Britt Jar is a very high level of shear, its estimated up to 6000 sl and that is a fairly realistic shear level that would exist on a paper machine.

Simon Champ

If your results are independent of the shear rate, then your results may be affected by your size measurement with the Malvern, but I don't know. It is something in which I have an interest in.