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Electrokinetic characterisation of cationic amylopectin starch; screening by salt and screening by nanosized silica particles

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Abstract

The screening of cationic amylopectin starch with salt has been investigated using the technique of electrokinetic sonic amplitude. The dynamic mobility was found to decrease as the electrolyte concentration increases. The experimental data were satisfactorily explained by applying a porous sphere model. The radius of the porous sphere could be used to evaluate the contraction of the amylopectin molecule as the electrolyte concentration increases. The screening of cationic amylopectin starch with nanosized silica particles was also followed using the technique of phase analysis light scattering. The formation of large macroscopic flocs could be explained in terms of available cationic and anionic sites of the initially formed polyelectrolyte complexes between one amylopectin molecule and a number of small silica particles.

Keywords: Starch; Silica; Electrokinetic; Electrokinetic sonic amplitude; Phase analysis light scattering; Polyelectrolyte complex; Retention aids; Mobility

1. Introduction

Starch and its derivatives are used in the paper industry as a retention and dewatering aid and to improve the dry strength of the paper. Cationic starch and nanosized silica particles are very efficient as retention aids, i.e., to incorporate fillers like clay and fines into the paper sheet [1]. The mechanism of how the retention aid operates is poorly understood but it involves ionic binding between the different components in the paper sheet. Therefore, an electrokinetic characterisation of the cationic starch and polyelectrolyte complexes of the cationic starch covered with the nanosized silica particles is important.

The starch used is from a recently derived strain of potato producing only amylopectin [2]. The molecular weight of amylopectin ranges from 10^7 g/mol up to 10^9 g/mol [3]. Typical values of the hydrodynamic radius are about 100 nm [4,5]. The amylopectin consists of glucose units connected with α(1-4) bonds in the linear parts and the branching points are α(1-6) bonds. Four to five percent of the links between the

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monomers are branching points [3,6]. The amylopectin probably has regions that are highly branched alternating with regions with linear polymer strands [5,7]. The branched regions can be modelled as a starlike structure with many arms [8]. The arms in the stars should be rather flexible due to the flexibility of the (α1-6) bonds in the branching points. The amylopectin molecule has often a bimodal distribution of chain length with the longer average chain length being 48–65 glucose units and a shorter length of 16–20 glucose units [9,10]. The different chains are further divided into A-, B- and C-chains. The C-chain carries the free reducing end group and is connected with B-chains that carry other B-chains and/or A-chains. The A-chain carries no other chain [7]. The ratio of A-chains and B-chains varies from 1:1 to 1.5:1 in most starch samples [7]. The branching density and distribution of chain lengths are very important for the molecular architecture of the amylopectin molecule. Callaghan and Lelievre [4] have concluded that wheat and potato amylopectin has the shape of an oblate ellipsoid (like a pancake) and the dimensions of wheat amylopectin is 120 nm for the long axis and 15 nm for the short axis.

An electrokinetic characterisation of charged polymers is a key issue in the understanding of their local geometry, i.e., if the polyions behave as cylinders, porous spheres or random coils. One of the first published electrokinetic characterisations of a polyion (polyvinyl sulphate) was by Nagasawa et al. [11] in 1958 using a moving boundary method. In 1971, Ware and Flygare introduced electrophoretic light scattering [12] which is much faster and a more reliable technique than the moving boundary method and does not require the build up of unstable concentration gradients. An improvement of the electrophoretic light scattering, namely phase analysis light scattering (PALS), was developed by Miller et al. [13] in 1991, which allows smaller particles to be followed and also allows nonpolar solvent to be used. The limitation of light scattering techniques is that the samples have to be very clean and dilute in order to obtain reliable results. This problem can be solved with the recently developed technique called electrokinetic sonic amplitude (ESA) [14] which is extremely rapid and does not require any sample cleaning. Furthermore, higher concentrations of the polymer in solution can be used.

In this paper, we have measured the dynamic mobilities of cationic amylopectin starch (CApS) samples dispersed in NaCl solutions of varying ionic strength using an ESA 8000 instrument. Furthermore, the electrophoretic mobilities of silica-covered amylopectin starch molecules were also investigated using phase analysis light scattering. This provides us with information on the local geometry and the size of the cavities in the amylopectin molecule.

2. Experimental

Materials.—Potato amylopectin starch was supplied by Lyckeby Stärkelsen, Kristianstad. For the preparation of cationic amylopectin, 3-chloro-2-hydroxypropyltrimethylammonium chloride (QUAB 188, obtained from Degussa) was used. The nanosized silica particles (NSP) was a gift from Eka Chemicals. The surface area determined by Sears titration [15] was 500 m^2/g, which corresponds to a spherical diameter of 5.4 nm.

The synthesis of cationic amylopectin.—In order to obtain a uniform distribution of the cationic charges the following synthesis procedure was used, as based on a method developed by Carr and Bagby [16]: 25 g native amylopectin was dissolved in 1200 g water at 95 °C for 30 min in a nitrogen atmosphere. At 55 °C, 9.15 g of a 66.7% 3-chloro-2-hydroxypropyltrimethylammonium chloride (QUAB 188) solution and 51.04 g 1 M sodium hydroxide were added separately. The solution was cationized (during the night $\approx$ 15 h), pH was then lowered to below 7 with hydrochloric acid and cooled to room temperature to stop the cationization process. The amylopectin was precipitated in isopropanol. The precipitate was washed five times in a mixture of 3:1 isopropanol–water by light centrifugation 3000 rpm in ten minutes to remove any residual salt. To get rid of any residual water it was centrifuged twice with isopropanol. The precipitate was dried at 55 °C for 24 h to remove the isopropanol. The yield was 60% by weight of added amylopectin and the precipitate was stored dry. The degree of cationization is the number of positively charged groups per 100 glucose monomers and was measured by Lyckeby Stärkelsen using the classical Kjeldahl method. The degree of cationization was found to be 5.2%.

Screening by salt.—Electrokinetic sonic amplitude (ESA). When an alternating electrical field is applied to a colloidal suspension, charged material will move electrophoretically. The surrounding liquid has to compensate for the mass flux of colloidal particles and ions towards or away from the electrodes. This generates an alternating pressure wave. This effect is

called the electrokinetic sonic amplitude (ESA) [14]. For dilute suspensions (up to a volume fraction of about 2%) the magnitude of the ESA signal is related to the dynamic mobility, μ_d, of the hydrated colloid by [17]

$$\mathrm{ESA}(\omega) = P/E = c(\omega)\mu_d\phi(\Delta\rho/\rho) \quad (1)$$

where P is the amplitude of the sound wave, E is the amplitude of the applied electric field, ω is the frequency of the applied electric field, c is an instrument factor, $\Delta\rho$ is the density difference between the particles and the solvent, ρ is the density of the solvent and ϕ is here the volume fraction of particles in suspension.

A similar expression is also valid for electrolyte solutions [18] where the term $\phi(\Delta\rho/\rho)\mu_d$ is replaced by,

$$\frac{\sum_j n_j e z_j \Delta M_j / f_j}{\rho} \quad (2)$$

where n_j is the number of ions per unit volume of type j of valency z_j and frictional coefficient f_j. ΔM_j is the mass of ion j corrected for buoyancy.

As can be seen there are two limits in the treatment of the polyelectrolyte. If the polyelectrolyte moves only a very short distance in the applied electric field, different parts of the polyelectrolyte can be considered as somewhat independent of each other and the electrolyte method is applicable. Zana and Yeager [19] treated this theoretically in the case where a sound wave is passed through a polyelectrolyte suspension giving rise to an alternating potential. In our case the applied electric field, as calculated from the lowest and highest measured dynamic mobilities respectively, moves the cationic starch between 3 to 10 Å. Therefore, the molecules move atomic distances and should not be treated as different parts of the molecule moving independent of each other. So the colloidal approach is used in our case. It should be noted that the dynamic mobility obtained is a mass average of the hydrated polyelectrolytes and the ESA signal obtained is not frequency-dependent in the available measuring range of the ESA apparatus. It should also be noted that for solid spherical particles, when $\Delta\rho$ and ζ are small, the dynamic mobility is equal to the electrophoretic mobility (within 10%) and independent of particle size up to 300 nm radii [20]. It will therefore be assumed that the polydispersity of the cationic starch does not affect the obtained dynamic mobility (the ESA signal).

In order to obtain the dynamic mobility, μ_d, in Eq. (1), it is necessary to evaluate the term $\phi(\Delta\rho/\rho)$. The volume fraction of the hydrated polyelectrolyte is extremely difficult to obtain and instead another approach is used. Wade et al. [21] has pointed out that the relation

$$(\rho_{\mathrm{suspension}} - \rho_{\mathrm{solvent}})/\rho_{\mathrm{solvent}} = \phi(\Delta\rho/\rho) \quad (3)$$

can be used, so the individual values of the volume fraction and density of a polymer are not required to calculate the dynamic mobility.

ESA measurements. The ESA measurements were performed on an ESA 8000 instrument (Matec Applied Sciences) using the high sensitivity PPL-80 cell, which requires about 4 mL of CApS sample. Each data point is an average of 10 measurements. The field strength was about 500 V/cm and the frequency 0.9–1.0 MHz. Measurements are sensitive to air bubbles, measurements were therefore made twice for each sample with the sample being taken out of the cell and reinserted in between, in order to check that the measured values were the same (within 4% or less of each other). In order to obtain the ESA signal for the CApS, the measured ESA signals were corrected for the background signal (from the electrolyte) according to the procedure outlined by Desai et al. [22]: The measured ESA ($\mathrm{ESA}_{\mathrm{meas}}$) is a vector sum of the ESA for the CApS ($\mathrm{ESA}_{\mathrm{true}}$) and that of the background electrolyte ($\mathrm{ESA}_{\mathrm{bkgd}}$). This can be written,

$$\mathrm{ESA}_{\mathrm{meas}} = \mathrm{ESA}_{\mathrm{true}} + \mathrm{ESA}_{\mathrm{bkgd}} \quad (4)$$

This equation can be resolved into its two components

$$|\mathrm{ESA}_{\mathrm{meas}}|\cos\theta = |\mathrm{ESA}_{\mathrm{true}}|\cos\beta + |\mathrm{ESA}_{\mathrm{bkgd}}|\cos\phi \quad (4a)$$

and

$$|\mathrm{ESA}_{\mathrm{meas}}|\sin\theta = |\mathrm{ESA}_{\mathrm{true}}|\sin\beta + |\mathrm{ESA}_{\mathrm{bkgd}}|\sin\phi \quad (4b)$$

where θ, β and ϕ here are the phase angles of the measured, true and background ESA signals respectively.

The cationic amylopectin starch was dissolved in double deionized water at 97 °C for 30 min at the concentrations used in the ESA apparatus. The solutions were cooled to room temperature (around 20 °C) and the appropriate amount of NaCl was then added to the amylopectin solution with gentle stirring. The concentration of the samples where checked

according to the method of Dubois et al. [23], except that the concentration of phenol in water was 10% wt instead of 5% wt.

The porous sphere model. The dynamic mobility of a porous sphere has been investigated only for relatively large particles (> 1 μm) [24]. It will here be assumed that the dynamic mobility is equal in magnitude to the electrophoretic mobility of a porous sphere of a radius of 300 nm or less, as has been found for solid spherical particles (within 10%) when $\Delta\rho$ and ζ are small [20].

The porous sphere model as developed by Hermans [25], can be used to convert the charge density to an electrophoretic mobility. If β and $\mu \gg 1$, the simplified expression

$$\mu_e = \frac{\rho}{vf}\left(1 + \frac{\mu^2(2+\mu/\beta)}{2\beta(1+\mu/\beta)}\right) \quad (5)$$

can be used, where

$$\rho = 0.052ve_0 \quad (6)$$

is the density of fixed charges on the polymer ion with the charge $e_0 = 1.602 \times 10^{-19}$ C, and

$$v = \frac{N}{4\pi R^3/3} \quad (7)$$

is the density of polymer beads in the porous sphere with radius R and N is the number of beads. The polymer ion is treated as if it consists of a large number of beads which are enclosed in a porous sphere with the same viscosity as the polymer. The number of beads is fixed in this treatment and therefore the porosity of the sphere can change as the radius of the sphere changes.

$$f = 6\pi\eta a \quad (8)$$

where f is the friction coefficient of one bead with radius a, η is viscosity of the solvent.

$$\mu^2 = 2\sigma^2/3 \quad (9)$$

μ here is a dimensionless parameter and σ is the Debye shielding ratio,

$$\sigma = \sqrt{vfR^2/\eta}\,. \quad (10)$$

The Debye shielding ratio describes the friction between the polymer and the solvent. If σ is large, the porous sphere will behave as a compact sphere with the same radius. If σ approaches zero, the molecule is free-draining and the frictional force becomes equal to NfU, where U is the electrophoretic velocity of the polymer.

$$\beta = \kappa R \quad (11)$$

κ is the reciprocal screening length. Both β and μ should be large compared with unity for Eq. (5) to hold. Note that β is 5 with no added salt and otherwise always above 10. μ is around 50 so the simplified expression is valid for the CApS polymer.

For the porous sphere model, the number of beads N is 434,600 as calculated from static light scattering measurements where the molecular weight of the amylopectin molecule was found to be 70.4×10^6 g/mol. The radius of the beads, a, is 2.5 Å as calculated from bond lengths and bond angles in α-D-glucose [26]. The radius of the spheres was chosen to be the only fitting parameter. The charge density is fixed, i.e., 0.052 of the beads contains a charge.

Screening by nanosized silica particles.—Phase diagram. The flocculation behaviour between the cationic amylopectin and the nanosized silica particles were tested according to the following procedure: CApS solutions with weight fractions between 0.01–1.0% after mixing and silica solutions with weight fractions between 0.01–1.0% after mixing were mixed vigorously in test tubes for 10 min using a vertical shaker. The pH was 8.0 and the NaCl concentration was 5 mM in all solutions. The mixed solutions were left overnight and the detection method was visual observation. The mixed solutions were characterised as either a homogenous or heterogenous solution. In the heterogenous solutions flocs were formed and were characterised as either transparent flocs or white flocs. The mixing order was checked by adding the silica to the starch solution and vice versa. The mixing order did not affect the visual result.

Phase analysis light scattering (PALS). When an electrical field is applied to a colloidal suspension, charged material will move electrophoretically. The velocity from the charged particles can be followed by measuring the change in phase of laser radiation scattered from the sample. This method is called phase analysis light scattering (PALS) [13]. PALS can distinguish the electrophoretic mobility from other velocity components such as Brownian motion, sedimentation, thermal convection, by applying a movable fringe pattern which shifts the phase relative to the incident light. The phase shift is directly proportional to the position of the scattering particle, so the

mean phase change is proportional to the electrophoretic velocity. This can be written as:

$$< Q(t) - Q(0) \geq < A > q[v_c t + \mu_e E_0\{\cos(\phi) - \cos(\omega t + \phi)\}/\omega] \quad (12)$$

where

$$\delta Q = A\,\delta\phi \quad (13)$$

A is the amplitude and ϕ is here the phase of the complex Doppler signal, q is the optical scattering vector, v_c is a term taking care of all velocities except the electrophoretic one, t is time, μ_e is the electrophoretic mobility, E_0 is the initial amplitude of the applied field, ω is the frequency of the applied sinusoidal field. Hence, a PALS experiment can generate the electrophoretic mobility and determine the sign. Eq. (12) is known as the amplitude-weighted phase difference (AWPD) function.

PALS measurements. The samples were prepared by vigorously mixing the CApS and the NSP solutions at pH 8 and with 5 mM sodium azide for 30 s. The final concentration of CApS was 1 mg/mL. The PALS measurements were performed at 25 °C and each result is an average of 500 runs. The change in mass ratio m_{NSP}/m_{CApS} were obtained by changing the silica concentration. The mass ratios were chosen to be on both sides of the flocculation region where macroscopic flocs are formed (see Fig. 2).

3. Results and Discussion

Screening by salt.—ESA measurements. In Fig. 1 the variation of the (corrected) ESA signal for CApS as a function of the concentration of CApS is shown. The ESA signal increases linearly with increasing CApS concentration. This shows that the background correction procedure works. However, it should be noted that the results are more difficult to reproduce at high electrolyte concentrations due to the dominance in the measured ESA signal from the background electrolyte (around 90%). This is the reason why the points at 2 mg/mL CApS is not shown for 50 and 100 mM added sodium chloride.

From the slope of the curves the dynamic mobility can be calculated, provided that the product $\phi(\Delta\rho/\rho)$ is known. As mentioned earlier, this product is equal to $(\rho_{suspension} - \rho_{solvent})/\rho_{solvent}$, an experimentally accessible quantity. This quantity was measured with an Anton Paar densitometer at added sodium chloride concentrations between 0–100 mM and 1 mg/mL CApS. The results are shown in Table 1. The results

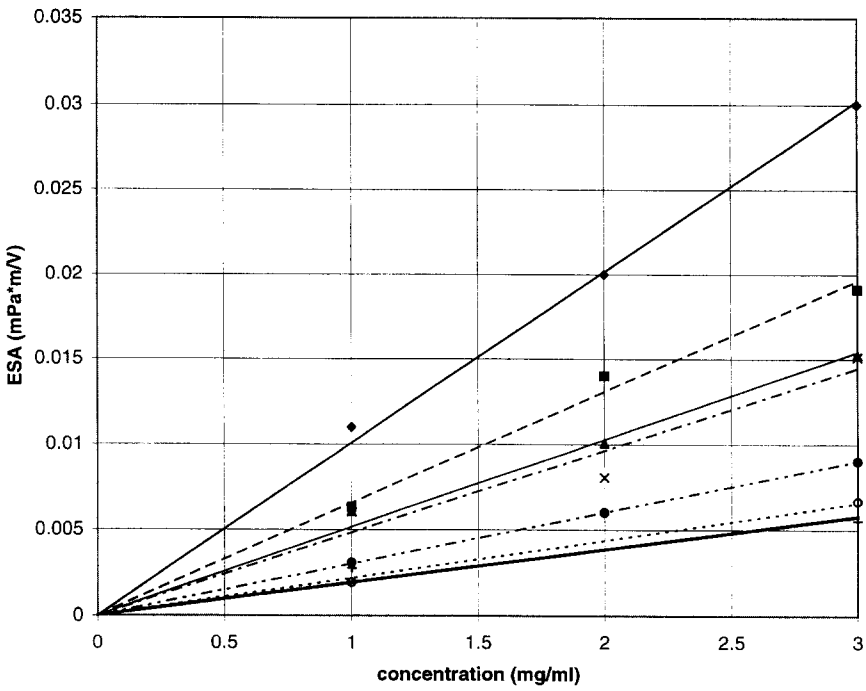

Fig. 1. The ESA signal as a function of amylopectin concentration. Seven different electrolyte concentrations have been used. Concentrations of NaCl solution added: ◆ 0 mM; ■ 2 mM; ▲ 5 mM; x 10 mM; ● 25 mM; + 50 mM; ○ 100 mM; ——— Linear (0 mM); —Linear (2 mM); ——— Linear (5 mM); -·-· Linear (10 mM); -· · - Linear (25 mM); ——— Linear (50 mM); · · · · · · Linear (100 mM).

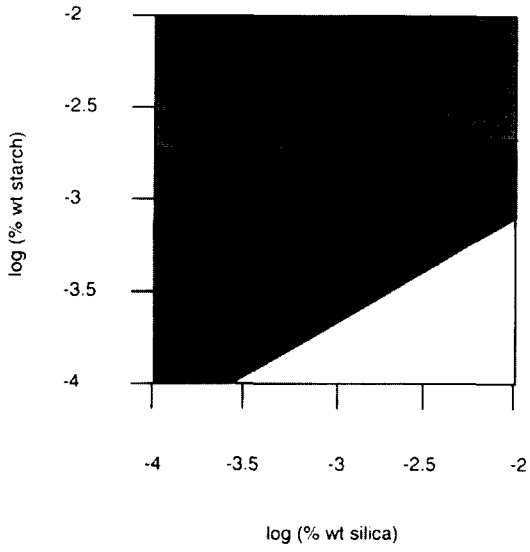

Fig. 2. A schematic phase diagram for mixtures of the cationic amylopectin starch polymer and the nanosized silica particles in 5 mM NaCl and at pH 8.0. In the black areas there are transparent flocs and in the grey area there are white flocs. In the white area there are no visible flocs. The axis refers to weight fraction of starch and silica respectively in water.

changed slightly and therefore the correction for every salt concentration was performed. The uncertainty in the obtained values were about $\pm 0.3 \times 10^{-4}$, due to the difficulty in determining the correct polysaccharide concentration. This value can now be used together with the best fit of the corrected ESA value at 1 mg/mL to calculate the dynamic mobility, μ_d, at each salt concentration. The result is shown in Table 2. The dynamic mobility decreases with increasing ionic strength as expected. Based on conductivity measurements 0 mM added NaCl has been given an ionic strength of 0.1 mM.

Amylopectin from potato contains one phosphate ester group per 100–500 glucose units [5,27,28]. This means that the cationized amylopectin is of a slightly amphoteric nature. According to the manufacturer this amylopectin contains one phosphate ester group per 250 glucose units. This is roughly 8% of the total number of charged groups, and therefore the anionic phosphate ester groups will be neglected in our treatment and only the cationic groups considered.

By using only one fitting parameter, namely the radius of the porous sphere, it was possible to obtain a perfect fit of the obtained dynamic mobilities with the calculated electrophoretic mobilities. The calculated radii for each investigated electrolyte concentration is shown in Table 3. This can be interpreted as an estimate of how much the size of the amylopectin molecule changes with an increased electrolyte concentration. The molecule contracts quite a lot as the electrolyte concentration increases especially at low salt concentrations. At low ionic strength the cationic groups maximize the distance between themselves in order to minimize the electrostatic energy. As the electrolyte concentration increases the cationic charges are screened from each other and the polymer behaves as an uncharged polymer. This behaviour has also been found for highly charged cationic starch with a degree of substitution of 0.32, where the dimensions of the starch decreased as the electrolyte concentration increased over the whole range studied (1–100 mM) [29]. This has also been shown theoretically for linear flexible polymers [30].

Screening by nanosized silica particles.—Phase Diagram. It was found that only white flocs were detected in a narrow region for dilute starch solutions (Fig. 2). Otherwise transparent flocs were formed if only enough starch was available. If the starch concentration was around the overlap concentration 4 mg/mL or above, white flocs were always formed. At low concentrations of starch and high concentrations of silica no visible flocs were formed. The size of the white flocs formed in the dilute starch region

Table 1
The obtained values of $(\rho_{suspension} - \rho_{solvent})/\rho_{solvent}$ as a function of electrolyte concentration

Electrolyte concentration (mM)	$(\rho_{susp} - \rho_{solv})/\rho_{solv}$
0	3.2×10^{-4}
2	3.2×10^{-4}
5	2.9×10^{-4}
10	3.3×10^{-4}
25	3.4×10^{-4}
50	3.9×10^{-4}
100	3.9×10^{-4}

Table 2
The dynamic mobility, μ_d, as a function of electrolyte concentration

Electrolyte concentration (mM)	μ_d ($m^2\ V^{-1}\ s^{-1}$)
0	2.15×10^{-8}
2	1.38×10^{-8}
5	1.17×10^{-8}
10	0.97×10^{-8}
25	0.60×10^{-8}
50	0.33×10^{-8}
100	0.38×10^{-8}

Table 3
The radius, R, of the porous sphere as a function of electrolyte concentration. The best fit of the obtained dynamic mobility, μ_d, with the electrophoretic mobility, μ_e, calculated from the porous sphere model implying that $\mu_d = \mu_e$. The radius of the porous sphere is used as a fitting parameter

Electrolyte concentration (mM)	R (nm)
0	253
2	110
5	88
10	76
25	70
50	79
100	57

were checked with laser diffractometry. The white flocs were typically around 60 μm in radius. Every white floc contains a large number of complex molecules while the transparent flocs contain only a few. The reason for this flocculation behaviour was not clear and therefore an electrokinetic study was performed which will be discussed in Section 3.2.2.

PALS measurements. The ESA-technique was not suited for measurements of silica covered CApS samples because the free silica particles dominated the ESA-signal. This is also expected because of the large density difference ($\Delta\rho \approx 1.2$ g/cm^3) for silica, compared to the cationic amylopectin molecules covered with silica particles (probably $\Delta\rho < 0.1$ g/cm^3). Therefore phase analysis light scattering (PALS) was used instead.

The mass ratios m_{NSP}/m_{CApS} are chosen to be on both sides of the region where macroscopic flocs are formed. It can clearly be seen in Table 4 that at low mass ratios m_{NSP}/m_{CApS} the electrophoretic mobility is virtually constant, but at higher mass ratios the charge of the cationized amylopectin is almost completely screened. The nanosized silica particles can not reverse the sign of CApS polymers even at high mass ratios, indicating that macroscopic flocs between silica-covered CApS polymers are not formed at complete neutralisation of the polymers. The highly-charged silica particles that are not bound to any cationic amylopectin might be too small (5 nm radius) to be observed by the PALS-apparatus and simply act as a background electrolyte signal.

Table 4
The electrophoretic mobility, μ_e, at constant starch concentration, 1 mg/mL, and different silica concentrations at 5 mM sodium azide and at pH 8.0

NSP Concentration (mg/mL)	μ_e (m^2 V^{-1} s^{-1})
0	4.82×10^{-9}
0.2	8.47×10^{-9}
0.3	3.69×10^{-9}
0.4	3.81×10^{-9}
0.5	4.95×10^{-9}
3.5	2.46×10^{-9}
4	2.41×10^{-9}
4.5	6.21×10^{-10}

The flocculation process can be considered as a kind of bridging flocculation where the comparatively large polymers (radius about 100 nm) are the kinetic unit and the small particles (radius about 5 nm) are the bridge-forming agent. The interaction between the silica particles and the cationic starch molecules are probably of a pure electrostatic nature. (No flocs are formed between an uncharged amylopectin molecule and the silica particles.) The interaction might therefore be explained in terms of available cationic and anionic sites. The flocculation process occurs in two steps [31]: First, the cationic polymer and the silica particles 'meets' and forms polyelectrolyte complexes. After that the polyelectrolyte complexes can bind to each other under certain conditions which will be discussed below. The different regions in Fig. 2 below the overlap concentration of the polymer will be discussed in terms of increasing amount of silica particles and compared to the electrophoretic mobility data in Table 4.

The CApS polymer is stabilized against aggregation by the cationic charges placed at the exterior of the 'bushy' polymer structure. Negatively-charged silica particles are electrostatically attracted to the CApS polymer. At low contents of silica particles every particle might be bound with a number of electrostatic bonds to one amylopectin molecule. In other words the silica particles are completely embedded in the amylopectin molecule and therefore there are no available anionic sites for further flocculation. The electrophoretic charge of the amylopectin molecules is not affected by the small amount of embedded silica particles.

As the number of silica particles increases, the number of electrostatic bonds between one silica particle and one CApS polymer decreases, because there is an increased competition between the silica particles of available cationic sites. Collisions between silica-covered amylopectin molecules will, of course, occur and therefore cationic sites on one polymer can bind to the anionic sites on silica particles bound to another polymer. Thus producing

macroscopic flocs where the silica particles are the bridge-forming agent.

At even larger numbers of silica particles all available cationic sites at the exterior of the polymers will immediately be bound to the silica particles. No available cationic sites will prevent any further flocculation. The amylopectin molecules are molecularly dispersed because the silica particles reverses the sign of the charge of the exterior of the polymer to be anionic instead. The positive electrophoretic charge is reduced because more silica particles are bound to every amylopectin molecule.

Why does the sign of the charge of the polyelectrolyte complexes at high mass ratios m_{NSP}/m_{CApS} not change? The silica particles can not penetrate very far in the highly-branched amylopectin structure. Therefore the cationic sites inside the 'bushy' amylopectin molecule are not available in the flocculation process but they are still measured in an electrophoretic measurement. This prevents the electrophoretic charge to be changed in the measurements even if the cationic charges on the exterior of the 'bushy' amylopectin molecule is completely screened by the silica particles. It seems likely that most of the charges in this amylopectin are kept in the interior of the molecule.

4. Conclusions

(I) A linear relationship between the ESA-signal and CApS concentration (up to 3 mg/mL) was obtained, indicating that the dynamic mobility of non-interacting CApS molecules can be evaluated from ESA measurements.

(2) The dynamic mobility decreases with increasing electrolyte concentration.

(3) The porous sphere model gives a reasonable description of the measured mobilities for CApS obtained for different electrolyte concentrations.

(4) The radii of the porous sphere can be used as a parameter describing the contraction of the CApS molecule at increasing electrolyte concentration.

(5) PALS can be used to investigate the screening of CApS by nanosized silica particles.

(6) Increased amount of nanosized silica particles increases the screening of the CApS polymer, but the electrophoretic charge of the polymers is still positive at high mass ratios m_{NSP}/m_{CApS}.

(7) Most of the charges in the amylopectin molecule are kept in the interior of the 'bushy' structure.

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