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Surface forces between cellulose surfaces in cationic polyelectrolyte solutions: The effect of polymer molecular weight and charge density

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KEYWORDS: Cellulose, Surface forces, Adhesion, Polyelectrolyte, Atomic force microscope (AFM)

SUMMARY: The purpose of this study was to gain a better understanding on how the cationic polyelectrolytes influence the forces between the cellulose surfaces and the importance of these forces in papermaking. The role of molecular weight and charge density of the polyelectrolytes was of particular interest. Surface forces between cellulose spheres in the presence of cationic polyelectrolytes were analysed with an atomic force microscope. The repulsion between the cellulose surfaces decreased when a small amount of high charged, low molecular weight cationic polyelectrolyte was added. Charge reversal took place at high polyelectrolyte concentrations. Surface forces at large distances were well explained by the DLVO theory, implying that the origin of repulsive interactions at large distances was purely electrostatic. The situation clearly changed, when a low charged, high molecular weight polyelectrolyte was added to the solution. Purely electrostatic behavior turned into steric repulsion at high polymer concentrations. The forces on separation were also different. While a sharp minimum was found in the presence of a polyelectrolyte with high charge density and low molecular weight, the detachment was gradual with attractive forces observed at separation of hundreds of nanometers for a polyelectrolyte with low charge density and high molecular weight. The pull-off force was at its largest near the charge neutralization point, where the surfaces were only partially covered and the polyelectrolyte was able to effectively bind the surfaces together. The difference between high charged, low molecular weight and low charged, high molecular weight polyelectrolytes indicates that the flocculation mechanism is bridging, but the effect of molecular weight is different. These observations on a molecular level can clearly be correlated with the flocculation and floc strength observed for fiber flocs in papermaking suspensions.

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It is important to control the surface interactions between cellulose fibers during papermaking. This can be accomplished e.g. by adding cationic polyelectrolytes to modify the surface interactions (Solberg, Wågberg 2003; Wågberg, Lindström 1987). They can introduce attractive forces, such as bridging, or diminish the electrostatic repulsion by neutralizing the surface charges of fiber, thereby increasing the importance of the attractive van der Waals forces. In these cases, polyelectrolytes act as flocculants. They can also act as a stabilizer, if their adsorption changes the forces between the surfaces to repulsive, such as steric repulsion or electrostatic repulsion due to charge reversal. The role of polyelectrolyte is a matter of dosage (Stenius 2000).

Studying fibre flocculation with cationically modified polyacrylamide (C-PAM), Wågberg et al. (Solberg, Wågberg 2003; Wågberg, Lindström 1987) found that the maximum flocculation occurred when the coverage of surface area was about 50% while redispersion was obtained close to 100% surface coverage. Polyelectrolytes also influence adhesive forces between cellulose surfaces. The strength of the fiber flocs is probably due to a combination of surface forces between cellulose surfaces and forces in cellulose-polyelectrolyte-cellulose systems (Wågberg, Lindström 1987).

The polyelectrolyte properties affect the mechanism behind flocculation and floc strength. High charged, low molecular weight polyelectrolytes cause flocculation due to charge neutralization or patchwise attraction. The flocs are sensitive to polymer dosage and break easily due to shear (Lindström 1989). Low charged, high molecular weight polyelectrolyte molecules are able to bind more particles together from a larger distance than high charged, low molecular weight polyelectrolytes. The flocculation is due to bridging (Lindström 1989; Swerin, Ödberg 1997). These flocs can resist high shear forces (Dickinson, Eriksson 1991).

Generally, surface forces have been widely studied with direct force measurement methods (Claesson et al. 2005; Hartley 1999; Hodges 2002). The connection between measured electrostatic forces and the DLVO theory is well known (Hartley 1999). Introducing polymer into the system produces more complex behaviour and the observed forces cannot always be explained with the DLVO theory (Hodges 2002). Uncharged polymers can introduce steric forces, the range of which is dependent on the gyration radius of the polymer coil in solution, but solvent effect or hydrophobic interactions, causing either attraction or repulsion, can also affect the interactions (Claesson et al. 2005; Hartley 1999; Hodges 2002). Low adsorbed amount of polyelectrolyte on an oppositely charged surface decreases the surface charge and, thus, decreases the electrostatic repulsion between surfaces (Claesson et al. 2005). Further adsorption leads to recharging and electrostatic repulsion increases again. Steric contribution on interactions is also possible. Attractive forces, such as bridging, may also be detected. Decreasing the charge density of the polyelectrolyte, the layer thickness of polyelectrolyte increases, which leads to a decrease in the pull-off force and steric repulsion near the charge neutralization point (cnp).

It is important to use cellulose model surfaces when studying the effect of polymers on cellulose fibres, because cellulose is a polymer itself and, thus, cellulose surface behaves differently compared to the inorganic surfaces in the polyelectrolyte adsorption (Poptoshev, Claesson 2002a; Poptoshev et al. 2000a; Salmi et al.

2003). The first surface force measurements between cellulose surfaces were made using the interferometric surface force apparatus (Neuman et al. 1993), while the first force measurements with cellulose using atomic force microscopy (AFM) were made in 1997 (Rutland et al. 1997). Since then, several studies on the interactions between cellulose surfaces and the effect of polyelectrolytes on these have been reported (Holmberg et al. 1997b; Österberg 2000; Paananen et al. 2004; Poptoshev et al. 2000b; Poptoshev, Claesson 2002a; Zauscher, Klingenberg 2000a and 2000b).

Nevertheless, there are many fundamental questions regarding the molecular behaviour of various polyelectrolytes on cellulose surfaces that still need to be understood. Thus, although the effect of molecular weight (M_w) and charge density (CD) of the polyelectrolyte on the fibre flocculation has been studied in bulk experiments with fibre suspensions, the effect of these parameters on the forces between cellulose surfaces has not been previously studied in a systematic manner by direct measurements of molecular interactions. Furthermore, their influence on flocculation mechanisms has not been unambiguously verified.

The aim of this study was to obtain a better understanding of the effects of cationic polyelectrolyte on the interactions in cellulose systems and to test the mechanisms suggested by bulk measurements by measuring the surface forces between model cellulose surfaces. A more general aim was to deepen the understanding of interactions in papermaking stock at a molecular level. Interactions were studied as a function of the polymer concentration and the ionic strength of solutions using an AFM. Polyelectrolyte properties were systematically varied to evaluate the effect of charge density and molecular weight.

Experimental

Materials

Poly(dimethyldiallylammonium chloride)s, PDADMACs, (Allied Colloids Ltd., England) and cationic polyacrylamides, C-PAMs, (Kemira Chemicals Oy, Finland) with various M_w and CD were used to study the effect of M_w and CD (Fig 1 and Table 1). Polyelectrolytes were ultra filtrated with different cut-offs to restrict M_w distribution and M_w was determined from intrinsic viscosity. CD was determined by polyelectrolyte titration using sodium polyethylene sulphonate and the point of equivalence was determined using a particle charge detector (Mütek PCD 03, Germany). The NaCl and NaHCO₃ were of analytical grade. The de-ionized and distilled water was further purified using Elga UHQ system, UK.

The precipitated spheres of cellulose II regenerated via viscose process were manufactured by Kanebo Co., Japan. They were 5–35% crystalline and slightly negatively charged (Carambassis, Rutland 1999). Their radius was 15–30 μm , as determined *in situ* in electrolyte solution by using an optical microscope and a digital camera. The radius in air was 10–20 μm indicating a 20–50% swelling.

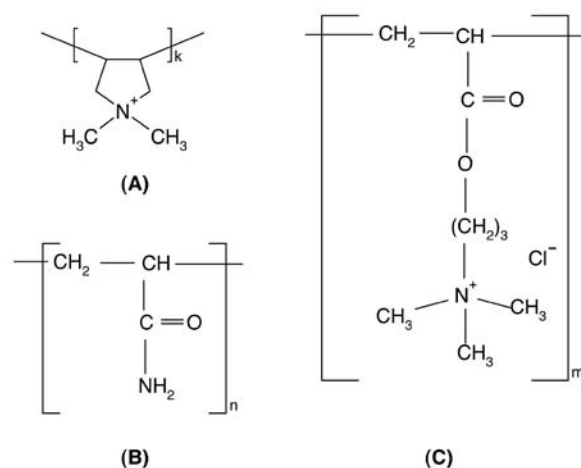


Fig 1. Molecular structures of (A) PDADMAC, (B) uncharged and (C) cationic unit of C-PAM.

Table 1. The properties of the used PDADMACs and C-PAMs. DS is the degree of substitution of charged unit.

Substance	M_w 10^5 g/mol	CD meq/g	DS mol-%
PDADMAC	less than 1 (low)	6.1 (high)	100
	3.9 (int)	6.1 (high)	100
C-PAM	4.0 (int)	3.1 (int)	38
	3.2 (int)	1.1 (low)	9
	14.0 (high)	1.8 (low)	17

int = intermediate

Force measurements using AFM

An atomic force microscope (NanoScope IIIa multimode, Digital Instrument, Santa Barbara) was used to measure surface forces. One cellulose sphere was glued to the tipless end of the AFM cantilever with a reported spring constant of 0.06 or 0.12 N/m (Veeco Instrument, US) and another cellulose sphere was glued to a freshly cleaved mica sheet. The forces between the two spheres were measured using the colloidal probe technique (Butt 1991; Ducker et al. 1991). The spring constants of the cantilevers were determined by the thermal noise method and the result was controlled by the reference spring method (Hutter, Bechhoefer 1993; Torii et al. 1996; Tortonese, Kirk 1997). The accuracies of the thermal noise method and the reference spring method were 5–20% and 10–30%, respectively (Hodges 2002). Standard deviation of the thermal noise method was about 10%.

Cellulose spheres were let to equilibrate in an electrolyte solution over night before the measurements. When changing the solution, the system was allowed to stabilize for one hour. Furthermore, the surfaces were allowed to relax for at least 10 minutes between the measurements. No changes in the surface interactions were detected on the time scale of stabilization or relaxation. This procedure has been found to provide reliable and reproducible results (Paananen et al. 2004). The cantilever velocity was about 500 nm/s.

All experiments were reproduced at least three times. For the sake of clarity, only one representative curve per system is shown in the figures. The standard deviation of the surface potentials determined from the force curves

was about 30%. Within the same measurement, the variation at high polyelectrolyte concentration was about 15% (standard deviation of surface potentials). Despite the variation in magnitude of the force, the shape of the force curves and the trends were reproducible.

The raw data (cantilever deflection vs. piezo movement) were converted into force curves (force vs. separation) using the Scanning Probe Image Processor (SPIP, Image Metrology, Denmark) and further handled in Origin (OriginLab Co., USA). The cantilever sensitivity was determined separately for each measurement from the raw curve obtained when using the maximum loading force i.e. in hard wall contact. The deflection was calculated by dividing the deflection voltage by the cantilever sensitivity. The surface separation was calculated relative to hard wall contact. Forces were calculated as the product of the spring constant and the deflection (Hooke's law). To facilitate a comparison to other studies, the forces in this study were normalised with the radii of the interacting cellulose spheres.

Fitting to DLVO theory

The results were fitted to the interactions predicted by the DLVO theory of colloidal stability, i.e., assuming that only van der Waals and electrostatic interactions were of importance. To analyse the electrostatic interaction energy, the linearized Poisson-Boltzmann equation for constant charge (1) and constant potential (2) was used as presented in the following equations:

$$W_{\sigma}(X)_{ft/ft} = 2Z^2 n_i kT \left(\frac{e\psi}{kT} \right)^2 \kappa^{-1} \left(\coth \frac{\kappa X}{2} - 1 \right) \quad [1]$$

$$W_{\psi}(X)_{ft/ft} = 2Z^2 n_i kT \left(\frac{e\psi}{kT} \right)^2 \kappa^{-1} \left(1 - \tanh \frac{\kappa X}{2} \right) \quad [2]$$

which are valid at distances larger than the Debye length and provided the surface potential of cellulose surfaces is low (< 25 mV) (Derjaguin et al. 1987). Here, $W_{ft/ft}$ is the energy between two flat plates, X the surface separation, Z the valency, n_i the ion concentration, k the Boltzmann constant, T the temperature, e the electron charge, ψ the surface potential and κ^{-1} the Debye length. Van der Waals energy of interaction was calculated using the following equation:

$$W_{vdW}(X)_{ft/ft} = -\frac{A_H}{12\pi X^2} \quad [3]$$

where A_H is the Hamaker constant. To obtain the DLVO interactions, the equations (1) or (2) and (3) were summed. In the van der Waals part of the DLVO theory, the Hamaker constant of $0.8 \cdot 10^{-20}$ J was used for cellulose in water (Bergström et al. 1999). For fitting, surface forces (F) were normalized by radii (r_i) of spheres using the Derjaguin approximation (4) (Derjaguin 1934).

$$F_{DLVO}(X)_{sph/sph} = 2\pi \frac{r_1 r_2}{r_1 + r_2} W_{DLVO}(X)_{ft/ft} \quad [4]$$

The fitting parameter was the surface potential, ψ . Instead of using Debye length (κ^{-1}) as a fitting parameter, a constant value depending on the ionic strength of the solution was used. Using Poisson-Boltzmann equation for constant charge (1), data fitted slightly better to the DLVO theory and only DLVO forces using Eq (1) are represented in the figures for clarity, except for Fig 4 where both approximations are represented. The relative errors of the surface potential, in cases fitted to theory, were under 5%. The coefficient of determination between theory and data was often better than 0.9. The effect of the polyelectrolyte and its counterions should not largely influence the Debye length, because of their low bulk concentration and the depletion zone (concentration near surface is lower than in bulk) after charge reversal at high polymer concentrations (Dahlgren, Leermakers 1995).

The linearized Poisson-Boltzmann equations (1) and (2) underestimate the surface potential. Hence, the potentials obtained here should only be used to compare the results reported in this paper; the absolute values are only tentative. One should remember that the surface potentials were also affected by the possible experimental errors in the spring constant, sphere radii and the apparent zero separation. The zero separation also influenced in a theoretical aspect, because it was treated as a plane of charge in the fittings.

The hydrodynamic forces were not included in the fittings, but measures were taken to minimize their influence on the experimental results. Thus, the approach velocity of the cellulose beads to each other was kept fairly low and its effect was tested. However, the possibility that the hydrodynamic forces could contribute to the results at short distances and polymer layers could enhance the effect of the hydrodynamic forces still exist.

Results and Discussion

The forces between the cellulose surfaces in the presence of various cationic polyelectrolytes were measured in order to understand the suggested flocculation mechanisms which are based on bulk studies of cellulose fibre suspensions. The effect of M_w , ionic strength and the polyelectrolyte concentration on the interactions was investigated for two different systems: high charged PDADMAC and low charged C-PAM. The difference between these two systems and the effect of charge density will be discussed separately.

Surface interactions between cellulose surfaces

To check the cleanliness of the system, the forces between pure cellulose surfaces before the addition of the polyelectrolyte was always measured. Two force regimes, steric and electrostatic, were observed between the two pure cellulose surfaces (open squares in Fig 2 and the following figures). The short-range interactions were not unambiguously dependent on the ionic strength and, therefore, we assume that they were mainly of steric origin. The range of the steric force for cellulose was fairly short.

The surface potentials obtained for cellulose were bet-

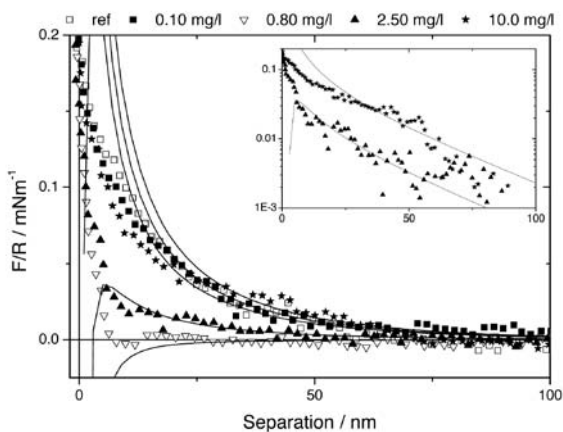


Fig 2. The effect of intermediate molecular weight PDADMAC concentration on surface forces between approaching cellulose surfaces in 0.10 mM NaCl. Solid lines represent DLVO fitting results assuming constant charge: surface potentials are -12.7, -13.8, 0, 7.5 and 14.9 mV, respectively, and Debye length is 30.3 nm. Inset graph shows 2.50 mg/l and 10.0 mg/l data in semi-logarithmic scale.

ween -13 and -16 mV at ionic strength 0.10 mM. The sign of the charge cannot be deduced from the calculations, but we can assume that the cellulose surfaces carry a weak negative charge and we know the added polyelectrolytes are positive. The results were in agreement with the values observed in the surface force measurements using similar cellulose spheres (-11 to -17 mV) (Carambassis, Rutland 1999; Rutland et al. 1997), using other type of model cellulose surfaces (-20 to -21 mV) (Poptoshev et al. 2000a; Zauscher, Klingenberg 2000a and 2000b) and only slightly lower than zeta potentials for cellulose and microcrystalline cellulose (-21 to -30 mV) (Brandrup et al. 1999; Pelton 1993). The pull-off force between pure cellulose surfaces varied from 10 to 80 $\mu\text{N/m}$. This is also in agreement with the previous observations of low pull-off force (Holmberg et al. 1997a; Zauscher, Klingenberg 2000a).

The interactions between cellulose surfaces in the presence of PDADMAC

Forces between cellulose surfaces were recorded as a function of polyelectrolyte concentration and ionic strength. Polyelectrolyte used was high charged cationic PDADMAC with two different M_w (Table 1).

Before any polyelectrolyte was added into the solution, the interactions between two cellulose spheres were monotonically repulsive in 0.10 mM NaCl (Fig 2). When polyelectrolyte was adsorbed, the electrostatic repulsion decreased at low concentration of intermediate M_w PDADMAC until it reached the charge neutralization point (*cnp*). This occurred in 0.80 mg/l PDADMAC solution, according to the fittings to the DLVO theory. In general, *cnp* was located in the concentration range of 0.80–1.0 mg/l.

When the concentration of PDADMAC was further increased, the repulsion increased due to overcompensation of the cellulose surface charge. Thus, we can assume that the net surface charge was positive. The forces at long distances were explained by the DLVO theory implying that at long distances the origin of the interaction was purely electrostatic. The surface potential increased from 0 mV to 14.9 mV when the PDADMAC con-

Table 2. Pull-off force (A) between cellulose surfaces as a function of polyelectrolyte concentration. For the sake of clarity, error limits are given only in representative cases.

Mw CD c mg/l	PDADMAC		C-PAM		
	Low High A $\mu\text{N/m}$	Int High A $\mu\text{N/m}$	c mg/l	Int Low A $\mu\text{N/m}$	Int High A $\mu\text{N/m}$
0	65	17 ± 18	0	11	0
0.1	32	103 ± 58	50	23	1
0.8	44	144 ± 39	100	4	5
1	nd	180 ± 101	150	8	10
2.5	148	148 ± 70	200	6	20
5	nd	122 ± 79	300	0	100
10	18	73 ± 53			

Int = intermediate
nd = not determined

centration increased from 1.0 mg/l to 10.0 mg/l.

The pull-off force was at its highest close to the *cnp*. This probably occurred because a high amount of the adsorbed polyelectrolyte molecules was able to bind to the opposite surface and also because the electrostatic repulsion between the surfaces was low (Table 2). When more polyelectrolyte adsorbed, the pull-off force decreased. Occasionally, an attractive force was observed on approach. A maximum in the attraction was also observed near the *cnp*. The range of this attraction was about 10 nm.

The effect of polyelectrolyte concentration on the interactions between the cellulose surfaces in the presence of low molecular weight PDADMAC ($M_w < 1 \cdot 10^5$ g/mol) are presented in Fig 3. The effects were similar to the trend observed with the intermediate molecular weight PDADMAC. First, the electrostatic repulsion decreased with increasing adsorption, i.e. an increasing polyelectrolyte concentration, but this occurred at a higher concentration than for the higher M_w PDADMAC. A clear repulsion between the surfaces in 0.8 mg/l PDADMAC still existed. The surface potential was -14.0 mV, but a minor attractive contribution to the surface force was detected at short separations. The repulsion rapidly

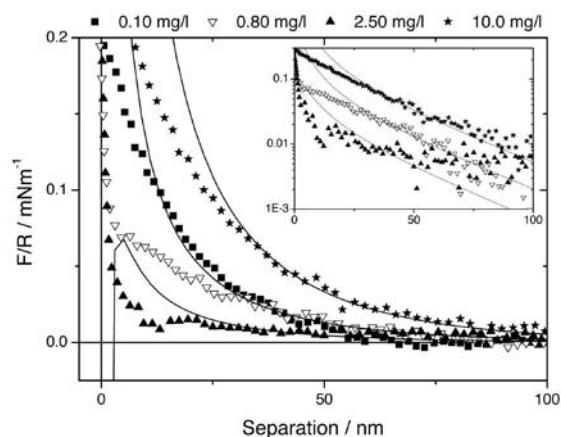


Fig 3. The effect of low molecular weight PDADMAC concentration on surface forces between approaching cellulose surfaces in 0.10 mM NaCl. Solid lines represent DLVO fitting results assuming constant charge: surface potentials are -13.3, -14.1, 8.7 and 22.2 mV, respectively, and Debye length is 30.3 nm. Inset graph shows 0.80 mg/l, 2.50 mg/l and 10.0 mg/l data in semi-logarithmic scale.

decreased and the charge neutralization occurred at PDADMAC concentrations between 0.80 and 2.5 mg/l. The surface forces in 2.5 mg/l PDADMAC were approximately equal for both PDADMACs. The surface potential indicated for a 2.5 mg/l solution of low molecular weight PDADMAC was +8.7 mV. The highest attractive contribution to the surface forces was detected in 2.5 mg/l PDADMAC and its range was from 7 to 14 nm. The highest pull-off force (148 $\mu\text{N/m}$) was also observed at this concentration (Table 2). When the polyelectrolyte concentration was further increased, the repulsion increased. The surface potential was 22.2 mV in 10 mg/l PDADMAC, which was higher than the one observed with the intermediate M_w PDADMAC.

The effect of ionic strength on the interactions between PDADMAC-coated cellulose is illustrated in Fig 4 for the intermediate M_w polymer. PDADMAC was adsorbed onto the cellulose spheres from a 2.5 mg/l solution at low ionic strength and then the NaCl concentration was successively increased to 0.1, 1.0 and 10 mM. When the electrolyte concentration in the solution was increased, the long-range repulsion decreased as predicted by the DLVO theory. Two force regimes were clearly apparent from the change of the slope: the electrostatic repulsion at large separation and the steric repulsion at short separations (see arrow in Fig 4). No systematic change of the surface potential as a function of the ionic strength was observed. The surface potential was approximately 10 mV. This may indicate that the surface charge density increases. The pull-off force decreased with an increasing ionic strength: 82, 47 and 33 $\mu\text{N/m}$ in 0.1, 1.0 and 10 mM NaCl, respectively.

The reason for the decrease in the pull-off force with the increasing ionic strength may be that the PDADMAC layer became slightly more compact as the ionic strength increased. Notably, the results indicate that PDADMAC was adsorbed in a flat conformation before the ionic strength was changed. Since the already adsorbed polyelectrolytes stick firmly on the cellulose surfaces, the rearrangement is very slow and the increase in ion concentration was not able to drastically change that conformation (Claesson et al. 2005). However, since the range of the intra and intermolecular electrostatic repulsion decreased, the layer could somewhat flatten (Dahlgren et al. 1995; Miklavic, Marcelja 1988).

The interactions between cellulose surfaces in the presence of C-PAM

The influence of molecular weight and charge density was studied using three different C-PAMs (see Table 1). When the effect of adsorption of a low charged and low molecular weight C-PAM was analysed, no unequivocal change in the surface forces between the cellulose surfaces was observed in the concentration range of 0 - 300 mg/l. The pull-off force also remained unchanged (Table 2). It can be concluded that the low charged, low M_w C-PAM did not adsorb on the low charged cellulose. In the adsorption studies of low charged, low M_w C-PAM on Langmuir-Blodgett layers of cellulose with a quartz crystal microbalance (QCM-D), it was observed that the

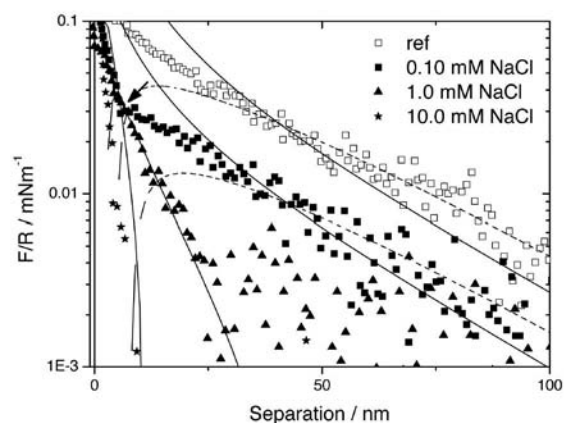


Fig 4. The effect of the ionic strength on surface forces between approaching cellulose surfaces in 2.50 mg/l PDADMAC solutions. Solid lines represent DLVO fittings in 0.10, 1.0 and 10 mM NaCl assuming constant charge with Debye lengths 30.3, 9.6 and 3.0 nm, respectively. The dotted lines represent fittings assuming constant potential for Debye length 30.3 nm. The fitted surface potentials (assuming constant charge) are -16.0, +10.1, +8.2 and +11.9 mV, respectively. An arrow indicates where steric forces start to dominate.

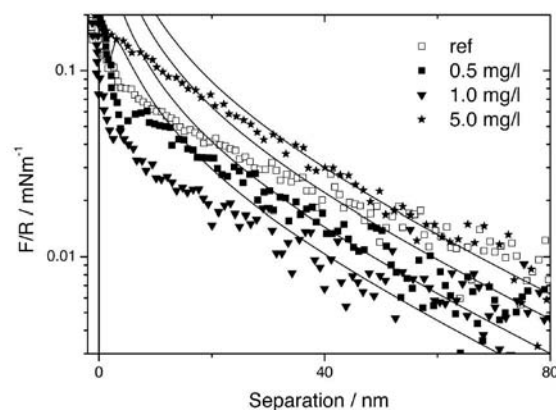


Fig 5. The effect of intermediate charged and low molecular weight C-PAM concentration on surface forces between approaching cellulose surfaces in 0.10 mM NaHCO_3 . Solid lines represent the DLVO fittings assuming constant charge: surface potentials are -14.3, -12.1, -10.3 and 17.2 mV, respectively, and Debye length is 30.3 nm.

polymer adsorbed only to a low extent (Salmi et al. 2003), which supports our observations in this study.

The interactions observed for an intermediately charged, low M_w C-PAM (Fig 5) were quite similar to the trends found for PDADMAC. The polymer adsorbed on the cellulose surfaces. The repulsion in 0.10 mM NaHCO_3 decreased with an increasing concentration of C-PAM from 0 to 1.0–2.0 mg/l and then increased until the concentration of C-PAM was 5.0 mg/l. Changes in the surface forces were rapid around the cnp , which was located in the range of 1.0–2.0 mg/l C-PAM, and however the exact cnp for the system was not located. The observed surface potentials were -10.3 mV in 1.0 mg/l C-PAM and 17.2 mV in 5 mg/l C-PAM. At concentrations higher than 5.0 mg/l, the repulsion remained unchanged, i.e. no further adsorption of polyelectrolyte occurred. In contrast to the PDADMAC case, neither attraction on approach nor a maximum in pull-off force was observed (Table 2). This may, however, be due to the fact that the exact optimum concentration for attraction was not found. The pull-off force seemed to be lower between the C-PAM

coated surfaces than between the pure cellulose surfaces.

When a high M_w , low charged C-PAM was added into the solution, the electrostatic repulsion between the cellulose surfaces decreased, because the net surface charge was lowered by the C-PAM adsorption (Fig 6). A repulsion minimum was observed in 5.0 mg/l C-PAM solution. The *cnp* was located between 5.0 and 10.0 mg/l C-PAM. The range of the attraction between approaching surfaces was from 17 to 29 nm. A pull-off force maximum (95 $\mu\text{N/m}$) was detected in the same concentration range, supporting the presence of the attractive forces (Table 2).

At high polymer concentrations (e.g. 100 mg/l), the measured surface force did not follow the DLVO theory even at large separations. It is suggested that this deviation from the DLVO theory is of steric origin. The C-PAM adsorption further increased with the increasing polyelectrolyte concentration. This led to a thick and loose layer of C-PAM on cellulose, which is typical for low charged, high M_w polyelectrolytes. The range of steric interaction was about 300–400 nm, i.e. 150–200 nm per layer on the cellulose beads. The observed range was consistent with the results obtained by other research groups on low charged polyelectrolytes (Poptoshev, Claesson 2002a; Zauscher, Klingenberg 2000a and 2000b). Comparing this to the hydrodynamic radius observed for similar C-PAMs in solution (420 nm for DS 20% and M_w 1.4 million, Mabire et al. 1984) suggests that the molecules adopt a slightly flatter conformation when adsorbing.

The pull-off force was stronger at a high polymer concentration, than between pure cellulose surfaces, but lower than the one observed around the *cnp* (Table 2). The attraction on separation extended to a significant distance (Fig 7). We suggest that the polyelectrolyte layers are entangled when forced into contact. When the surfaces were pulled apart, the molecules did not have enough time to rearrange themselves. This led to gradual and long-range detachment. Similar phenomena have been observed previously e.g. by Poptoshev et al. (2000a).

The effect of the ionic strength on the high M_w , low charge C-PAM system was studied by increasing the NaHCO_3 concentration from 0.10 to 10.0 mM in 20.0 mg/l C-PAM solutions (Fig 8). The range of repulsion decreased with an increasing ionic strength, but not as much as predicted by the DLVO theory, further confirming that the origin of the surface force is not purely electrostatic.

When the experiment was performed the other way around, adsorbing C-PAM from a 10 mM NaHCO_3 solution and then decreasing the electrolyte concentration to 0.1 mM the behaviour was similar, but the steric contribution was weaker than previously (not shown in the figure). Apparently, the conformation of the adsorbed polyelectrolytes reflects the history of the experiment and may not be the most favourable conformation at that ionic strength. This effect should not be confused with the very rapid re-conformation of the polyelectrolyte that occurs within seconds after adsorption or the change in thickness of the diffuse layer upon changing the electrolyte concentration.

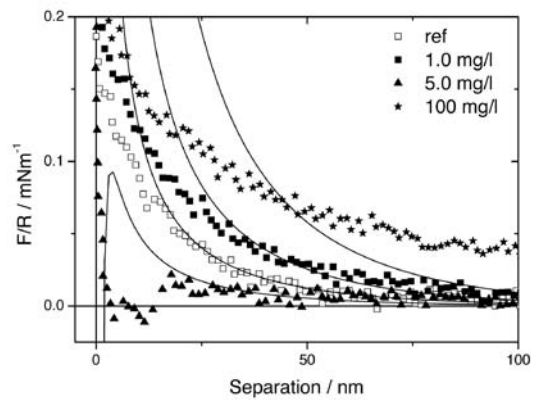


Fig. 6. The effect of low CD and high M_w C-PAM concentration on surface forces between approaching cellulose surfaces in 0.10 mM NaHCO_3 . Solid lines represent DLVO fitting results assuming constant charge: surface potentials are -13.7, -19.5, -9.28 and 29.25 mV, respectively, and Debye length is 30.3 nm.

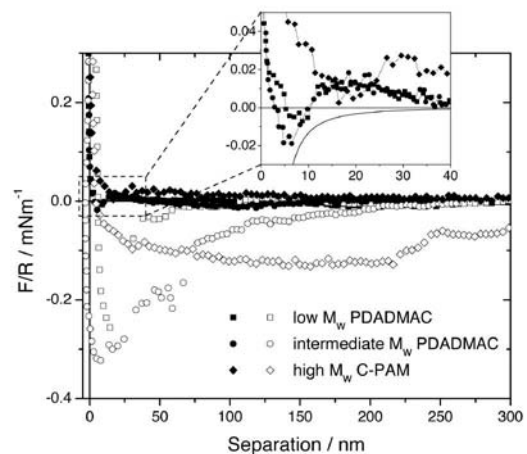


Fig 7. Approaching (filled symbols) and retracting (open symbols) force curves of low molecular weight PDADMAC (1.0 mg/l), intermediate molecular weight PDADMAC (2.5 mg/l) and low CD , high M_w C-PAM (5.0 mg/l). Curves show a maximal effect of attractive force on approach in a particular case. Ionic strength was 0.10 mM. Inset graph shows magnified data about the attraction on approach and the theoretical van der Waals attraction (solid line). Points are connected for clarity.

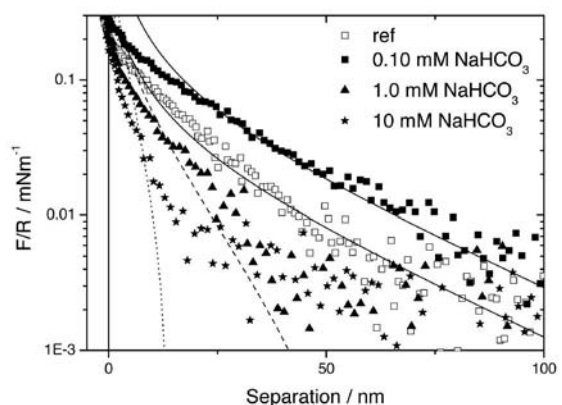


Fig 8. The effect of the ionic strength on surface forces between approaching cellulose surfaces in 20.0 mg/l high molecular weight C-PAM solutions. Solid lines represent DLVO fittings with Debye length 30.3 nm whereas dashed and dotted lines represent the fittings with Debye lengths 9.6 and 3.0 nm. The fitted surface potentials are -12.8, +16.6, +11.2 and +14.7 mV, respectively.

Since the polymer has a low charge density, the electrolyte concentration will not have a very strong effect on the conformation of the adsorbed polyelectrolyte. However, one can assume a slightly more compact conformation in higher electrolyte concentration. This explains why the steric contribution was overall lower in the case where C-PAM was adsorbed at high electrolyte concentration as compared to the case where the polymer was adsorbed at low electrolyte concentration.

The effect of the charge density and molecular weight on the attractive forces

An attractive contribution to the forces on approach was observed near the *cnp* of both PDADMACs and low *CD* and high M_w C-PAM. This attraction, as well as the forces on separation are shown in more detail in *Fig 7*. The range of the attraction in the force curve was 17–29 nm for C-PAM and around 10 nm for both PDADMACs. In the case of the PDADMAC, the interactions may be explained by the attractive van der Waals forces, while for the C-PAM case, the range of attraction clearly suggests a bridging attraction.

In all cases, the maximum pull-off force occurred at the same concentration as the maximum contribution of the attractive force on approach. The pull-off force was slightly stronger with high M_w than with low M_w PDADMAC (180 vs. 148 $\mu\text{N/m}$), but the pull-off force in both PDADMAC systems was clearly higher than the one in the C-PAM system (95 $\mu\text{N/m}$). The pull-off force in C-PAM solutions ranged to a significant distance and the detachment of the surfaces was gradual, which suggests a thick and loose layer structure (*Fig 7*). A similar long-range pull-off force, gradually stretching over 200 nm was observed by Poptoshev (2001), using a 10% charged, random copolymer of acrylamide and cationic [3-(2-methylpropionamido)propyl]trimethylammonium chloride (AM-MAPTAC-10).

The differences in the range of attraction on approach as well as the variation in pull-off forces led us to the notion that the effect of molecular weight on the attraction varied between polyelectrolyte studied. In the case of PDADMAC, the attraction was short-range and independent of the molecular weight. In addition, the pull-off force was quite strong and the force minimum was observed at a small separation. This is consistent with the notion that the origin of the attraction in PDADMAC solutions was mainly due to bridging of short and strongly bound molecules and the conformation of PDADMAC on the cellulose surface was quite flat. In the bridging attraction, molecules adsorbed to one surface attract the other surface, if there is a free adsorption spot. Obviously, this attraction is the strongest close to the *cnp*, when surfaces are partially covered. The flat layer of PDADMAC also seems reasonable, because the range of attraction is independent of the molecular weight and the bridging range is short. The bridging seems to be the most reasonable attraction mechanism, although a patchwise flocculation is typical to systems containing high charged polyelectrolytes, which adsorb in a flat conformation. However, it should be noted that the possibility to

detect the patchwise attraction in the force measurements has been criticized, because the measurement system used is static, not freely rotating, and surfaces are macroscopic (Poptoshev 2001).

The origin of the attraction in the case of C-PAM (high M_w , low *CD*) appears to be also bridging. This, together with a looser layer structure, would explain the gradual detachment on retraction seen from pull-off force data and the long-range attraction on approach. Joints formed via bridges can be assumed to be thick and flexible, which leads to a gradual detachment of surfaces keeping them connected at large separation, because bridges of different lengths detach one by one. Indeed, it was observed that the range of bridging attraction was longer with low charged C-PAM than the one with high charged polyelectrolytes, but, at the same time, it was weaker. Clearly, this is due to conformation of polyelectrolyte. It has been shown that the attraction is stronger with high charged polyelectrolytes than with low charged ones (Poptoshev 2001; Sjöström 1998). Attraction, which was concluded to be due to bridging, has been detected earlier in various cationic polyelectrolyte solutions (Dahlgren et al. 1993; Poptoshev 2001; Poptoshev, Claesson 2002a; Poptoshev et al. 1999). All these were high charged and only one had a molecular weight of over a million g/mol. An adhesion maximum caused by bridging has been previously reported (Biggs 1995; Biggs, Proud 1997; Zauscher, Klingenberg, 2000a and 2000b).

The effect of the molecular weight on the interactions

The effect of molecular weight was different for polyelectrolytes with high and low charges. The high charged PDADMAC with intermediate M_w gave rise to a stronger attraction and pull-off force than the one with low M_w . The differences were, however, minor and do not allow for definite conclusions. At high polyelectrolyte concentrations, the magnitude of the electrostatic repulsion was stronger for the low M_w PDADMAC than for the one with an intermediate M_w . Surface potentials in 10.0 mg/l PDADMAC were 22.2 and 14.9 mV, respectively. This indicates that more molecules with low M_w adsorbed onto cellulose than molecules with high M_w . It is probably easier for the smaller molecules to fit on the surface more densely than it is for the larger molecules. The colloidal probe measurements do not give any indication of the adsorbed amount or the thickness of the layer, which should be larger for the high M_w molecules, however, the results indicate that the surface charge increases more with smaller molecules.

The effect of the molecular weight was different for the low charged C-PAMs as compared to PDADMAC. The C-PAM with low M_w did not adsorb onto cellulose at all, but the one with high M_w did, resulting in a steric contribution to surface forces at high concentrations of the polyelectrolyte. As discussed above, bridging was also observed with high M_w C-PAM. The reason for this difference may be that the electrostatic attraction between the low charged cellulose and low charged C-PAM is too weak to induce adsorption, but when the molecular weight of the polyelectrolyte increases the adsorption is

driven by the decrease in the polymer solubility and for entropic reasons.

The effect of charge density on the interactions

Comparison of the low M_w polyelectrolytes leads to the conclusion that the higher the charge density, the more polyelectrolytes adsorb on the cellulose surfaces and the more the forces are affected. In contrast to PDADMAC, an attraction was not observed with C-PAM. Due to its higher charge density, PDADMAC molecule evidently had the higher affinity to cellulose surface and thus drew surfaces together more strongly than C-PAM, which favored the attraction. For the same reason the pull-off force was lower with C-PAM than with PDADMAC (Table 2). A similar disappearance of attraction has been previously detected when the polyelectrolyte charge density decreases (Claesson et al. 1994; Poptoshev 2001), because a polymer with a low charge density has a lower affinity to the surface than the one with a high charge density. C-PAM reached the maximum adsorption and surface potential in solutions with lower charge concentration than PDADMAC, but surface charge neutralization occurred approximately in the same charge concentration range and final surface potentials were roughly equal in both cases.

Papermaking relevance

The effect of polyelectrolyte dosage on flocculation and re-stabilization of papermaking stock has been thoroughly investigated (Lindström 1989; Wågberg, Lindström 1987). The influence of the dosage on the flocculation and stabilization suggested in these studies were clearly confirmed by our measurements. In addition, the mechanism behind the flocculation in different polyelectrolyte systems could be further clarified. Obviously, one must be careful when comparing results between this static model system and the papermaking environment, which is chemically much more complex and has totally different hydrodynamics. However, we suggest that the difference in flocculation behaviour observed in this study may be even emphasized in the fast papermaking process where polymers do not have time to change conformation after adsorption.

When the polyelectrolyte concentration increases, the repulsion first decreases because of the surface charge neutralization and then increases because of the charge reversal. A maximum attraction on approach and a maximum pull-off force were observed near the charge neutralization point. Correspondingly, it has been observed that fiber flocculation passes through a maximum close to cnp (Solberg, Wågberg 2003; Swerin et al. 1996).

Despite the differences observed between the high charged, low M_w and the low charged, high M_w polyelectrolytes, it could be fairly unambiguously verified that the mechanisms behind the attraction was bridging in both cases. The observed variations provide an explanation of the behaviour of the various polyelectrolytes in papermaking stock. The attraction on approach and the pull-off force was clearly different in these two cases. High charged, low M_w polyelectrolytes showed an attrac-

tion on approach and the highest pull-off force on retraction close to the cnp that could be explained based on the DLVO-theory and a short-range bridging that was independent of molecular weight. Although charge neutralization and patchwise flocculation cannot totally be ruled out as a mechanism for fibre flocculation using high charged, low molecular weight polymers, we suggest based on the results in this study that also bridging plays a role in these systems.

Low charged, high M_w polyelectrolytes, on the other hand, induced long-range attraction on approach that could not be explained based on DLVO-theory. In addition, the surfaces gradually detached upon retraction and attractive forces were still present at separations above 150 nm. Similar observations have been made in fiber flocculation experiments (Lindström 1989; Swerin, Ödberg 1997). Optimal bridging was attained when the degree of substitution of the polyelectrolyte was 0.2 (Wågberg, Lindström 1987), agreeing with our observations.

Interactions at a high polymer concentration of high charged polyelectrolytes were mainly electrostatic, but a steric contribution was observed in the case of low charged, high M_w C-PAM. Evidently, the layer formed by low charged, high M_w polyelectrolyte is thick and flexible. It is easy to understand why particles, once they are in contact, stay together even in shear. It has been observed in papermaking stock, that the flocs can resist the shear better when the mechanism of flocculation is bridging (Dickinson, Eriksson 1991). According to our results, bridges should also be long and flexible enough in order to resist the shear.

Conclusion

Clear differences were observed between high charged, low M_w and low charged, high M_w polyelectrolytes. When adsorbed, both gave rise to attraction between cellulose surfaces on approach and to a maximum pull-off force near the charge neutralization point, but the attraction was longer range and the pull-off force was gradual, keeping surfaces connected at a larger distance in the case of the high M_w polyelectrolyte. These differences were due to different layer structures. Polyelectrolytes with high charge formed a flat layer on the cellulose surfaces and gave rise to attraction between surfaces and its range was independent of molecular weight, whereas high M_w polyelectrolyte formed a thick layer and caused bridging ranging further. Steric forces were observed at a high polymer concentration for the case of low charged, high M_w polyelectrolyte, while the interactions in polyelectrolyte solutions with high charge were mainly electrostatic. These observations on a molecular level can clearly be correlated to the flocculation and floc strength observed for fiber flocs in papermaking suspensions.

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